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To be published as a chapter in the book,
"Technique of Inorganic Chemistry"

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UNIVERSITY OF CALIFORNIA

Lawrence Radiation Laboratory
Berkeley, California

Contract No. W-7405-eng-48

THE USE OF ELECTRIC DISCHARGES IN CHEMICAL SYNTHESES

William L. Jolly

December 14, 1960

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INTRODUCTION

Aim of Chapter -

Many chemical systems which are unreactive under ordinary conditions undergo vigorous reaction in the presence of an electric discharge. Although such reactions often yield thermodynamically stable products (e.g., ammonia may be prepared from nitrogen and hydrogen), they are seldom of practical interest since thermodynamically stable materials can generally be made by other methods which are simpler and more economical. On the other hand, discharge reactions having products which are thermodynamically unstable with respect to the starting materials are usually of interest to synthetic chemists. Sometimes discharge syntheses of thermodynamically unstable compounds compete favorably with other synthetic techniques such as electrolysis. For example, although ozone may be prepared by the electrolysis of aqueous sulfuric acid solutions, the electric discharge technique is the only commercially feasible preparative method. However, sometimes a discharge synthesis is often the only known method for preparing a compound. For example, although diboron dichloride may be prepared by the passage of boron trichloride through a mercury discharge tube, no direct chemical method for the preparation has yet proved successful.

As one might expect, many fascinating compounds of unusual structure have been isolated from reactions carried out in electric discharges. Thus, although such syntheses often have low energy efficiencies, they are still of interest to synthetic chemists who hope to discover new types of compounds.

In this chapter, the main types of electric discharges are discussed with particular emphasis on the experimental techniques involved in their use in laboratory syntheses. A wide variety of synthetic examples has been used to emphasize the versatility of the general method.

Types of Electric Discharge -

If the electric potential between two metallic electrodes in a gas is gradually increased from zero, practically no current passes until a critical voltage, the sparking potential, is reached. The sparking potential (V_s) for a particular gas is a function only of the product of the pressure and the distance between the electrodes (pd). The form of the function for air is shown in Figure 1, where V_s is plotted vs. pd. If an impedance is in series with the electrode circuit, the increase in current which occurs during the initial sparking is accompanied by a decrease in the potential between the electrodes. This decrease in potential with increasing current is represented by the extreme left side of the curve in Figure 2, where the discharge tube voltage is plotted against the logarithm of the current. Most gaseous discharge tubes are operated in the region AB of this curve (the glow discharge region). If the impedance of the circuit is lowered sufficiently, the operating point of the discharge tube will move beyond point B into the region where the voltage increases with increasing current. However, at point C the temperature of the cathode (or of both electrodes in the case of a.c. operation) will have increased to the point where thermionic emission of electrons is significant. Then a transition to the arc region (DE in Figure 2) occurs. Arcs are characterized by low potential drops, high current

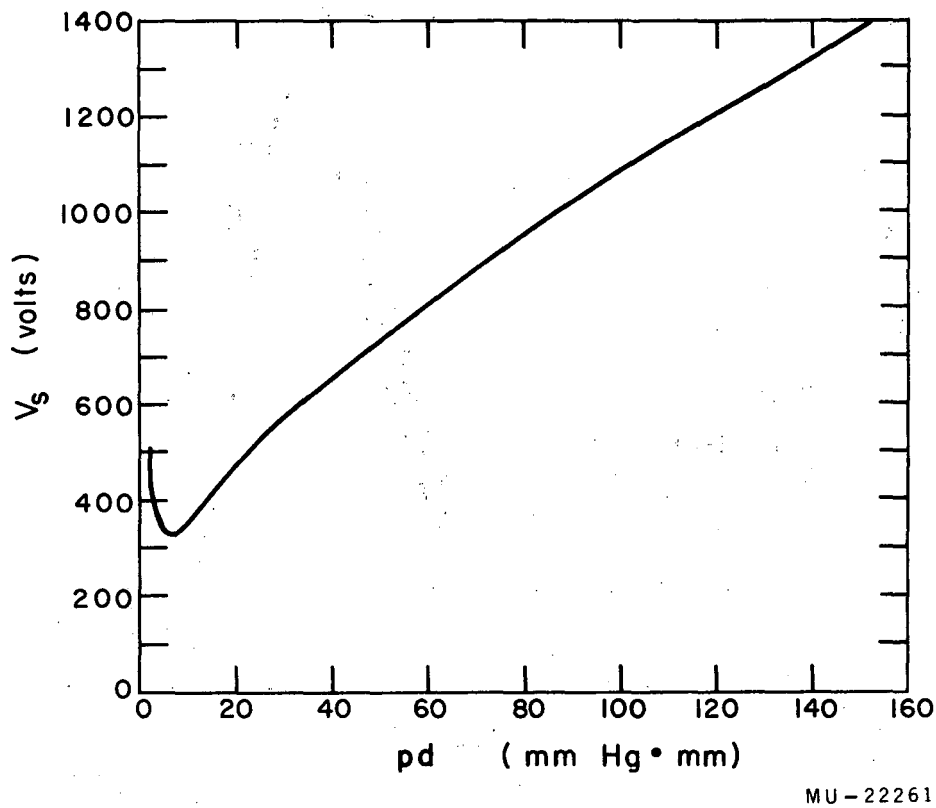

Fig. 1. The Sparking Potential for Air vs. the Product of the Pressure and the Distance between Electrodes. (From data given by Loeb (40)).

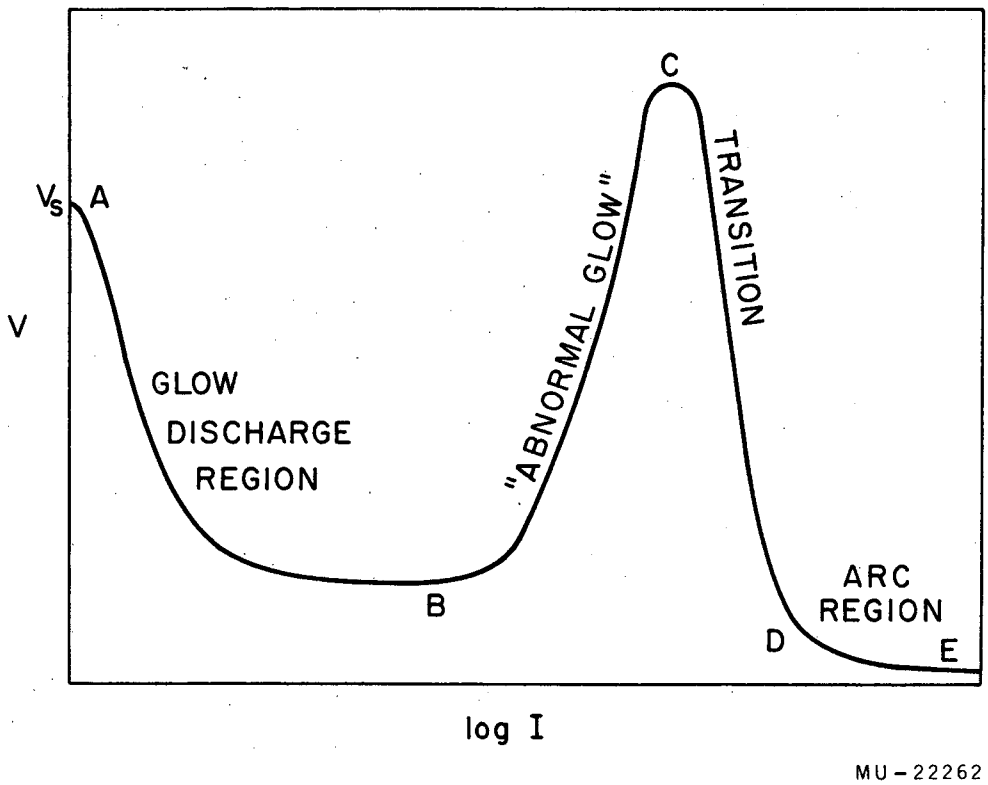

Fig. 2. The characteristic Voltage-Current Curve for a Discharge Tube.

densities, intense luminosities, and high temperatures (sometimes as high as $25,000^{\circ}$).

In some types of electrodeless discharge, the electrons and ions within the discharge zone are subject to an externally applied electromagnetic field. Then one speaks not of a potential between electrodes, but rather of an electric field strength. Since the latter quantity is difficult to measure, and since current loses its simple significance in such a discharge, the above-described criteria for glow and arc discharges are inapplicable. Under these conditions, one usually makes a qualitative distinction between the two types of discharge: an arc discharge is much hotter than a glow discharge. In this chapter we shall be principally concerned with discharges operated in the glow discharge region.

GLOW DISCHARGES

"Electrode Discharges" -

Apparatus; Circuit stabilization. The classical glow discharge tube consists of a glass tube (perhaps 3 cm. diameter and 30 cm. long) at each end of which is an electrode with an electrical lead sealed through the glass wall of the tube. If a constant potential of several kilovolts is applied across the electrodes while the tube contains a gas at atmospheric pressure, no appreciable current will pass. However, if the tube is gradually evacuated, pd will eventually reach a value such that V_s equals the applied potential, and a spark will pass between the electrodes. If there is no impedance in the circuit between the discharge tube and the source of potential, the current will quickly grow either until some part of the circuit breaks down (e.g., a fuse blows or the electrodes melt away), or until the current is stabilized in the "abnormal glow" region of the characteristic curve (Fig. 2), where the voltage increases with increasing current. It is almost always the first of these alternatives that happens, since most apparatus is not designed for the large currents beyond point B in Figure 2.

However, consider the resistance-stabilized D.C. circuit pictured in Figure 3. Here $E = V + IR$, where E is the overall potential supplied to the circuit and R is the resistance of the variable resistor. It will be noted that the current through the discharge tube may be regulated either by adjusting R, the variable resistance or by changing E, the overall potential. Although E must be at least as great as V_s in order to start a discharge, E may be reduced to values considerably less than V_s after the discharge has

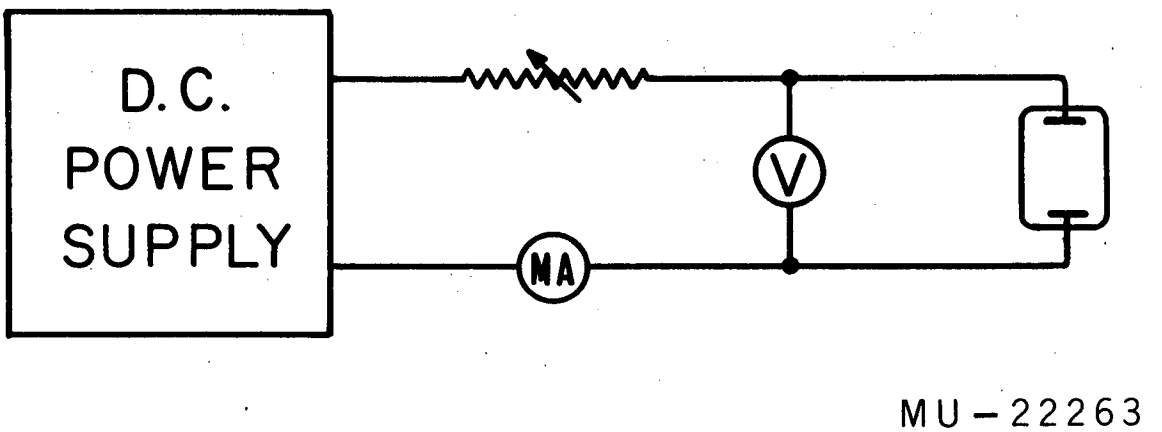

Fig. 3. A Resistance-stabilized D.C. Discharge Circuit.

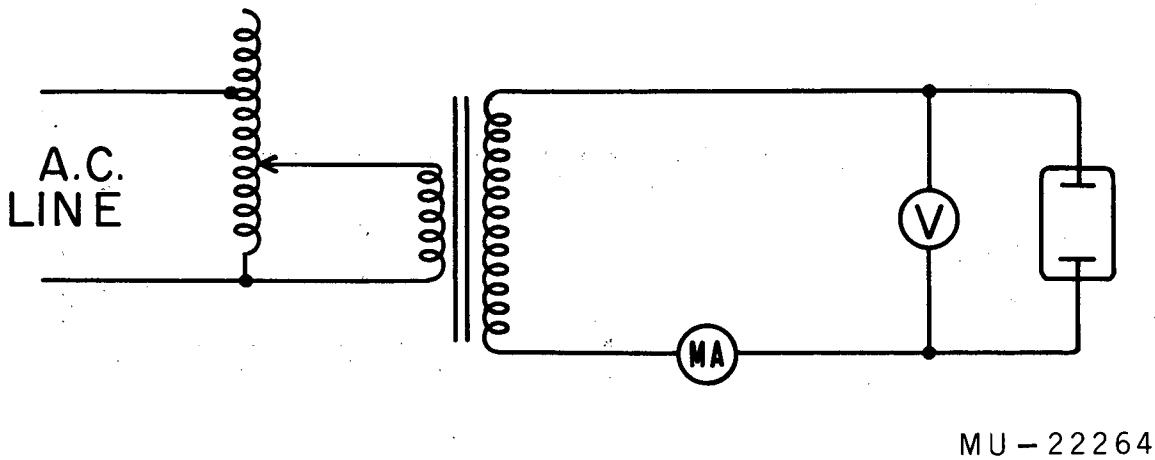

Fig. 4. A Typical A. C. Discharge Circuit.

been established. The voltmeter pictured in Figure 3 is preferably of the moving coil type and graduated such that the highest voltage likely to be used is about 3/4 of full scale (generally about 2 or 3 kilovolts). (The range of a voltmeter may be readily extended by adding an appropriate resistance in series with the meter.) The milliammeter should be of low resistance and capable of handling any anticipated current. (Most electrode discharge tubes operate with currents less than 500 milliamps.) The circuit should be suitably fused for protection of the milliammeter and the discharge tube.

Most glow discharge tubes are operated with alternating current supplied by a high voltage transformer. A typical set-up is shown in Figure 4. Here the output voltage of the high voltage transformer is controlled by means of an autotransformer which permits adjustment of the voltage applied to the primary winding. When the power for a discharge tube is supplied by a transformer, it is usually unnecessary to include a resistor in the circuit for current stabilization, since the leakage inductance and resistance of the secondary coil of the transformer provide sufficient impedance in the circuit to prevent the current from increasing without bound. A typical luminous tube transformer (110 v. primary/24,000 v. secondary) has a secondary coil impedance of 20,000 ohms.

The voltmeter across the discharge tube is preferably of the rectifier type (essentially a d.c. meter provided with a rectifier for converting the a.c. to d.c.) Such a meter, if it is to measure potentials above one kilovolt, must usually be in series with some known resistance. A series resistance of 20 megohms is typical for a full scale reading of 20 kilovolts. In

the absence of a voltmeter and milliammeter in the secondary (high voltage) circuit, one may use a voltmeter and ammeter in the primary coil circuit. If the voltage ratio of the high voltage transformer is known, a measurement of the voltage applied by the autotransformer permits one to estimate the voltage across the discharge tube. Similarly, by measuring the current through the primary winding, one can make a rough estimate of the current passing through the discharge tube.

Wood-Bonhoeffer tubes. Wendt and Landauer (78) found that an unusually reactive form of hydrogen was formed by the passage of hydrogen at low pressures through a discharge between metal electrodes separated by about 10 cm. They were able to detect reduction of the following species by the activated hydrogen: sulfur, nitrogen, arsenic, phosphorus and permanganate. They noticed that this activity of the hydrogen was catalytically destroyed by the action of various finely divided metals. Unfortunately, they incorrectly explained these phenomena in terms of triatomic hydrogen, H_3. Wood (82) and Bonhoeffer (5) studied the reaction of hydrogen in a similar discharge tube and correctly explained their results in terms of atomic hydrogen, H. Besides studying the reactions of atomic hydrogen with various substances, the latter investigators examined the spectrum of the glow discharge and were able to observe the Balmer series spectrum of atomic hydrogen.

The discharge tubes pictured in Figure 5, which are often called Wood-Bonhoeffer tubes, are characterized by discharge paths of one or two meters length. To operate a discharge tube of this type, a potential of 2 or 3 kv is required at 60 cycles. For hydrogen at a pressure of 0.5 mm., the current

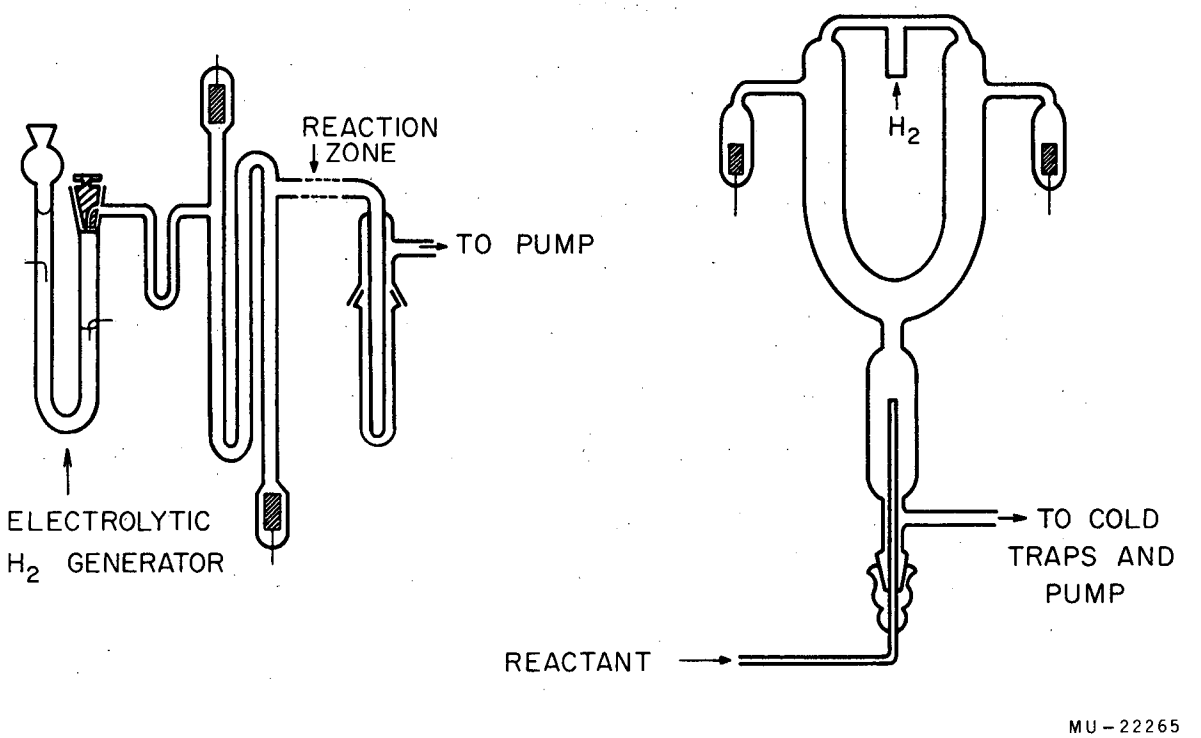

Fig. 5. Glow Discharge Tubes of the Wood-Bonhoeffer Type for Studying Reactions of Atomic Hydrogen.

is approximately 100 ma. The electrodes are usually cooled by fans, but it is also possible to use water-cooling (77).

The atomic hydrogen which forms in the discharge reacts to form molecular hydrogen much more slowly than would be expected from a consideration of bimolecular collisions. For example, under the conditions of most Wood-Bonhoeffer tubes, the half-life of the atomic hydrogen is about 0.3 second. This permits one to pump the atomic hydrogen from the discharge zone distances as great as a meter or so, and the atomic hydrogen may then be allowed to react with other gases, liquids or solids outside of the complicating discharge zone. The longevity of atomic hydrogen is explained by the fact that it recombines by a three-body collision, a rather rare event in a gas at a pressure less than 1 mm.

$$H + H + M \longrightarrow H_2 + M.$$

The third body (which may be molecular hydrogen or the wall of the apparatus) serves to carry off some of the heat of reaction, which amounts to 104.2 kcal/mole for the reaction as written. Similar mechanisms explain the longevity of other atomic species, such as atomic oxygen, chlorine, etc. It has been recommended that the inner walls of the discharge tube be coated with various substances such as syrupy phosphoric acid (50, 69) or Dry-film (81) (a mixture of dimethyldichlorosilane and methyltrichlorosilane). The increased yields which have been observed with such coatings have been ascribed to a reduction in the activity of the wall in catalyzing the recombination reaction. Most workers have found that a small amount of

moisture is beneficial to the formation of atomic hydrogen in a Wood-Bonhoeffer tube. The usual procedure is to use hydrogen which has been saturated at one atmosphere pressure with water at room temperature.

Atomic hydrogen (as well as other atoms and radicals) may be detected in a number of ways, including the calorimetric measurement of the heat of the catalyzed recombination, mirror removal, para-ortho hydrogen conversion and electron spin resonance. These and other methods are discussed by Steacie (63), whose monograph may be consulted for further information. A particularly accurate device for determining atom concentrations is the Wrede gauge (52, 83). With this gauge, the stream of atoms and molecules is led past a capillary whose diameter is smaller than the mean free path of the gas. Under these conditions, gas passes through the capillary only by diffusion. Since the glass surface of the capillary strongly catalyzes the recombination of the atoms, only molecules exist at the end of the capillary. Recognizing that, at steady state conditions, the rate of diffusion of gas through the capillary is the same in both directions, we calculate

$$n = \frac{100\,(P_1 - P_2)}{P_1\,(1 - 0.5\sqrt{2})}$$

where n is the volume percent of atoms and P_1 and P_2 are the pressures in the main gas stream and at the end of the capillary, respectively. Thus, by measuring these pressures with two Pirani gauges (one in the stream of atoms and one at the end of the capillary), the concentration of atoms may be determined. By the use of electrode glow discharges in hydrogen streams at

several tenths of a millimeter pressure, atom concentrations (as measured with a Wrede gauge) as high as 60 volume % have been observed.

Atomic oxygen may be produced in an electrode discharge in much the same way as is atomic hydrogen. However, in this case the electrodes not only act at catalytic surfaces for the recombination of the atoms, but in many cases they undergo oxidation and thus introduce impurities in the system. For these reasons atomic oxygen is generally prepared with electrodeless discharges (see Page 45).

When nitrogen is excited in certain types of discharge tubes, it exhibits greatly enhanced chemical activity and a yellow glow which persists after the excitation is removed, sometimes remaining visible for an hour or more. The afterglow consists of well-known band spectra of the nitrogen molecule. An enormous literature exists on the subject of active nitrogen, and it now appears established that the essential component of active nitrogen is atomic nitrogen (31). The longevity of this species is explained by the necessity of three-body collisions in bringing about recombination of the atoms.

In an ordinary electrode discharge nitrogen is dissociated to its atoms to the extent of only a few percent. However, yields of approximately 35% may be obtained by the use of an intermittent, or pulsed, discharge (17, 22, 25). A circuit for this type of discharge is pictured in Figure 6. Typically, a 3-5 kv. d.c. power supply charges a 5 μf. capacitance through a 20,000 ohm resistance. Depending on the sparking potential of the discharge tube and the applied voltage, an intense discharge will pass through the discharge tube 4 to 10 times per second. Sometimes an air spark gap is included in series with the

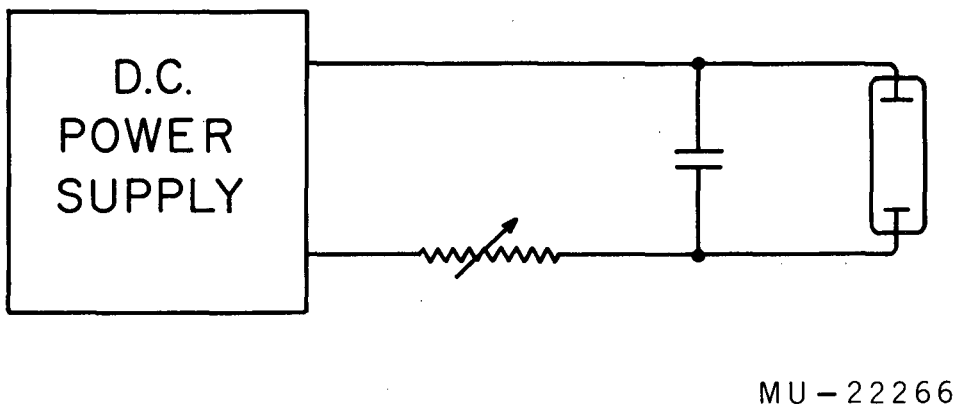

Fig. 6. A Pulsed-Discharge Circuit.

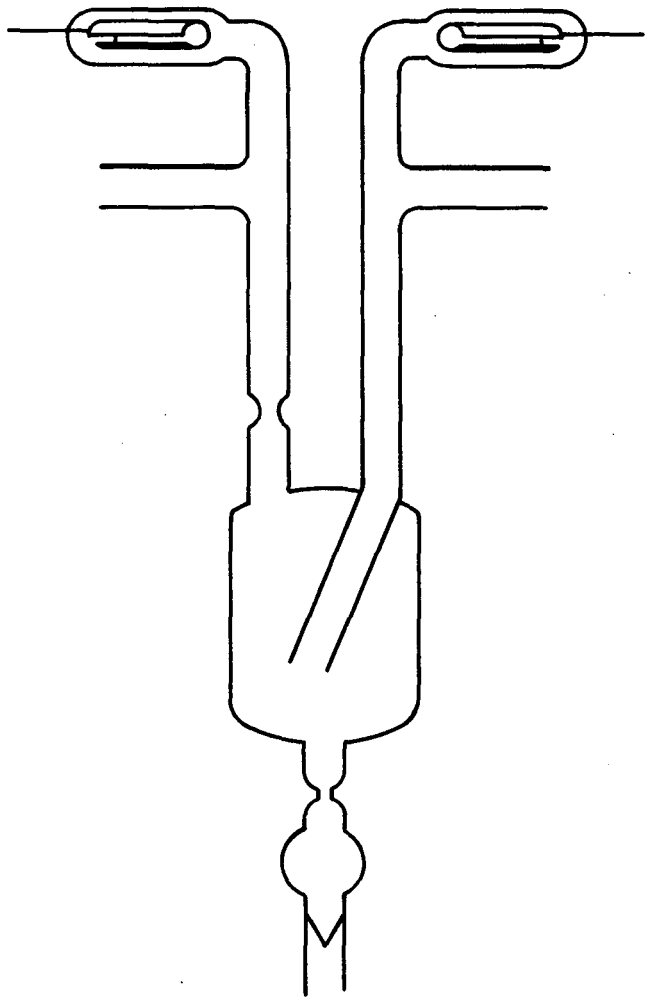

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Fig. 7. Discharge Tube for Preparing $(SiCl_3)_3N$.
(Pflugmacher and Dahmen)

discharge tube. The length of the spark gap is then another variable for controlling the discharge frequency. No good explanation has been given for the unusual effectiveness of the pulsed discharge in dissociating nitrogen.

Pflugmacher and Dahmen (48) prepared tris-trichloro-silylamine, $(SiCl_3)_3N$, by passing an equimolar mixture of nitrogen and silicon tetrachloride vapor through the discharge tube shown in Figure 7. The middle of the discharge path consisted of a trap to whose bottom was sealed a small bulb with a break-seal attached and whose inlet tube had a constriction for slowing the gas flow. After passing the gases at a pressure around 0.5 mm through the discharge for 25-40 hours, about 5 ml of a crude product collected in the small bulb. After sealing off the bulb and then attaching it to a suitable fractional condensation train, the $(SiCl_3)_3N$ was separated from a series of intractable polymeric materials. Two distinctly different modifications of $(SiCl_3)_3N$ were found: a stable form with a melting point of 78° and an unstable form with a melting point of 44°.

Schenk and his coworkers (10, 53) were the first to study the reactive sulfur oxide which forms when a stream of sulfur dioxide and sulfur vapor is passed through an electrode discharge. Meschi and Myers (44A) showed that the compound formed was disulfur monoxide, S_2O. These latter investigators used an apparatus due to Jones (33) which is pictured in Figure 8. In order to maintain an appreciable concentration of sulfur vapor in the discharge, the discharge tube was heated to 150° with a winding of resistance wire. It was necessary to have an air gap between the winding and the discharge tube in order to prevent the discharge from puncturing the glass walls to the resistance wire. The air jacket also served as an air thermometer. Gaseous disulfur

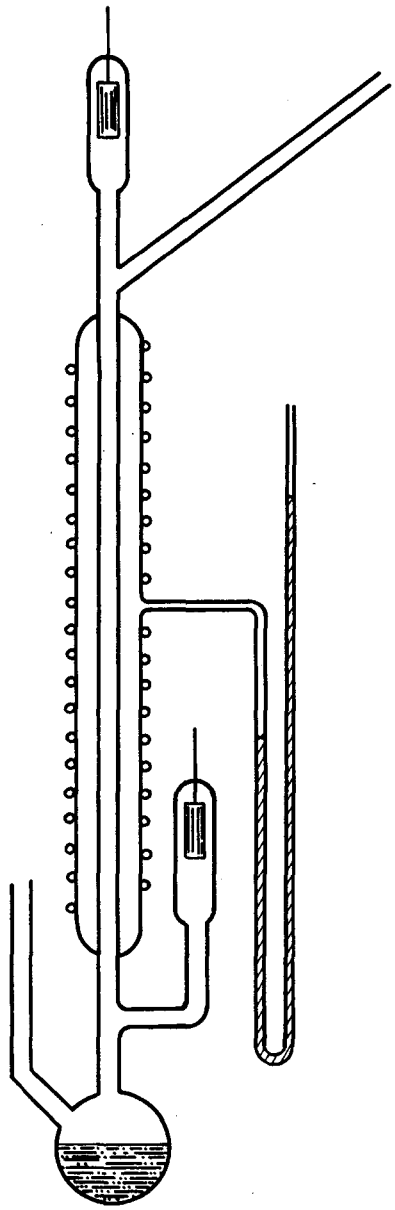

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Fig. 8. Discharge Tube for Preparing Disulfur Monoxide (Jones (33)).

monoxide is stable for hours at pressures of a few mm of mercury, but at pressures above 30 mm. it rapidly decomposes to sulfur and sulfur dioxide.

Mercury discharge tubes. If a glow discharge is established between two pools of mercury (which serve as electrodes) and the mercury is allowed to become warm, an appreciable amount of mercury vapor will be present in the gaseous discharge zone. Under the discharge conditions, this mercury vapor can reduce various non-metal chlorides to give mercurous chloride and polymeric chlorides of the non-metal.

Urry, Wartik, Moore and Schlesinger (68) prepared diboron tetrachloride (B_2Cl_4) and tetraboron tetrachloride (B_4Cl_4) by passing boron trichloride vapor through the mercury discharge tube pictured in Figure 9. The auxiliary apparatus pictured was used to automatically and repeatedly pass the boron trichloride through the discharge tube. In the following sentences we paraphrase the authors' description of the operation of the apparatus: Liquid boron trichloride was present in bulb A at -80°, at which temperature its vapor tension is 4 mm. During the downstroke of the mercury piston the boron trichloride evaporated from the bulb and passed through the discharge cell into the upper chamber of the mercury circulating pump. During this stage the electrical discharge was not operating. On the upstroke of the piston most of the boron trichloride in the upper chamber was forced back through the cell in which the discharge had then been established. The diboron tetrachloride formed during this stage, together with traces of other subchlorides and with unchanged boron trichloride, was condensed in bulb A. On the succeeding stroke of the piston, only the boron trichloride evaporated

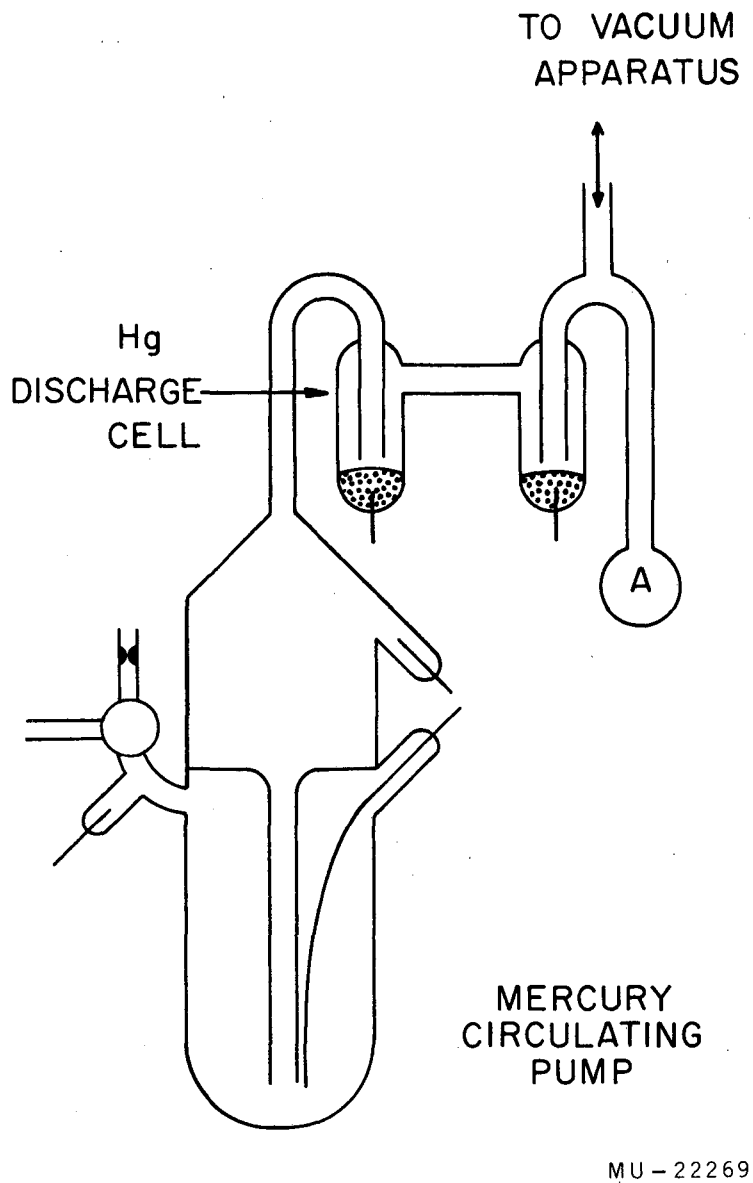

Fig. 9. Mercury Discharge Tube and Auxiliary Apparatus for Preparing B_2Cl_4 and B_4Cl_4. (Urry, Wartik, Moore and Schlesinger (68)).

from the bulb, since the subchlorides are essentially nonvolatile at -80°.

With continuous operation of such an apparatus, the authors obtained one gram of diboron tetrachloride (together with about 3 mg. of tetraboron tetrachloride) per week. The optimum voltage (60 cycle) was about 1000 v. for a 4 cm. path.

Using a similar apparatus, Finch (15) prepared diphosphorus tetrachloride (P_2Cl_4) from phosphorus trichloride. And Urry (67) similarly prepared various liquid perchloro polysilanes from silicon tetrachloride. When akyl chlorosilanes are passed through a mercury discharge, long reaction flames are observed and high yields or silicon-carbon chain compounds are obtained (67). It is believed that this type reaction proceeds by a free radical chain mechanism.

Wartik (75) has shown that the boron subchlorides may be prepared in yields around one gram per hour by using the discharge tube pictured in Figure 10. Here metallic copper, in the form of copper wool, serves as the reducing agent for the boron trichloride.

"Glow-discharge Electrolysis."

A glow-discharge electrolysis is an electrolysis in which one electrode is immersed in an electrolytic solution and in which the other electrode is suspended in the gas phase over the electrolytic solution. A typical apparatus for the glow-discharge electrolysis of aqueous solutions is shown in Figure 11. The suspended electrode is usually a platinum wire placed about 8 mm. over the surface of the solution. The electrolysis is carried out under reduced pressure (approximately the vapor pressure of the solution); during

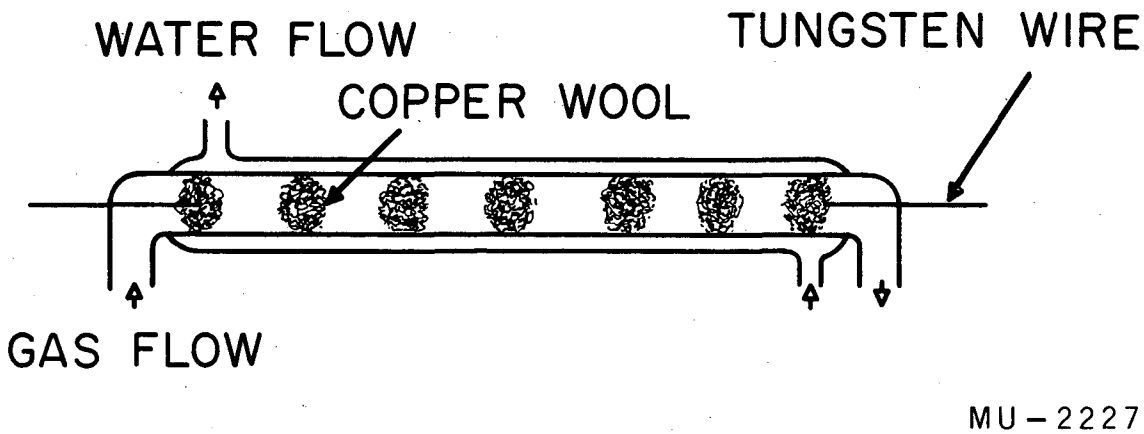

Fig. 10. Discharge Tube used for Preparing B_2Cl_4. (Wartik (75)).

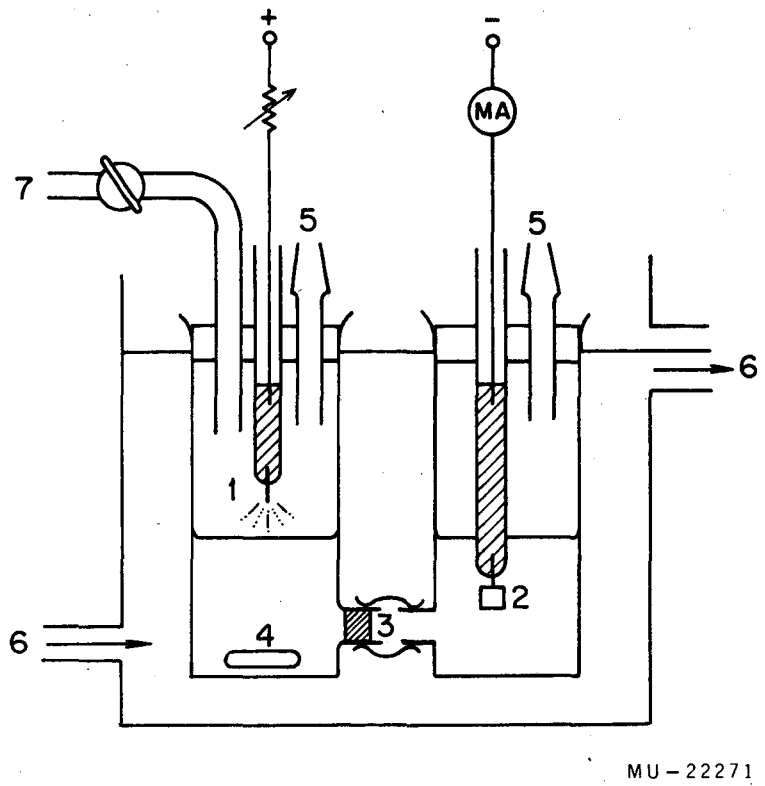

Fig. 11. Apparatus for Glow-Discharge Electrolysis of Aqueous Solutions. (Denaro and Hickling (14)).
(1) gas-phase electrode, (2) liquid phase electrode, (3) porous plug, (4) magnetic stirrer, (5) connections to vacuum line, (6) cooling water, (7) gas supply.

the electrolysis a cone-shaped luminous discharge is established between the gas-phase electrode and the solution. Direct current voltages between 500 and 1000 volts are usually applied across the cell; currents of 25 to 100 milliamps are usually observed. The discharge is initiated either by momentarily tipping the cell in order to make direct contact between the gas phase electrode and the electrolyte or by momentarily applying a high voltage a.c. pulse.

When the suspended electrode is made the anode (positive), chemical effects far in excess of those predicted by Faraday's Law are observed. Thus when an aqueous solution of an inert electrolyte such as $NaHCO_3$, Na_2HPO_4 or K_2SO_4 is electrolyzed, from 1.3 to 1.9 equivalents of hydrogen peroxide are formed per faraday of current (13). Electrolysis of aqueous sulfuric acid has given a mixture of hydrogen peroxide, peroxymonosulfuric acid and peroxydisulfuric acid in a total yield of 12 equivalents per faraday (35). Electrolyses of 0.3 M solutions of oxidizable species such as the ferrous, azide, ferrocyanide and cerous ions result in oxidation of these species to the extent of 5 to 7 equivalents per faraday (14). It is believed that these oxidations are caused by OH radicals which form from collisional processes in the discharge and at the solution-gas interface.

In the glow-discharge electrolysis of an ammonium nitrate solution in liquid ammonia (using a positive gas-phase electrode), hydrazine forms in yields of 2.5 moles of hydrazine per faraday (27, 29). When alternating current is used, yields of only 1.3 moles per faraday are obtained, indicating that hydrazine is only formed during the half-cycle when the gas-phase electrode is positive.

The glow-discharge electrolysis of liquid sulfur dioxide containing about 1% water gives both sulfur (4.2-8.5 g. atoms per faraday) and sulfuric acid (6.5-13.9 moles per faraday) (8A).

Electrodeless Discharges -

Capacitive coupling. If, instead of sealing electrodes through the glass walls of a discharge tube, the electrodes are simply placed on the outside wall, a discharge may still be established if alternating current is used and if the voltage is high enough. Placing the electrodes on the outside wall surface amounts to adding capacitors in series with the discharge circuit. The capacitance of two parallel plates of equal area may be calculated from the formula $C = 8.84 \times 10^{-14}$ KA/d where C is the capacitance in farads, K is the dielectric constant of the material between the plates, A is the area of one plate in cm^2, and d is the separation of the plate surfaces in cm. The capacitive reactance may be calculated from the formula $X_c = 1/2\pi fC$, where X_c is the capacitive reactance in ohms, f is the frequency in cycles per second and C is the capacitance in farads. Thus, when using capacitive coupling in a discharge circuit, it is advantageous to make the electrode areas large, to use thin glass walls, and to use a high frequency current source.

Metal foil is commonly used as the electrode material, although thin coats of Aquadag (a highly conductive paint consisting of a suspension of graphite particles) (18), mercury (51), or electrolytic solutions (71, 73) may also be used. When it is necessary to keep the discharge tube (including the electrode area) cold, it is convenient to use the cooling bath itself as an electrode. Thus, a 1% solution of concentrated hydrochloric

acid in acetone is a reasonably good conductor and freezes around -95°.

Although power supplies of radio frequency have been used with capacitive coupling (18), it is commoner to use the regular line frequency of 50 or 60 cycles per second. The usual discharge tube consists of two concentric glass tubes between which the discharge is established. This type device is called a Siemens ozonizer (or ozonator). A typical set-up is pictured in Figure 12. The capacitive reactance of an ordinary ozonizer is usually around 50 megohms, or several orders of magnitude greater than the impedance of the transformer. Therefore it is unnecessary to have any stabilizing resistance in the circuit. The ozonizer is usually used with applied potentials between 5 and 20 kv, and currents up to 5 ma are drawn.

Since the interesting products of most discharge syntheses are rather unstable molecules, it is important that the reaction products be removed from the discharge zone as rapidly as possible. For this reason, most syntheses are carried out in flow systems where the gases are rapidly passed through the discharge. Several syntheses of this type are dicsussed in the following paragraphs.

The most important application of the electric discharge (both industrially and in the laboratory) is the preparation of ozone. Oxygen or air, at one atmosphere pressure, is passed through a Siemens ozonizer or between two parallel glass plates with the electrodes on the outer surfaces. During the discharge, the gas space is filled with a diffuse glow which has been described as a series of brush discharges (21). The over-all discharge is actually intermittent; during each cycle of the alternating current there are two discharge periods and two dark periods. Oscillographic studies have shown that, during

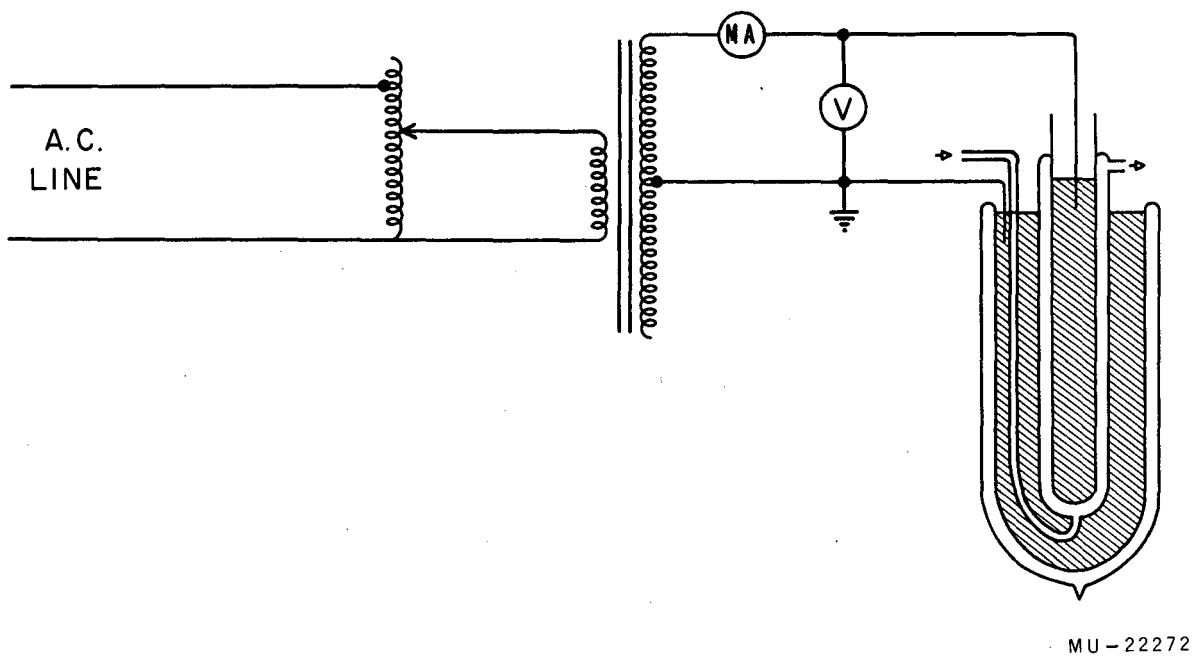

Fig. 12. Typical Siemens Ozonizer Set-up.

the discharge periods, the potential across the gas space is constant. The power input to an ozonizer may be calculated from the relation

$$W = 4fC_d e_0 \left[e_m - (C_g/C)\, e_0 \right]$$

where W is the power, f is the frequency, C_d is the capacity across the dielectric walls, C_g is the capacity of the discharge gap, C is the over-all capacity, e_0 is the discharge potential across the gas, and e_m is the peak voltage applied across the electrodes (42).

The conversion of oxygen to ozone is increased by raising the power input, but the increase in yield is less than proportional unless the flow rate is increased so as to maintain a constant ozone concentration. If oxygen is replaced by air, both the concentration and the energy yield of ozone are approximately halved. The presence of moisture has a very deleterious effect; as little as 0.02 mg of water per liter of gas can measurably reduce the yield of ozone. The lower the temperature of the ozonizer, the higher is the concentration of ozone (24).

A simple method for adapting an all-glass distillation condenser for use as an ozonizer has been described (38, 59). A more efficient laboratory ozonizer, capable of producing 8% (by weight) ozone with an oxygen flow of 5 to 6 liters per hour has also been described (79). A commercially available laboratory ozonizer (Welsbach Model T-23) produces 2% (by weight) ozone with an oxygen flow of 200 liters (S.T.P.) per hour (47). With lower flow rates, concentrations as high as 6% can be obtained. The energy efficiency of the best commercial ozonizers is about 140 g./ kw-hour, using oxygen (24).

Benson and Axworthy (4) have discussed the mechanism of formation and decomposition of ozone in an ozonizer. They propose three processes for the formation of ozone: the combination of atomic oxygen and molecular oxygen (Equation 1), a collisional de-excitation reaction (Equation 2), and a dissociative recombination of ions (Equation 3).

$$O + O_2 + M \longrightarrow O_3 + M \qquad (1)$$

$$O_2^* (^3\Sigma_u^+) + O_2 \longrightarrow O + O_3 \qquad (2)$$

$$O_2^- + O_2^+ \longrightarrow O + O_3 + \text{energy} \qquad (3)$$

They believe that ozone is destroyed in the discharge both by electron bombardment

$$O_3 + e^* \longrightarrow O + O_2 + e$$

and by thermal decomposition. Thus it is clear why over-all ozone yields increase with both increasing flow rate and decreasing temperature. The atomic oxygen which does not form ozone recombines to form molecular oxygen:

$$O + O + M \longrightarrow O_2 + M$$

Andreev (2) flushed the vapors of methyltrichlorosilane through an ozonizer-type discharge tube with a stream of hydrogen which finally passed through cold traps to collect the product. A mixture of polychloromethylsilanes containing chains of alternating silicon and carbon atoms was formed in yields

of about 50%. By fractional distillation of the liquid product, 1,1,1,3,3-pentachloro-1,3-disilabutane ($CH_3Cl_2Si-CH_2SiCl_3$), 1,1,1,4,4-pentachloro-1,4-disilapentane ($CH_3Cl_2Si-CH_2-CH_2-SiCl_3$), and various compounds of composition $C_3H_7Cl_7Si_3$ and $C_4H_9Cl_7Si_4$ were obtained. Andreev proposed a reaction mechanism involving CH_3 and $SiCl_3$ radicals and H atoms.

Kotlensky and Schaeffer (38) swept diborane (B_2H_6) through an ozonizer with a stream of helium and collected the condensible products in cold traps beyond the discharge. By fractional condensation it was possible to separate the products: B_4H_{10} (40% yield), B_5H_9 (20% yield), B_5H_{11} (30% yield), and small amounts of B_6H_{10} and B_9H_{15}.

Sometimes the products of a discharge tube reaction have sufficiently low volatilities that, once formed, they condense out on the walls of the discharge tube and are then safe from bombardment by high energy electrons and ions. In such cases a "static" discharge system may be employed wherein the reactants are kept in the discharge tube until completion of the reaction or wherein the reactants are continually fed into the discharge tube at a rate equal to their rate of reaction. Several examples of these "static" syntheses in ozonizer-type discharge tubes are discussed in the following paragraphs.

Schwarz and Achenbach reported the synthesis of sulfur tetroxide, SO_4, by the reaction between pure O_2 and SO_2 in a glow discharge (57). Wannagat has shown that when commercial oxygen containing traces of nitrogen is used in the preparation, the product is highly contaminated with dinitrosyl disulfate, $(NO)_2S_2O_7$, the presence of which confuses the product analysis (70). Using electrolytically-prepared oxygen, Wannagat and his coworkers have shown that SO_2-O_2 and SO_3-O_2 mixtures react in static ozonizer-type tubes to form

solid, unstable polysulfur peroxides, $(SO_{3-3.9})_x$, whose O:S ratios are dependent on the $SO_2:O_2$ ratios in the reacting gas mixtures (71, 73). These compounds are believed to have structures similar to that of β-SO_3, but in which a variable number of the linking oxide groups have been randomly replaced by peroxide groups:

$$\cdots\ SO_2\text{-}O_2\text{-}SO_2\text{-}O\text{-}SO_2\text{-}O_2\text{-}SO_2\ \cdots$$

The apparatus used in these studies is pictured in Figure 13. It will be noted that provision was made for cooling the discharge tube.

Using a discharge tube similar to that in Figure 13, static mixtures of thionyl fluoride and oxygen (1:1) have been converted at -50° to a liquid mixture containing monoperoxy-tetrafluorodisulfur(VI) oxide ($S_2O_5F_4$) and monoperoxydifluorodisulfur(VI) oxide ($S_2O_6F_2$) (72). These compounds, whose boiling points are 57° and 67°, respectively, are believed to have the structures indicated below.

$$S_2O_5F_4:\quad F_3SO\text{-}O\text{-}O\text{-}SO_2F$$

$$S_2O_6F_2:\quad FSO_2\text{-}O\text{-}O\text{-}SO_2F$$

Treatment of 1:1 mixtures of phosphorus trifluoride and oxygen in the same type of static discharge at -60° to -75° gives a solid, white compound of the approximate composition $P_7O_{10}F_{15}$ (74). When this material is warmed to room temperature, the volatile compounds PF_5, POF_3, and $P_2O_3F_4$ and the non-volatile

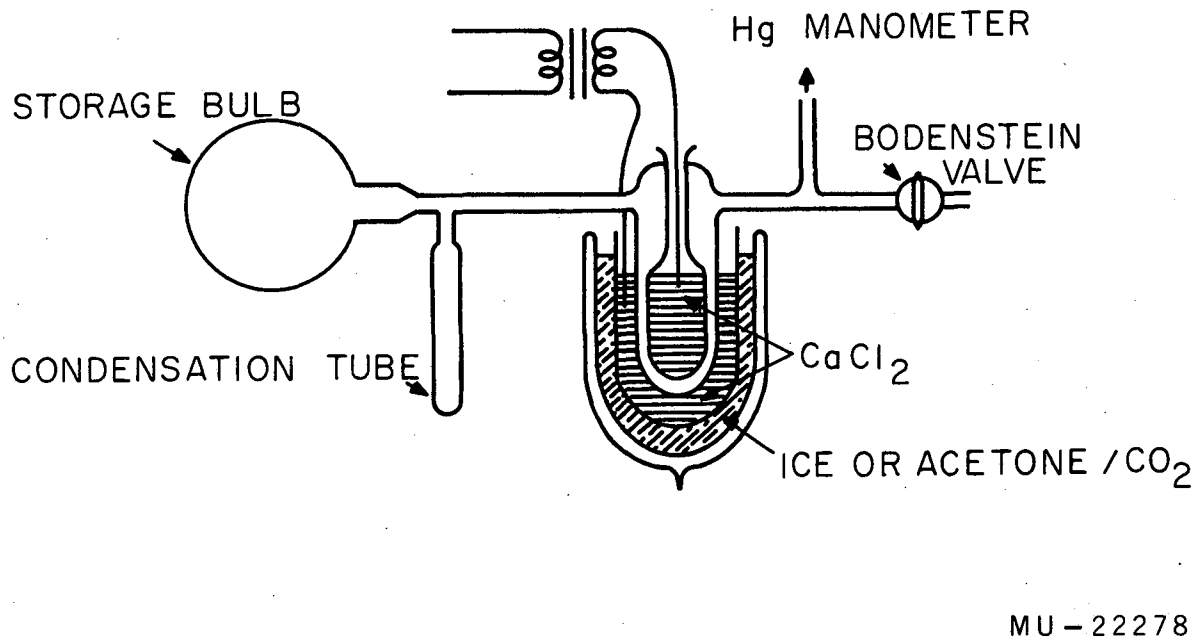

Fig. 13. Apparatus for the Preparation of Polysulfur Peroxides. (Wannagat et al).

polymer $(PO_2F)_x$ are formed. The latter two compounds are believed to have the structures indicated below.

$$P_2O_3F_4: \quad F_2PO\text{-}O\text{-}POF_2$$

$$(PO_2F)_x: \quad \cdots POF\text{-}O\text{-}POF\text{-}O\text{-}POF \cdots$$

Wartik and Rosenberg allowed a 3:1 mixture of carbon monoxide and boron trichloride to stand in an ozonizer discharge for 160 hours, during which time the pressure gradually decreased and a yellow film deposited on the walls of the discharge tube (76). From the observation that no boron trichloride and only about one-third of the original carbon monoxide remained in the gas phase, it was concluded that the solid had the composition $BCl_3 \cdot 2CO$. This polymeric material is believed to have a structure involving cross-linking of boron atoms by -O- groups, $-CCl_2-$ groups, and -CO- groups.

Organic compounds have been labeled with tritium by exposure of the compounds to tritium gas (80). A tremendous increase in the yield of labeled molecules is achieved by applying an external source of radiation during the tritium treatment (19). Lemmon and his coworkers (39) used the static ozonizer-type discharge tube pictured in Figure 14. By exposing 0.6 ml. of benzene to 40 millicuries of tritium in this discharge tube for one hour, 0.67 millicurie of activity was found to have been incorporated in 0.5 ml. of the purified benzene. Without the electric discharge, a total activity of only 4×10^{-5} millicurie would have been incorporated in the benzene.

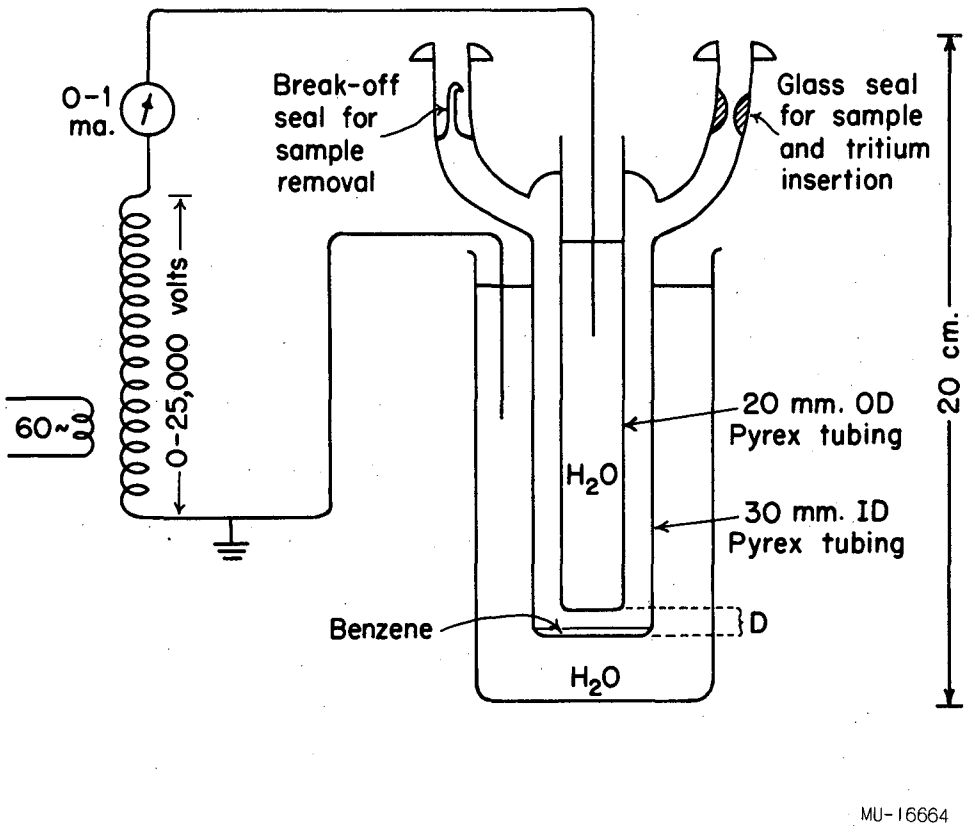

Fig. 14. Apparatus for Tritium Labeling of Benzene. (Lemmon et al (39)).

Inductive coupling. If a glass vessel containing a rarified gas is placed inside a solenoid through which an alternating current is passing, a discharge will be established if the current and frequency are sufficiently high. The electrons and ions in the gas will be accelerated by the rapidly changing magnetic field within the solenoid. Since the lines of magnetic force in the discharge tube are parallel to the axis of the solenoid, the charged particles in the discharge will be accelerated in circular paths around the solenoid axis. The energy which the electrons and ions acquire is proportional to the square of their distance from the axis (66). Hence, if the discharge tube is centered within the solenoid, the charged particles nearest the walls of the tube acquire the greatest energy. It is clear why this type of discharge is sometimes called a "ring discharge".

A very common form of electrodeless discharge tube consists of a glass tube passing through several turns of copper tubing, as shown in Figure 15. The copper tubing solenoid is supplied with power from a radiofrequency oscillator. The solenoid is usually an integral part of the oscillator circuit and its dimensions (number of turns, diameter, length) affect the actual frequency of the current. The efficiency of the coupling between the coil and the discharge is a function of the pressure of the gas and of the dielectric loss factor of the glass walls. If the gas pressure is too low, there are insufficient electrons and ions formed to give a highly conducting discharge phase; if the pressure is too high, the discharge may be quenched because of a too high sparking potential. Ordinarily, pressures around 0.5 mm of Hg are optimum for the production of radicals and atoms in discharge tubes. If the glass walls of the discharge tube are made of some glass like Pyrex

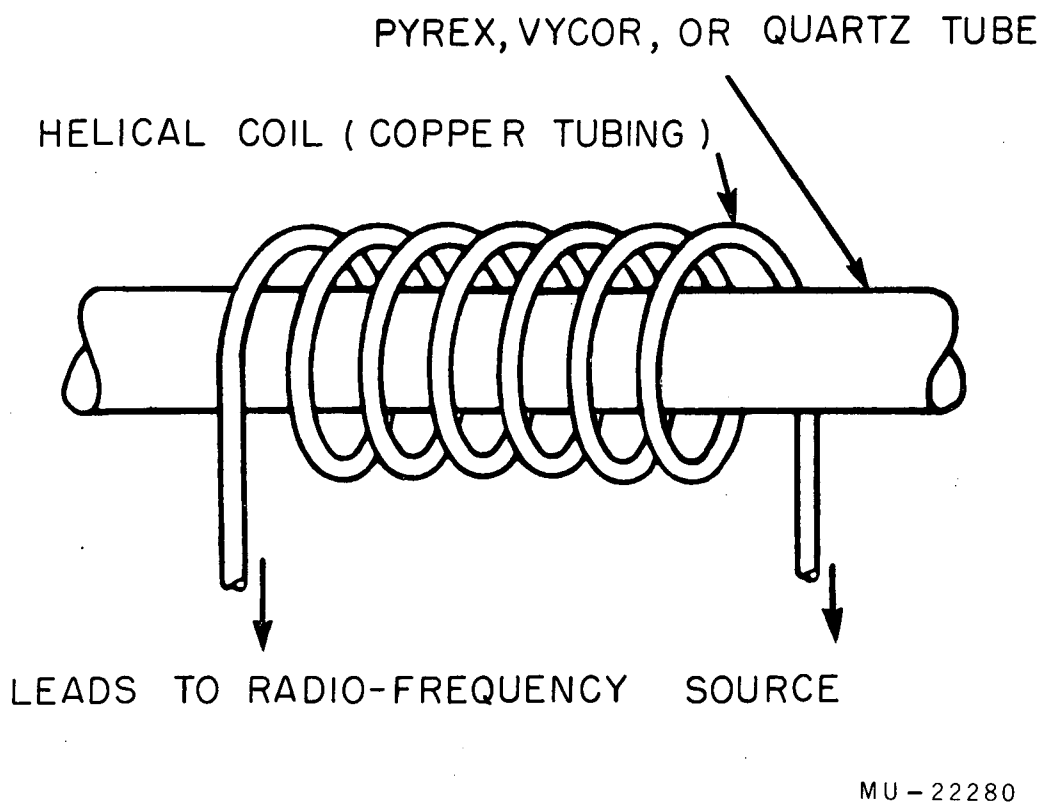

Fig. 15. Inductively Coupled Discharge Tube.

(loss factor = 2.1% at 1 mc/sec and 20°), a considerable amount of power from the oscillator will be wasted in dielectric heating of the glass. Thus not only is the glow discharge reduced, but the discharge reaction which is being studied may be deleteriously affected by the hot walls. If insufficient cooling is provided, the glass walls may melt and collapse. Silica glass is preferred over Pyrex not only because of its lower loss factor (0.04-0.2%) but also because of its higher melting point. Corning glass No. 7070 is a special low loss (0.24%) borosilicate glass which has the advantage that it may be sealed directly to Pyrex glass.

Oftentimes the discharge will spread throughout the vacuum system connected to the discharge tube, rather than remain in the vicinity of the coil. This spreading may be prevented by attaching copper foil strips directly to the outside glass walls (30).

Circuit diagrams for radio frequency power supplies have been published (8, 23, 54, 61), but many commercially available radio transmitters are quite satisfactory as power supplied for inductively coupled discharge tubes.

Jennings and Linnett (30) used a solenoid discharge tube (with a 9.7 mc/sec. oscillator of 350 watts power) to produce hydrogen atoms in a stream of hydrogen at 0.08 mm pressure. They found an atom concentration (as determined with a Wrede gauge) of 50-60% about 25 cm. downstream from the discharge.

Schumb, Gamble and Banus found that when boron triiodide was sublimed at a pressure of 1-3 mm. through a solenoid discharge tube powered by a 5 mc/sec. transmitter, diboron tetraiodide (B_2I_4), a lower iodide of boron (B_xI_y, with $x > y$), and free iodine were formed (55). The lower iodides of boron condensed out in the discharge tube and near its exit; the unreacted

boron triiodide and iodine condensed out in a liquid nitrogen trap. Forty percent of the boron triiodide decomposed in one pass; one third of the decomposed boron triiodide was recovered as diboron tetraiodide. B_2I_4 is a pale yellow solid which slowly disproportionates at room temperature:

$$B_2I_4 \longrightarrow BI_3 + 1/X\ (BI)_x.$$

Schumb and Rogers (56) found that the vapor of aluminum (III) iodide may be converted by a solenoid discharge to iodine and a product of empirical composition $Al_{1.22}I$. This material was believed to be a mixture of aluminum and some subiodide such as $(A\ell I)_x$.

Microwave discharges. If a microwave generator is coupled to a hollow metal container, standing waves will be established, whose pattern depends on the shape and dimensions of the cavity. Resonance cavities which are used for the excitation of discharge tubes are generally in the shape of cylinders, with the radiation being introduced from coaxial tubing via a loop. Since the glass discharge tube is usually placed along the axis of the cylindrical cavity, it is desirable that a mode of oscillation be established wherein the electric field lines near the center are parallel to the cavity's axis. This condition is fulfilled in the TM_{01} mode, for which it is required that the radius of the cylinder be equal to 0.383 λ, where λ is the wavelength of the microwave radiation (1, 20, 49). If the radiation enters from a coaxial wave guide at a point midway between the ends of the cylinder, it is best to have the loop (an extension of the inner conductor of the coaxial line) parallel to the

cylinder's axis, so that it is also parallel to the electric lines of force (1).

The comments which were made regarding the dielectric loss factor of the glass tubing used for solenoid discharge tubes (see above) applies equally well here.

Magnetrons are commonly used as microwave sources. Raytheon QK 60 and QK 61 magnetron tubes (which have been available as Navy surplus) are useful 50 watt sources of 10 cm. microwaves. One need simply provide filament voltage and a d.c. power supply with a voltage variable between 1000 and 1500 volts. Commercial diathermy units are convenient, self-contained microwave generators. The units manufactured by Raytheon Manufacturing Co. (Waltham, Mass.) and by Baird Associates, Inc. (Cambridge, Mass.) operate at a wavelength of 12.2 cm. with power outputs of approximately 100 watts. The Raytheon unit is pictured in Figure 16.

Microwave discharges have, in common with all electrodeless discharges, the advantage of having no metal electrodes in the discharge zone. McCarthy (41) has pointed out that microwave discharges have two unique advantages over other types of discharge with respect to chemical syntheses: (1) For many gases, a microwave discharge, after being initiated at a low pressure (5-30 mm Hg), persists as a glow discharge even if the pressure is increased above atmospheric. (2) The energy efficiency of a microwave discharge for radical production is much greater than that of other types of discharge. (This latter assertion has been challenged by Shaw (58)). McCarthy studied the energy yield of nitrogen, oxygen, and hydrogen atoms as a function of several variables such as the electric field strength and the pressure. He used a commercial generator which delivered up to 1500 watts of microwave

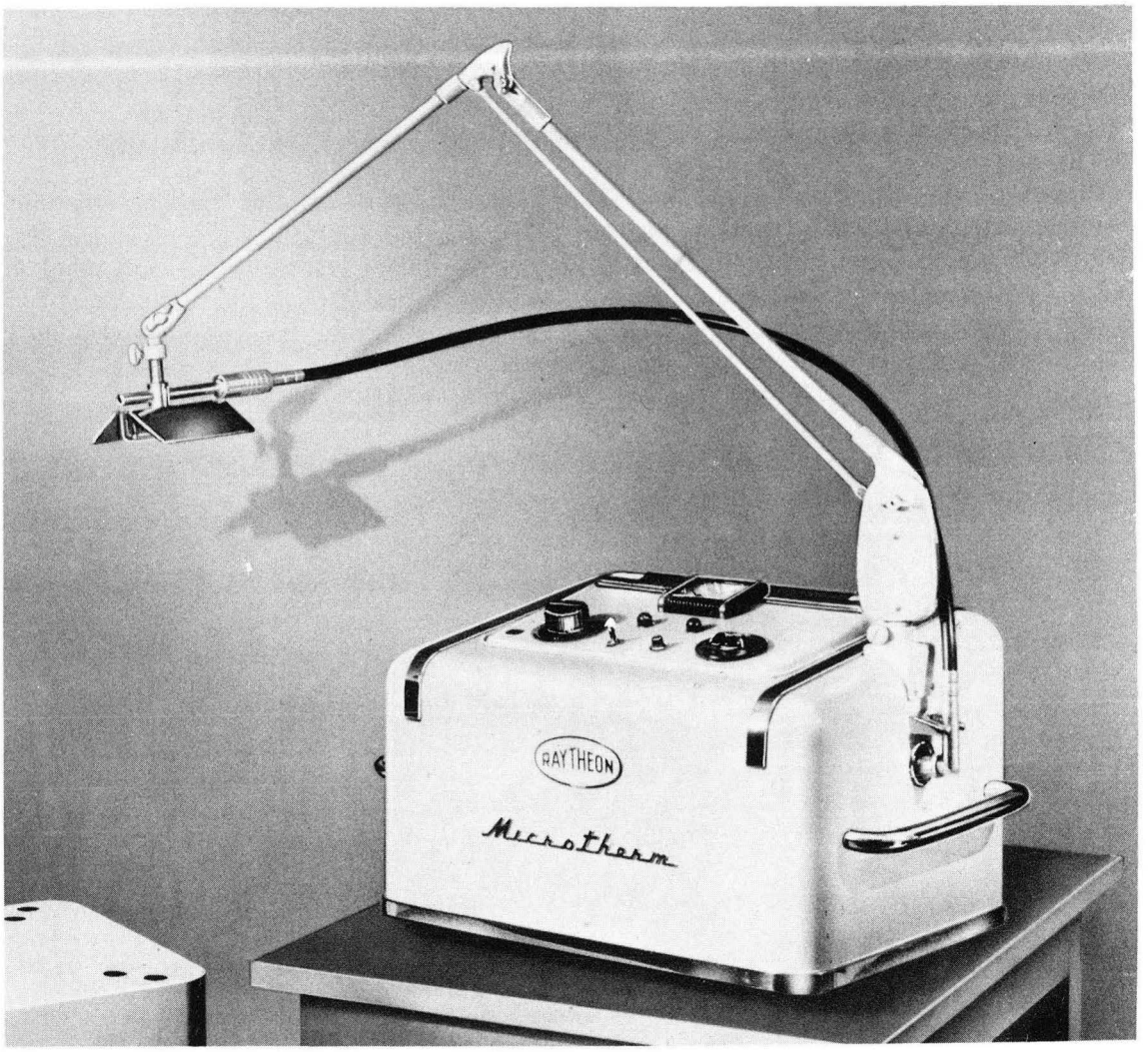

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Fig. 16. Microwave Power Generator. (Raytheon Model KV 104(NB); photograph courtesy of the Raytheon Manufacturing Co.).

power at a frequency of 2464 mc/sec. His best energy yields were 0.58 g atom/kw-hr for nitrogen, 0.80 g atom/kw-hr for oxygen, and 1.0 g atom/kw-hr for hydrogen. These yields are based on calorimetric determinations of the radicals, and may be too high because the calorimetric method cannot distinguish excited molecules from atoms. Nitrogen dioxide was prepared from air with a maximum yield of 0.77 mole/kw-hr. It was found that the reaction was most efficient when the energy supplied was just sufficient to sustain the discharge. At this point, the rate of production of electrons equaled their rate of diffusion to the walls. The production of excessive electrons reduces the efficiency, because then many electrons lose an appreciable amount of energy to the walls in high energy collisions.

Kaufman used a 700 watt generator of 3000 mc/sec microwaves in the production of atomic oxygen (34). He utilized the greenish yellow chemiluminescence of the reaction of atomic oxygen with nitric oxide to detect atomic oxygen:

$$O + NO \longrightarrow NO_2 + h\nu$$

A reaction much faster than the above reaction is the reaction between atomic oxygen and NO_2:

$$O + NO_2 \longrightarrow O_2 + NO$$

Hence it is possible to "titrate" oxygen atoms with NO_2 to the point of complete extinction of the chemiluminescence. It will be noted that the "titration" furnishes its own indicator. This titration method was used to

study the kinetics of the reactions of atomic oxygen with various species.

When boron trichloride is passed through a microwave discharge at low pressure, diboron tetrachloride and chlorine are formed (16):

$$2BCl_3 \longrightarrow B_2Cl_4 + Cl_2.$$

The diboron tetrachloride and unreacted boron trichloride may be condensed in a -112° trap and the chlorine in a -196° trap. Under similar conditions, germanium tetrachloride will react to give digermanium hexachloride and chlorine (32, 60):

$$2GeCl_4 \longrightarrow Ge_2Cl_6 + Cl_2.$$

A -18° trap is used to collect the crystalline Ge_2Cl_6; a -78.5° trap collects the unreacted $GeCl_4$, and a -196° trap collects the chlorine. The apparatus used for this latter synthesis is pictured in Figure 17.

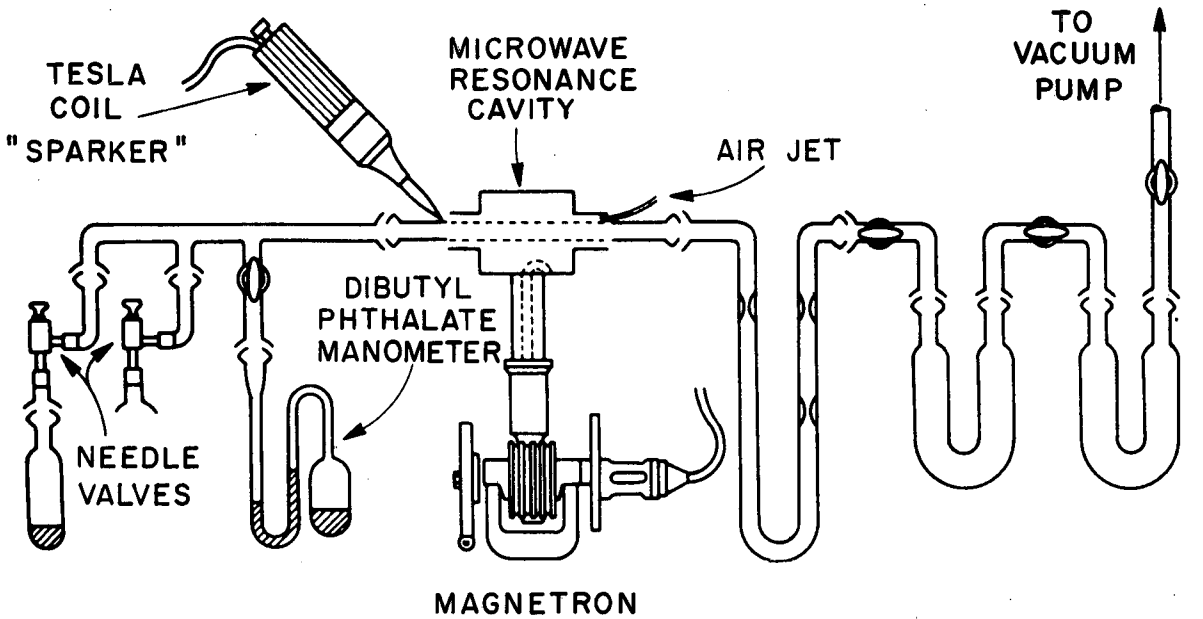

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Fig. 17. Apparatus for the Microwave Discharge Synthesis of Ge_2Cl_6 (Jolly (32)).

ARCS

Arcs under Liquids and Solutions -

Metallic dispersion. Colloidal suspensions of various metals may be prepared by forming arcs between metallic electrodes under liquids. By this technique (Bredig's method), suspensions of platinum, gold, lead, silver, mercury, aluminum, tin, iron, zinc, and calcium have been prepared (3, 7, 11, 26). The arc is usually formed by touching two wires of the metal under the liquid and then separating them a short distance. If the ordinary 110-volt current is used, a resistance of about 10 ohms should be in series with the electrodes.

Zinc arc reduction. If an arc is struck between zinc electrodes beneath a chemically reactive liquid, interesting reduction products may be formed. Stock, Brandt and Fischer used the zinc arc apparatus pictured in Figure 18 to prepare C_3S_2 from carbon disulfide, Si_2Cl_6 and higher perchlorosilanes from silicon tetrachloride, P_2Cl_4 and phosphorus from phosphorus trichloride, and B_2Cl_4 and boron from boron trichloride (64). In a typical experiment, a direct current of 4-5 amperes from a 110 volt source passed through the arc discharge and a regulating resistance in series. The potential drop across the electrodes was generally 20-25 volts. In the preparation of the C_3S_2, 180 mg. of C_3S_2 was obtained per gram of consumed zinc, corresponding to a 50% yield based on the equation

$$3CS_2 + 4Zn \longrightarrow C_3S_2 + 4ZnS.$$

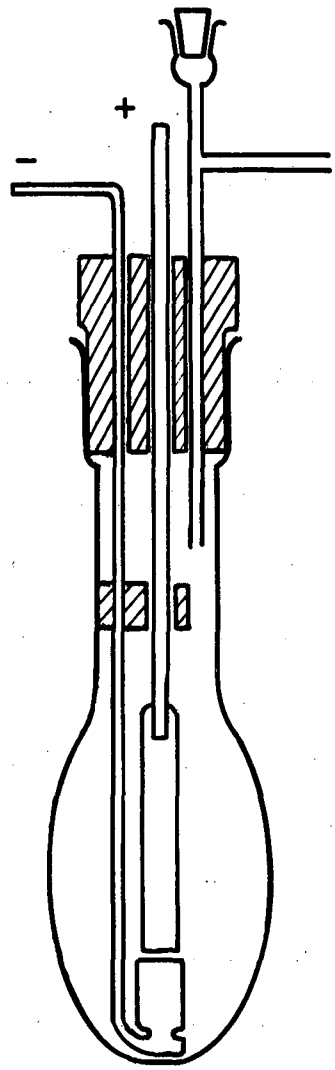

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Fig. 18. Zinc Arc Reduction Apparatus. (Stock, Brandt, and Fischer (64)).

Arcs in Flowing Gases -

Stanley (62) formed a discharge between two tungsten electrodes in a stream of nitrogen gas. The electrodes were separated by a short length of quartz capillary tubing through which the discharge and the flowing nitrogen passed. Although currents of only 500 ma at 5-10 kv were passed, the discharge was very intense in the region of the capillary and was called an arc discharge by Stanley. With this apparatus he was able to prepare active nitrogen at pressures as high as atmospheric.

If an arc between two electrodes is established in a stream of rapidly flowing gas, the hot discharge zone (the "plasma") will be pushed in the direction of flow. If the arc is formed in a properly designed chamber with an exit nozzle, it is possible to form a flame-like discharge or "plasma jet" wherein the electrons and ions are practically in the complete absence of an external electric field (46). A cross-sectional view of a commercially available plasma jet torch is shown in Figure 19. Plasma jet torches are manufactured by the Plasmadyne Corporation (Santa Ana, California) and the Thermal Dynamics Corporation (Lebanon, New Hampshire). In general, these torches consist of a chamber with a water-cooled tungsten cathode at one end and a water-cooled copper anode-nozzle at the other end. An inert gas such as argon is introduced near the tungsten cathode and is allowed to escape as a jet from the nozzle. A commercial plasma jet is available which is designed for continuous laboratory operation at 60 volts D.C. with power levels of 2 to 40 kw. Larger, industrial units may be operated up to 1200 kw. (65).

Hydrocarbons may be cracked in a hydrogen plasma jet to acetylene (2A, 65)

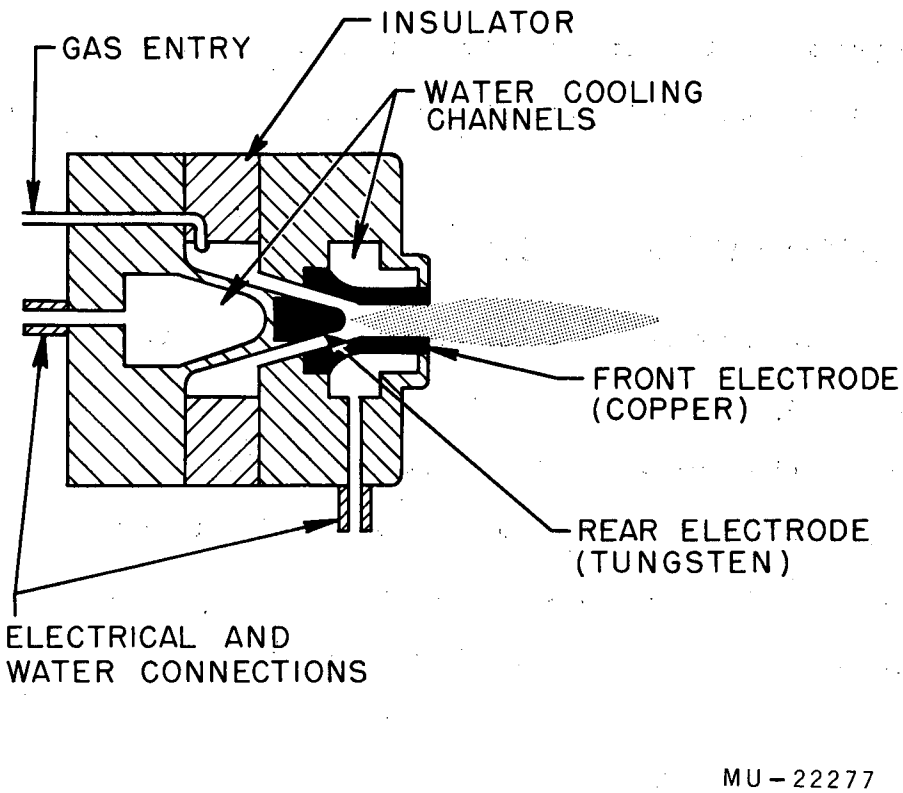

Fig. 19. Typical Plasma Torch (cross-section).

and carbon reacts with nitrogen in a nitrogen plasma jet to form cyanogen (65). Schematic drawings of the apparatus for these syntheses are shown in Figure 20. Thermodynamic studies indicate that it should be feasible to prepare hydrogen cyanide with a plasma jet containing hydrogen, carbon and nitrogen (43, 44).

Miscellaneous Industrial Application -

Electric arc discharges have found extensive industrial application in metallurgical and chemical processes. As isolated examples we may cite steel manufacture (the "electric arc furnace") (6), the preparation of nitrogen oxides (the outmoded arc method of nitrogen fixation)(12), the preparation of fluorocarbons (9), lower metal halides such as $TiCl_3$ (28), hydrides (45), hydrogen cyanide (36), and metal borides (37).

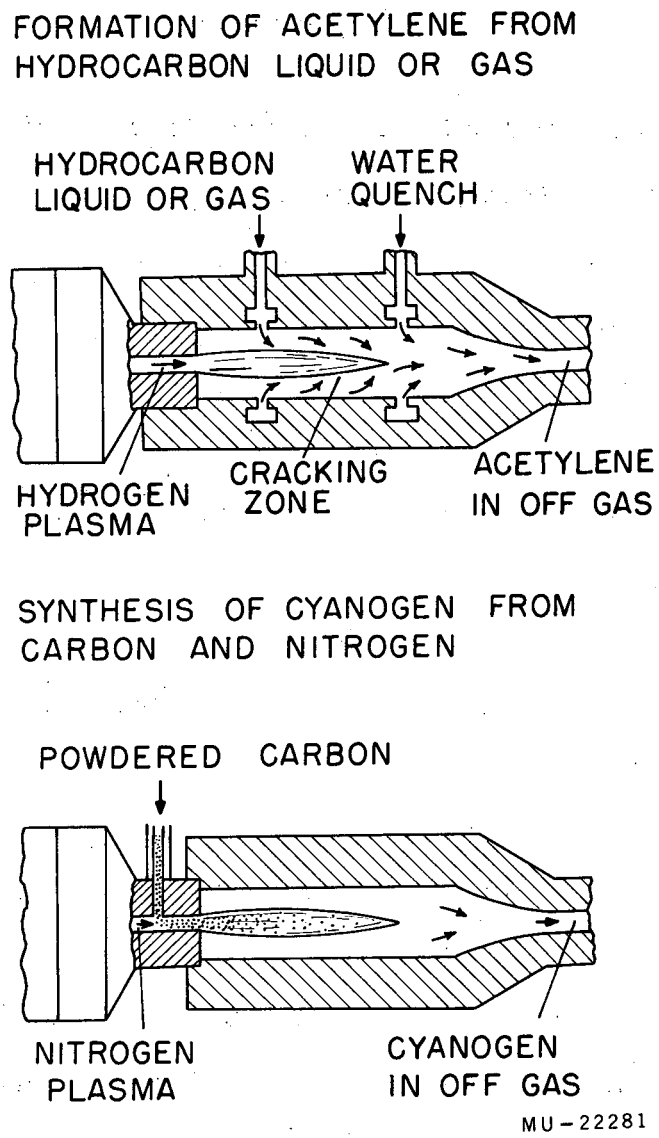

Fig. 20. Plasma Jets for the Synthesis of Acetylene and Cyanogen. (Courtesy of the Thermal Dynamics Corp.).

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