CHEMICAL REACTIONS IN ELECTRIC DISCHARGES

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I. Plasma Generators and the Nature of Electric Discharge Reactions

A. INTRODUCTION

The existence of unusual species in electric discharges has been known for many years and scientists have traditionally sought atomic and molecular spectra from arcs and sparks for analytical purposes. Recently there has been a new concern with electric discharges as devices for chemical synthesis, and it is this latter development which is to be emphasized in this chapter.

It is not the purpose of this chapter to trace the history of chemical reactions in electric discharges or to cover extensively all the investigations of discharge reactions reported. An extensive review on the subject was prepared 20 years ago by Glockler and Lind (*84*) and a more recent review appeared as a technical report by Jolly (*109*) in 1960. Rather it is intended here to point out the available devices and special techniques being used in modern studies of discharge reactions, and to cite some of the more recent work in the field illustrative of the importance of such studies. For example, an electric discharge synthesis is often the only convenient way to prepare compounds thermodynamically unstable at room temperature.

B. Plasma Generation Devices

An electric discharge is observed when a gas or vapor, across which a voltage gradient exists, becomes electrically conducting by transition to the plasma state. The condition necessary for the development of a plasma in any discharge is that the rate of generation of ions shall be sufficient to produce a potential maximum in the discharge container.

The fundamental types of continuous electric discharge are (1) the glow discharge, and (2) the arc discharge. These are self-sustained and can be maintained without the support of an external ionizing agency. On the other hand, excitation and thermal ionization of an isolated gas at a given reduced pressure can be obtained by application of an external source of energy.

1. The Glow Discharge

A glow discharge is maintained by electrons produced at the cathode by bombardment of particles and light quanta from the gas. The direct-current glow discharge is established in a tube containing gas at a pressure of a few millimeters of mercury. The appearance of the discharge depends on the operating conditions (*35*). The a.c. discharge does not differ significantly from the d.c. discharge. At low frequency and relatively short gaps, the time required for an electron to cross the gap is very short compared with the time of a half-cycle. Negative ions, formed by electron attachment, and positive ions cross the gap more slowly, but removal of ions and electrons from the gap occurs before the succeeding half-cycle. In long gaps ions oscillate only about a mean position near the point of their formation, and are subject to diffusion and recombination during the periods of low voltage. A discharge powered by an a.c. power supply is normally stabilized by an autotransformer which permits adjustment of the voltage applied to the primary. A resistance in series with the discharge tube is not necessary for stabilization as is the case in a d.c. discharge.

2. Electrodeless Discharges

The development of efficient high-frequency power sources has resulted in the wide use of electrodeless radiofrequency and microwave discharges and decreased interest in discharges between electrodes. Adoption of the electrodeless discharges can be attributed to a combination of factors such as ease of control, simplicity of construction of the discharge tube, greater stability, and, probably most important, greater purity of the discharge products since metallic electrodes, in contact with the discharge gases, are not required.

The transfer of radiofrequency energy into a discharge tube can be accomplished by inductance or capacitance. Also, efficient coupling can be accomplished with a microwave generator coupled to the discharge tube by various types of resonance cavities. Small amounts of radiofrequency power may be obtained from conventional power supplies and amplifiers. The three main types of high frequency-generating equipment for large power jobs (5–100 kw) are the spark gap converter, the vacuum-tube oscillator, and the motor generator set. A detailed discussion of high frequency generators is presented by Jordan (*112*).

In inductive coupling a metal solenoid surrounding the discharge tube can be used to induce an alternating current in the tube and create a plasma. At sufficiently high frequencies, a thin layer near the surface of the tube

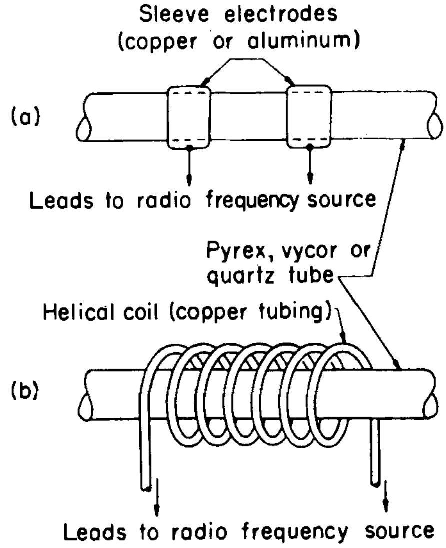


FIG. 1. Coupling arrangements for use with radiofrequency discharge; (a) capacitive coupling, (b) inductive coupling (*195*).

will carry nearly all of the current as required by the "skin effect" (*151*). Figure 1b shows a general arrangement of a high frequency discharge formed by inductive coupling.

Capacitive coupling (Fig. 1a) is accomplished by placing the discharge electrodes on the outside of the tube. This amounts to adding capacitors in series with the discharge circuit. A metal foil, a thin coat of aquadag, mercury, or an electrolytic solution of 1% HCl in acetone (f. p. = −95°) can be used as external electrodes. The tube can be powered by the regular line frequency of 50–60 cps (*146*).

Microwave coupling through a resonance cavity gives standing waves whose pattern depends on the shape and dimensions of the cavity (*6, 83, 171*). Shaw (*195*) has described conventional microwave coupling systems and a variety of microwave circuitry and components. The main critical point in the choice of the microwave discharge arrangement is that an impedance match between the discharge tube and the microwave power source is attained. Designs for microwave cavities are described in the literature (*33*), and microwave discharge sources are commercially available at various frequencies, e.g., the microthermic unit made by Raytheon has a frequency of 2400–2500 megacycles and a power output of 120 watts.

3. The Arc Discharge

The electric arc is a self-sustaining discharge of low voltage and high current. The arc is usually established by separation of contacts or by transition from a higher voltage discharge. It differs from the glow discharge by its low cathode fall of about 10 volts and its high current density. The transition from the relatively low current density and high voltage of the glow discharge requires an important change in the electron-emission processes at the cathode (*35*). Arcs are classified as low and high intensity arcs. The voltage drop across the plasma region in the low intensity arc accounts for the major portion of the arc voltage. As the current is increased, very little change will be noticed in the appearance of the arc and the current density remains the same. Further increase of the current results in a spread of the arc crater over the entire area of the anode tip. Figure 2 shows the appearance of a carbon arc as the total current is increased through the transition point from a low intensity to a high intensity arc (*196, 225*). The high intensity arc is characterized by a jet of gaseous material that proceeds from the anode surface known as the "tail flame." The jet comprises a mixture of vaporized anode components and infused ambient material.

The so-called Beck arc is an example of a high intensity arc characterized by an anode containing oxides and fluorides of cerium. The high current density at the anode leads to very rapid evaporation from the anode sur-

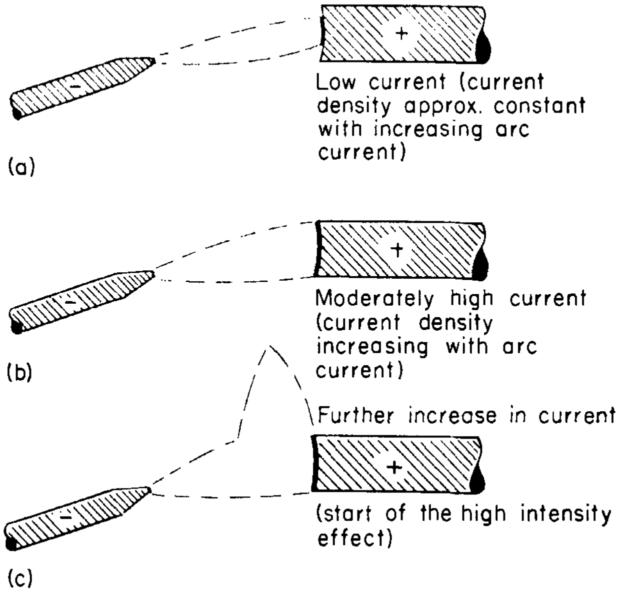


FIG. 2. Appearance of a carbon arc as the total current is increased through transition to the high intensity arc: (a) low intensity region, (b) just below transition point, (c) just above transition point (*225*).

face, and a plasma temperature of the order of 9000–10,000°K is attained. The possibility of introducing a variety of elements into the arc by placing the substances to be studied in the core of the carbon anode is convenient and unique. The rapid evaporation results in a high temperature jet at an initial velocity of 10^3–10^4 cm sec^{-1} (*137*).

4. Plasma Jet Generators

Besides the above mentioned form of the high intensity arc, the constricted arc is a well-developed device for producing high temperature plasmas. Whenever an arc is forced to burn through a narrow hole, the increased current density results in an increased magnetic force directed in such a way as to produce confinement of the arc. The magnetic pressure directed radially results in pressure release in both axial directions from the confining hole. The mechanism may be described as a kind of pump, which sucks gas sideways into a constriction and blows it out in an axial jet after heating the gas and transforming it into plasma.

The term plasma jet applies to any high current arc in which plasma is jetted through a nozzle. The plasma jet generator is an electric arc contained within a small tube through which the gas is also blown. The significant characteristic of this device is that it incorporates an ingenious cooling system, which keeps the electrodes from evaporating and helps to elevate the temperature of the plasma. The concept of increasing the plasma temperature depends on the "pinch effect" caused by the self-induced magnetic field, i.e., the "magnetic pinch," and on the "thermal pinch" resulting from the increased current density. By means of such techniques the plasma jet ejected from an orifice in one of the electrodes consists of a beam of highly excited particles with temperatures in the range 10,000–100,000°K.

The Gerdien arc (*80*) is the prototype of modern plasma jet generators.

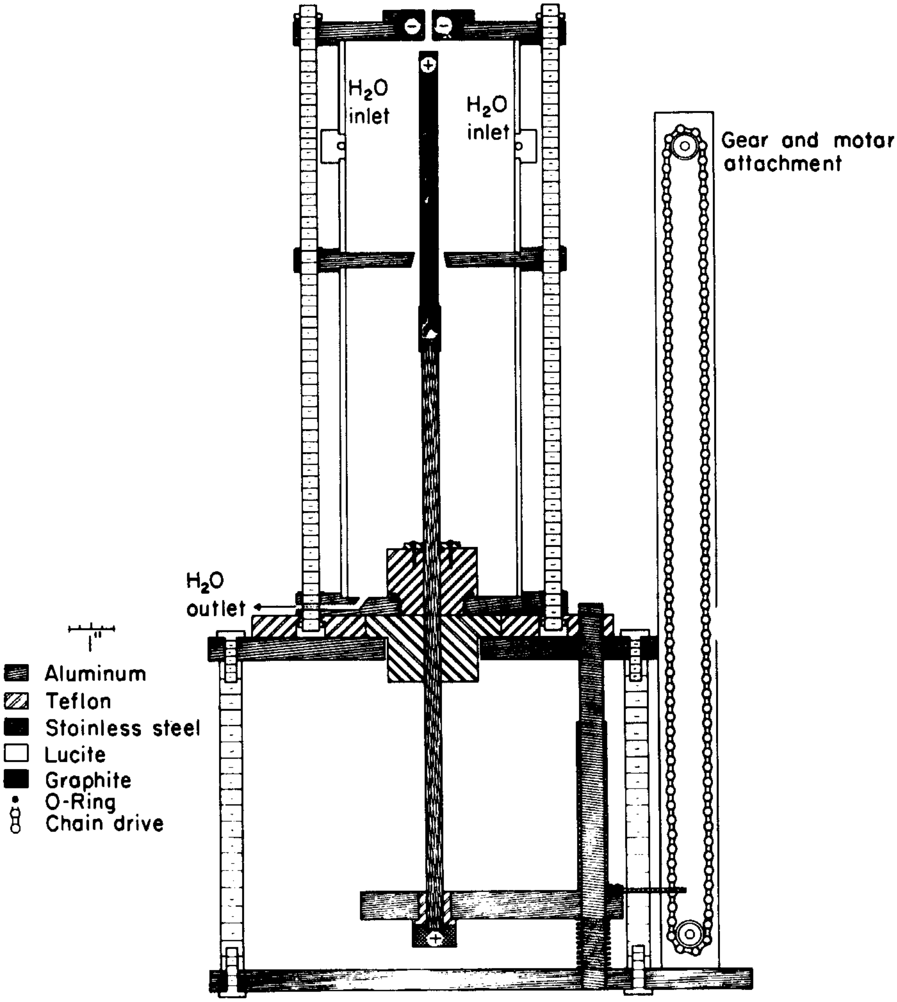


FIG. 3. Water-constricted plasma generator (*114*).

The arc is forced to pass through a narrow water-cooled constriction established by a copper diaphragm. The cooling effect of running water (or some other fluid) in direct contact with the arc column has proved to be of high efficiency. A cooling water column may be established by introducing water tangentially with enough energy to form a hollow vortex with almost parallel walls. Improvements of the Gerdien arc were reported by Maecker (*140*) and Weiss (*237*). A diagram of a water-constricted plasma generator based on the one constructed by Weiss is shown in Fig. 3.

Stabilization of the plasma jet generator is also possible by the use of a rare gas like argon or helium or a diatomic gas such as hydrogen or nitrogen. Stabilization in this case is either by vortex flow and formation of a gas sheath or by wall stabilization. Examples of these generators are presented in Figs. 4–6.

The distinction between the arc and the plasma jet is arbitrary. Usually the arc is considered as the portion of the discharge between the electrodes and carries current due to the excess supply of electrons. On the other hand, the plasma jet does not carry excess electrons from the external circuit. In a sense the plasma jet resembles a chemical flame in appearance, but differs from the flame by its high ionization and its almost unlimited supply of energy. In the plasma jet the source of energy is the electric power supplied to the arc generating the plasma jet. The plasma jet heated by the arc energy may be used as a heat source and to provide an environment for chemical reactions at temperatures higher than flame temperatures. On the other hand, direct contact of the reagent with the electric arc is avoided. Endothermic reactions are expected to take place when a reagent contacts the plasma stream outside the arc chamber. The rapid heating and fast

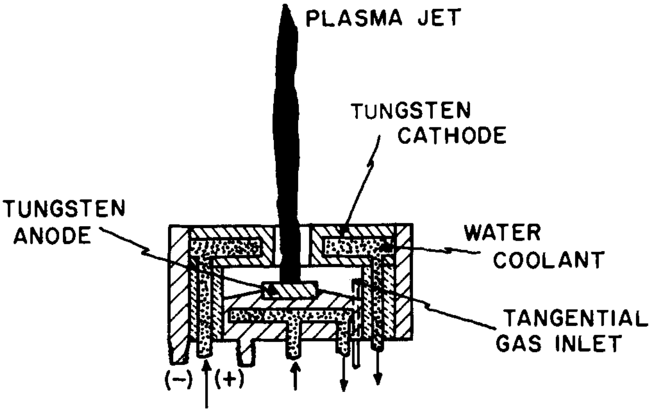


FIG. 4. Vortex-stabilized plasma generator (*222b*).

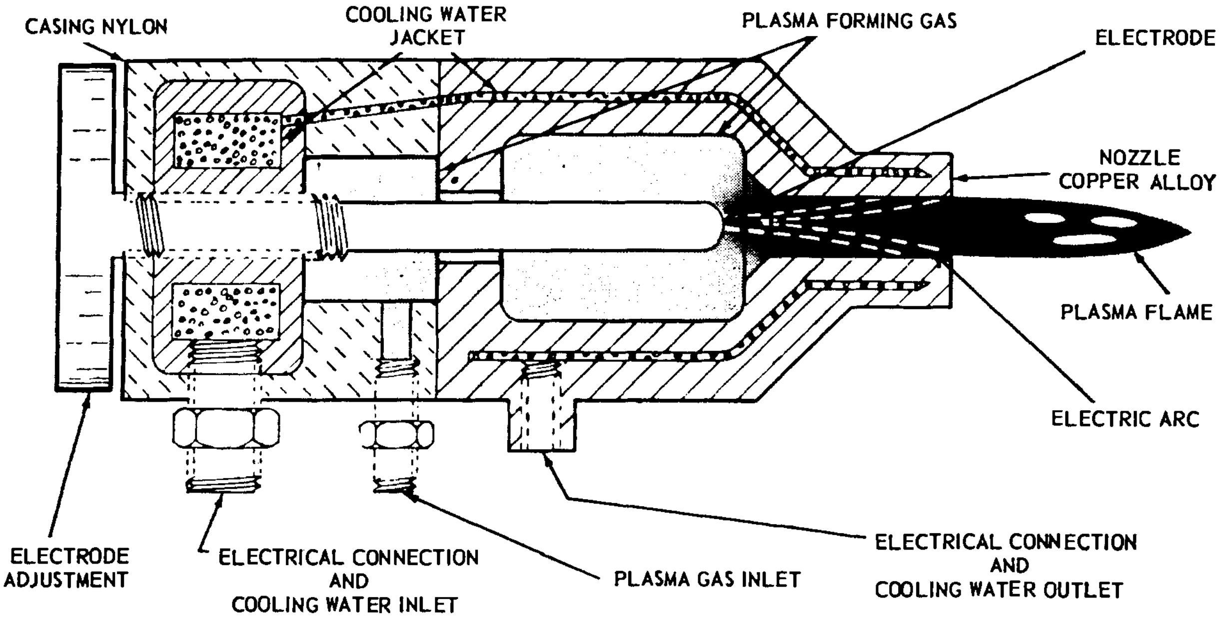


FIG. 5. Gas sheath-stabilized plasma generator (*222b*).

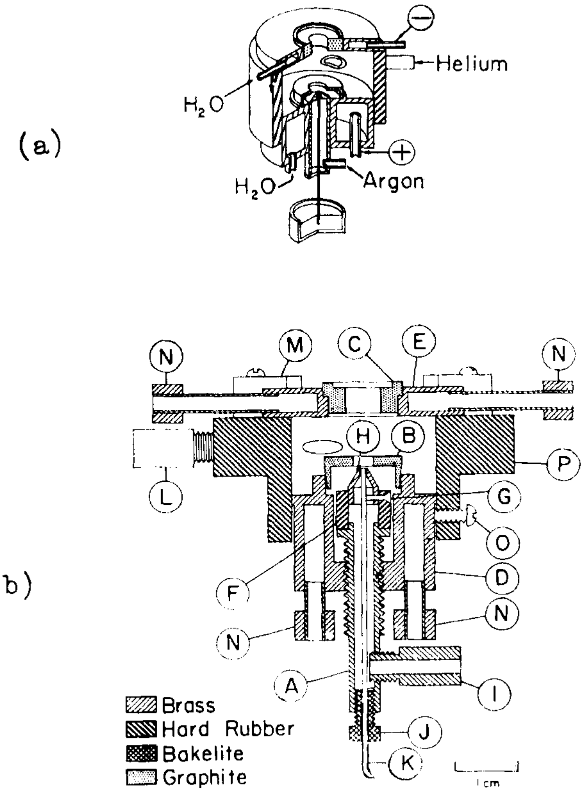


FIG. 6. The plasma jet as modified for a spectroscopic source: (a) schematic drawing, (b) detailed drawing: A, atomizer; B, anode; C, cathode; D, chamber holding atomizer and anode; E, cathode holder; F, hard rubber insulator; G, set screws for positioning capillary; H, atomizer tip; I, argon inlet; J, plastic screw holding capillary; K, capillary tube; L, helium inlet; M, cathode holder clamps; N, water connections; O, set screws; P, outer case *(162)*.

quenching of the reagents in the plasma stream are important factors in the utilization of the plasma jet in chemical processes.

5. Induction-Heated Plasma Torches

This type of plasma torch uses a radiofrequency field to maintain a thermal plasma, without the consumption of electrodes. The energy of the high-frequency electromagnetic field is transferred to a gas by interactions with the ionized gaseous molecules, atoms, and electrons and thus maintains a high degree of dissociation and excitation. By allowing recombination among these species, the absorbed energy is given off in the form of heat and light. This method of heating gases can best be understood in the same terms as general heating by induction. The plasma generation is started by forming a small volume of plasma by induction heating of a tantalum wire or a carbon or tungsten rod placed in the center of the coil. This, in turn, heats the gas around it, lowering its breakdown potential

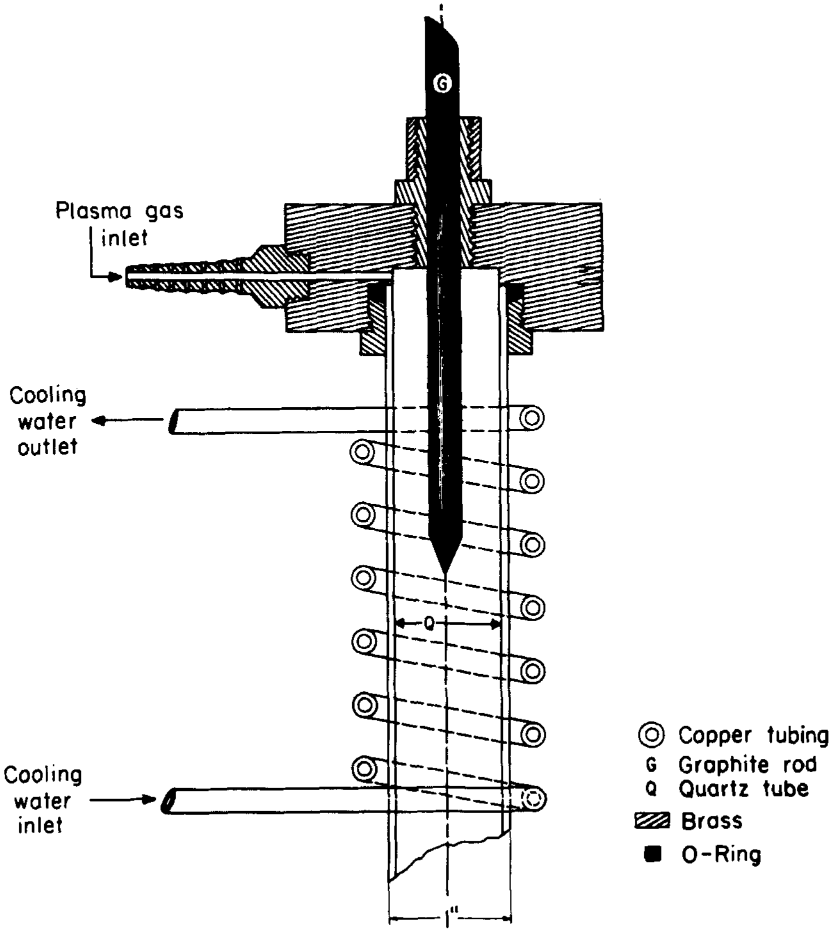


FIG. 7. Thermal induction plasma torch (*114*).

and giving rise to ionization of the gas and establishment of the plasma in the high radiofrequency field. As in other plasma jet generators, the plasma has to be stabilized to maintain itself against the gas flow. Vortex stabilization has proved to be convenient. A tangentially fed gas flows spirally down the walls of the torch tube, creating a low pressure area in the center of the tube. This causes some of the plasma to flow up the tube

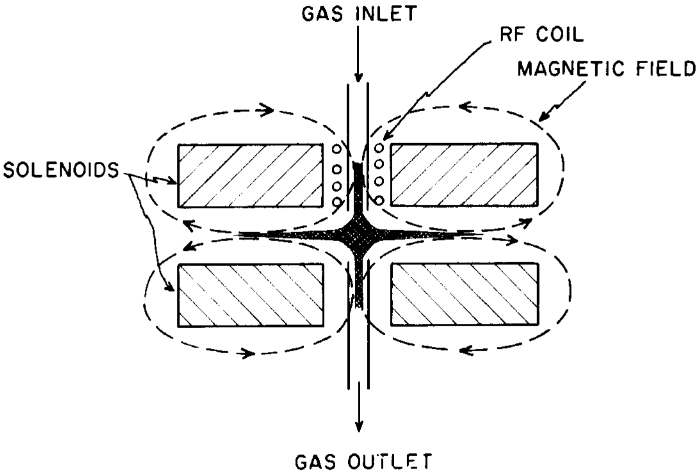


FIG. 8a. Plasma torch trapped in a cusp-shaped magnetic field (*85*).

countercurrent to the main flow. The flow along the walls tends to keep the plasma centered and away from the walls, thus keeping the tube walls cool and making it possible to operate at higher power levels (*88*, *175*, *177*). The field producing the energy may be from either an ordinary high-frequency or microwave transmitter. A frequency of 4 megacycles was used by Reed (*175*) and in this laboratory. Frequencies of the order of 25–28

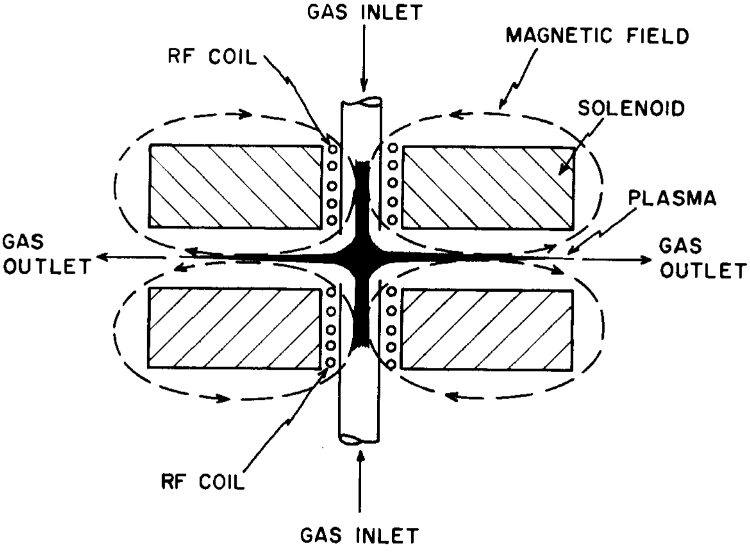


FIG. 8b. Plasma torch confined by a steady magnetic field (*85*).

megacycles were used by Grosse (*88*), and a 5-kw source at 915 megacycles was utilized by Friedman (*76*). Figure 7 shows a sketch of an induction-heated torch.

Magnetic confinement of the plasma generated in a radiofrequency torch has been reported by the Plasmadyne Corporation (*85*). A diagram of such a torch is shown in Fig. 8. Figure 8b shows a design expected to be of use in chemical studies, while the torch configuration of Fig. 8c has the advantage of jet formation where a high velocity plasma is desired.

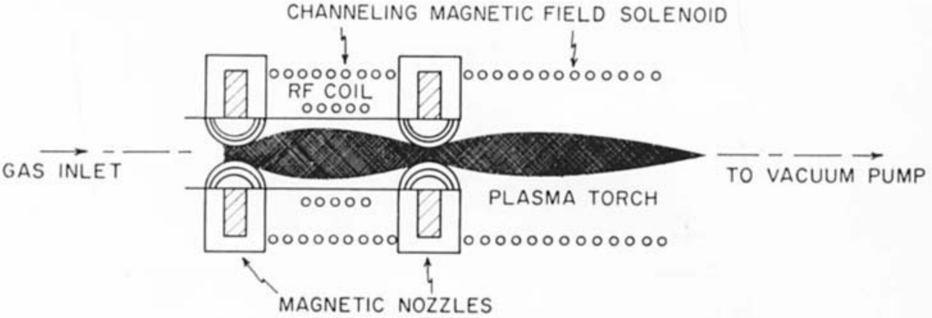


FIG. 8c. Plasma torch with a magnetic nozzle (*85*).

C. IONIZATION- AND EXCITATION-ACTIVATED REACTIONS

Chemical reactions of substances in an electric discharge are widely varied. Decomposition, formation, and/or transformation of a given substance may take place according to the nature of the substance and the discharge parameters. The reactions which may take place vary in complexity, depending on the number of highly active species which are produced as intermediate fragments, and their lifetimes.

The main activating processes which may induce chemical reactions in an electric discharge reactor may be categorized as thermal-, excitation-, or ionization-activation processes. Considerations of the mechanism of a given reaction involve the energy of the electrons produced in the discharge and the site of the reaction in the reactor. One of the first general attempts to explain the mechanism of electric discharge reactions was that of Lind (*135*), where an ion-cluster theory was proposed to explain the high yield of chemical reactions in a discharge. Brewer and Westhaver (*28–31*) explained the formation of NH_3, O_3, and the oxidation of hydrogen in electric discharges on the basis of ion-activation processes. On the other hand, Lunt and Mills (*138*) and Emeleus and Lunt (*60*) denounced the ionic mechanism and interpreted the reactions on the basis of a free radical mechanism. In support of the free radical mechanism, Bradford and Finch

(*27*) considered the production of free radicals by electronic excitation processes as opposed to thermal ones. Burton and Magee (*38, 39*) suggested that electronic excitation may be perceived by considering the role of low energy electrons (0.5–4 ev) in electric discharges, and argued that molecular electronic states of very high energies can be excited by moving the molecule up a succession of closely spaced electronic energy steps. They favor electron impacts, rather than radiation, as responsible for the excitation on account of the rapid mechanism of the first. In support of this view Wiener and Burton (*238*) cited the decomposition of methane in an electric discharge. They suggested the excitation of CH_4 where the initial excitation furnishes sufficient CH_3 radicals to start the process. CH_2 radicals are then formed in high concentration as evidenced by the formation of CH_2D_2 in presence of D_2, while CHD_3 and CH_3D are formed in small amounts. The formation of C_2H_2 in this process was assumed to follow the steps:

$$\begin{aligned} CH_4 &\rightarrow CH_4^* \\ CH_4^* &\rightarrow CH_3 + H \\ CH_3 &\rightarrow CH_3^* \\ CH_3^* &\rightarrow CH_2 + H \\ CH_2 + CH_3 &\rightarrow C_2H_5 \\ C_2H_5 &\rightarrow C_2H_3 + H_2 \\ C_2H_3 &\rightarrow C_2H_2 + H. \end{aligned}$$

Reddy and Burton (*174*) used the same argument in explaining the decomposition of C_2H_4 in an electric discharge to give C_2H_2.

In the event that ionization serves as the rate-determining step in electric discharge reactions, one would predict that a given reaction would set in at the ionization potential of the reactant involved. This still does not exclude the possibility of excited species also acting as reactive centers. Metastable states, on account of their relatively long lives, may be effective in the activation of certain reactions. Further, one has to take into account the effect of thermal activation, especially in high temperature plasmas. Although support for various views can be deduced from experimental data on a specific reaction, it is clear that the mechanisms of chemical reactions in discharges do not all follow the same path.

D. PRODUCT COLLECTION AND IDENTIFICATION

The occurrence of a given chemical reaction depends on activation of the appropriate species, and this explains the unique role which an electric discharge might play in producing a particular product molecule. In certain cases the electric discharge may be needed to activate a single species, which contacts a second reactant at lower temperature outside the discharge zone.

In other instances both reactants may be found in the discharge zone where contact and interaction take place under the activating condition of the discharge. In any case, the nature of the products determines the kind of discharge and the system to be used in the synthesis. For example, if rather unstable products are of interest they should be removed from the discharge zone as rapidly as possible, and a flow discharge system is used. If stable products of low volatilities, which condense out on the walls of the reactor and do not undergo further reactions, are synthesized, a static discharge system may be used. In certain cases where intermediates or byproducts are undesirable, the discharge reactors may be immersed in a low temperature bath. This can also be done when the products are volatile to provide for their continuous condensation by such cooling.

The uses of the plasma jet devices for studies of chemical reactions differ from those of other electric discharge devices, in that the hot gas stream may be utilized either as a heat source or as the source of chemical species which participate in a chemical reaction. In the first case the plasma gas is a relatively inert gas, such as argon or helium, and serves as a source of heat by heat exchange. Of course, the electrons and excited species of the plasma may also participate in some chemical reactions with other substances present in the plasma reactor. In the case of other plasma gases, such as nitrogen, hydrogen, or oxygen, one has introduced into the system species which can take a more active part in the chemical reaction. When these substances are present in the plasma stream, they either react (after being activated to the right energy state or decomposed into the appropriate intermediate fragments) among themselves or form new compounds by combination and transformation with other materials introduced into the plasma gas stream. In many cases, a well-known gas cannot be used as a plasma gas directly. Maintenance of the discharge requires a critical temperature to perpetuate the electric conductivity, and, in addition, corrosive decomposition products may react with the electrodes and change the discharge characteristics, leading to instability and extinction of the arc.

Various techniques can be used to inject materials of interest into a plasma stream. The nature of such substances, their state, and the best predicted conditions under which a reaction is expected to take place, help determine which one to use. A description of some typical reactors is given below.

A general arrangement for a plasma jet reaction chamber is given in Fig. 9. The reaction chamber is fitted with an opening through which variously shaped "cold fingers" may be inserted. For collecting solids the cold finger is set close to the feed ring to quench the products. The same

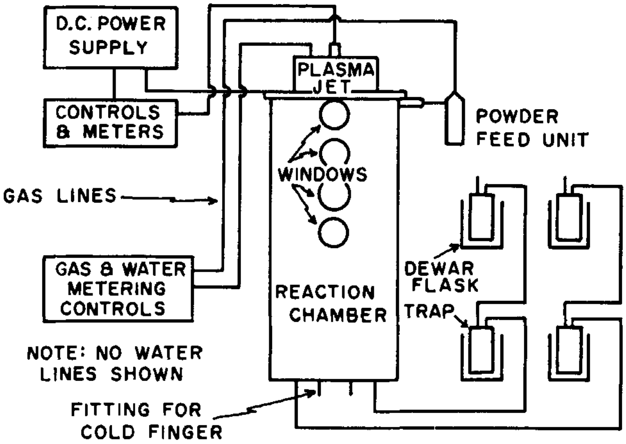


FIG. 9. Plasma jet reaction chamber and collection system (*204*).

setup can be used to quench the reaction products when gaseous compounds are prepared. In this latter case, cold traps are used with either liquid nitrogen or dry ice. A somewhat similar arrangement by Grosse *et al.* (*88*) allowed for passage of the gas from the quenching chamber through a glass tube packed with glass wool (intended to retain finely divided soot which is found in $(CN)_2$ preparation) (Fig. 10).

In those cases where the reactant gas is heated by the stream of hot plasma outside the discharge chamber, the reactor may consist of two sections: the first for mixing the reactant gas with the plasma and initiating reaction, and the second to provide for cooling and quenching the products. A reactor-quencher combination is shown schematically in Fig. 11. The quenching chamber consists basically of a water-cooled double-walled tube to which the plasma generator is bolted by means of flanges and the joint is made gastight with 0-ring seals.

Due to the variety of reactions and their needs for different environmental conditions, one cannot give a general account of all the possibilities for product and reactant handling. Figure 12 gives a general idea of several of the different methods by which a plasma torch can be utilized for chemical reactions. Grosse *et al.* (*90*) reported the feasibility of liquid-phase chemical reactions in a plasma reactor at temperatures above 4000°K. Their reactor consisted of a centrifugal furnace with a reaction section of three concentric tubes: (1) oxides, carbides, nitrides, or graphite, (2) insulating material, and (3) the water-cooled external metal cylinder. Using aluminum as a test material, and alumina as the internal tube of the reactor, the alumina tube partially melted and by rotation of the furnace served

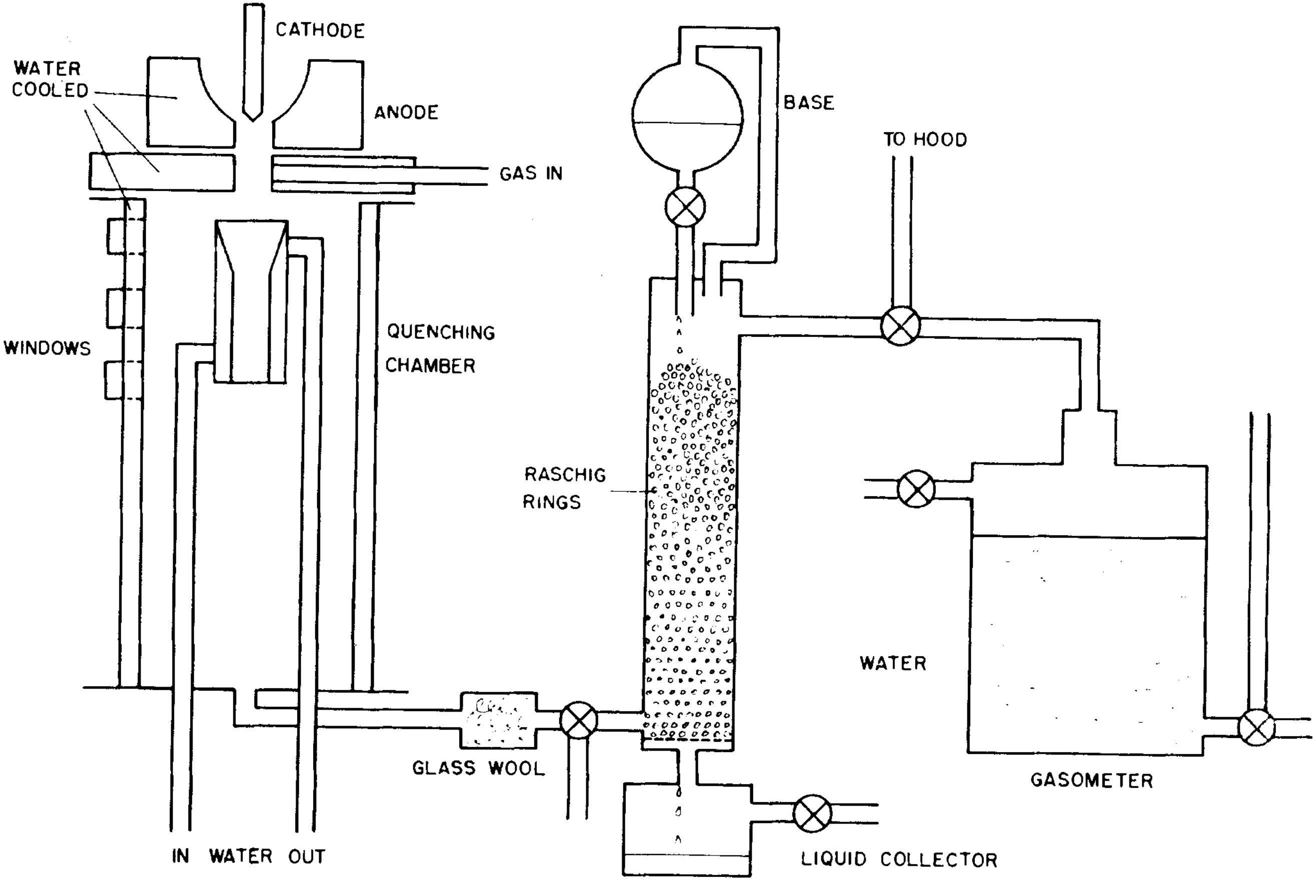


FIG. 10. Plasma jet reaction chamber and product collection system (*88*).

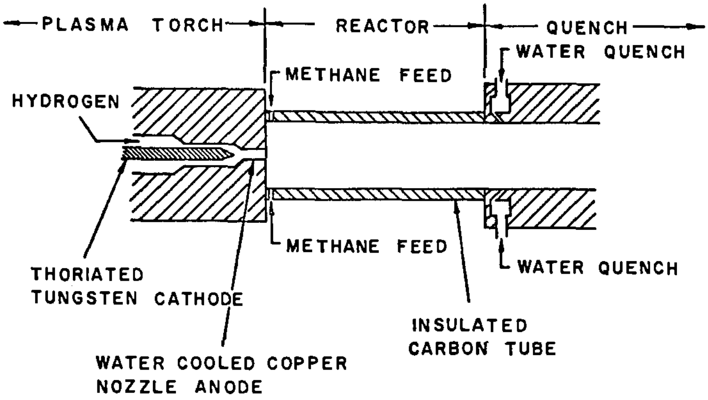


Fig. 11. Plasma reactor and quencher combination (*7*).

as a liquid crucible. Other refractories were also used as liquid containers in such a reactor.

For product analysis one utilizes all of the conventional analytical techniques along with gas chromatography, optical spectroscopy, and mass spectrometry in identifying the products. In certain cases, intermediate fragments can also be detected by spectroscopic techniques, and such identification of intermediate free radicals should aid in establishing the steps of a given reaction mechanism.

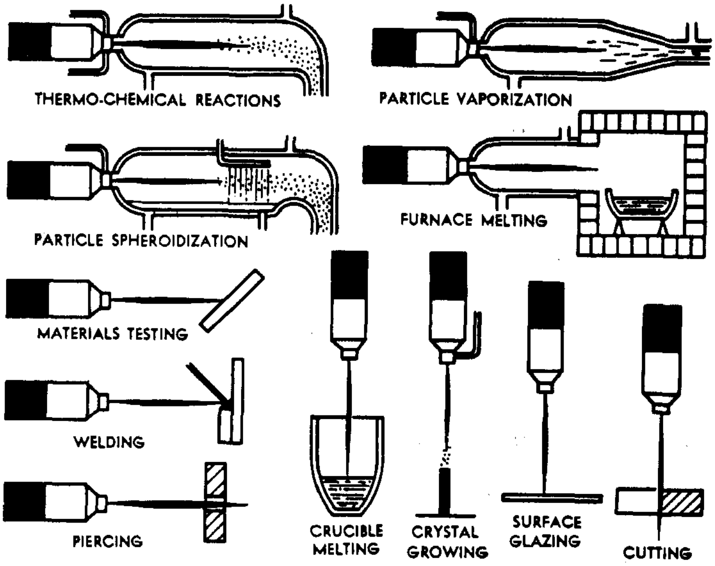


Fig. 12. Various arrangements for plasma jet reactors (*222a*).

II. Chemical Reactions in Glow and Arc Discharges

The current state of knowledge of chemical reactions in glow and arc discharges will be elucidated in this section by fairly comprehensive reviews of research covering reactions of boron, silicon, sulfur, titanium, phosphorus, oxygen, nitrogen, hydrogen, various halides, and inorganic and organic carbon compounds.

A. Boron and Its Compounds

1. Boron Halides

Diboron tetrachloride, B_2Cl_4, was first prepared by Stock *et al.* (*202*) in 1925 by striking an arc between two Zn electrodes immersed in liquid boron trichloride. Wartik *et al.* (*234*) synthesized the same compound by passing BCl_3 at a pressure of 1–2 mm Hg through a glow discharge between Hg electrodes, as described schematically in Fig. 13. The volatile products of the reaction were passed through a trap at −78°C where the B_2Cl_4 was retained. Urry *et al.* (*223*) suggested the following step mechanism for the reactions in the discharge:

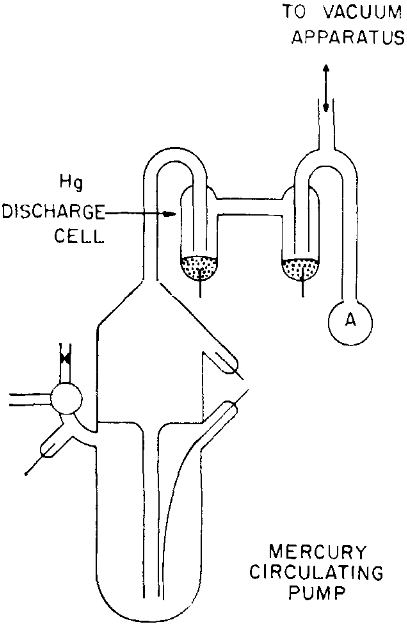


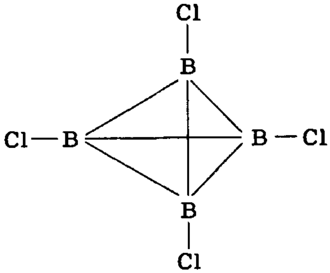
Fig. 13. Mercury discharge tube for preparation of B_2Cl_4 and B_4Cl_4 (*223*).

$$BCl_3 \rightarrow BCl_2 + Cl$$
$$Cl + Hg \rightarrow HgCl \text{ and/or } HgCl_2$$
$$2BCl_2 \rightarrow B_2Cl_4.$$

The interference of metallic electrodes was eliminated by Frazer and Holzman (*74*, *75*), who used microwave radiation to excite BCl_3 vapor under a pressure of 44 mm Hg as it passed through a resonating cylindrical cavity maintained at a temperature below 0°C. The microwave exciter unit operated at a wavelength of 12.2 cm with a power of 30–40 watts, and B_2Cl_4 was condensed in a trap at -111°C. Free chlorine produced in the reaction was removed from the trap, along with small amounts of BCl_3, by fractional distillation. Investigation of the spectra of the emitted light in the process suggested the presence of the BCl molecule as an intermediate species in the reaction (*102*):

$$2BCl_3 = B_2Cl_4 + Cl_2.$$

The absence of spectroscopic evidence for the species BCl_2 shows that either the location of the spectrum of BCl_2 lies outside the investigated region (2000–7000 Å) or the energy absorbed is higher than the dissociation energy of BCl_2, resulting in immediate rupture. Other investigations of the preparation of B_2Cl_4 and similar compounds, in electric discharges of various types, were reported by Wartik (*234*). Two other boron subchlorides were reported by Schlesinger *et al.* (*189*). B_4Cl_4 was formed as a by-product in the reaction of BCl_3 in an electric discharge, while the main product was B_2Cl_4. The structure of B_4Cl_4 is believed to consist of a tetrahedron of boron atoms with chlorines at each apex:



The second by-product was $(BCl)_x$, which appeared as a coating on the walls of the discharge tube. The monochloride was assumed by Rosenberg and Wartik (*179*) to be the result of B_2Cl_4 decomposition:

$$xB_2Cl_4 \rightarrow (BCl)_x + xBCl_3.$$

Rosenberg and Wartik (*179*) obtained the corresponding monobromide from an electric discharge through BBr_3.

$$x\mathrm{BBr_3} \rightarrow (\mathrm{BBr})_x + x\mathrm{Br_2}.$$

On the basis of the chloride reaction, Diener and Pflugmacher (*57*) suggested the formation of B_2Br_4 from BBr_3 in an electric discharge where Hg was used as a reducing agent.

Schumb *et al.* (*190*) found that BI_3, when sublimed under a reduced pressure of 1–3 mm Hg through a silent discharge tube powered by a 5 Mc/sec transmitter, gives B_2I_4. This compound is pale yellow in color and disproportionates at room temperature:

$$\mathrm{B_2I_4} \rightarrow \mathrm{BI_3} + 1/x(\mathrm{BI})_x.$$

The nature of $(BI)_x$ is unknown.

2. *Boron Hydrides*

The decomposition of diborane in a silent discharge in the presence of an inert gas was described by Kotlensky and Schaeffer (*128*). Diborane passed slowly and at reduced pressure through an ozonizer-type discharge yields a mixture of boron hydrides. A yield of 40% B_4H_{10}, 20% B_5H_{11}, small amounts of B_5H_{10}, and a previously unidentified B_9H_{15} was reported. Gibbins and Shapiro (*81*) reported that their mass spectral studies of the discharge products indicated the presence of a hexaborane having a minimum of 12 hydrogen atoms, as the mass spectrum differed distinctly from B_5H_{10}. Decaborane-16 was also formed in an electric discharge between copper electrodes through a stream of hydrogen and pentaborane-9. Grimes *et al.* (*86*) explained the formation of decaborane by loss of one molecule of hydrogen between two molecules of pentaborane, and then the formation of boron-boron bonds between the remaining units according to

$$2\mathrm{B_5H_9} + \mathrm{H_2} \rightarrow \mathrm{B_{10}H_{16}} + 2\mathrm{H_2}.$$

3. *Metal Borides*

TiB_2 was formed when a mixture of TiO_2, H_3BO_3, and C was exposed to an electric arc (*113*). The powder charge was arranged so that the evolved CO protected the reaction zone from atmospheric oxygen. Kahlswa (*113*) described an arc system applicable to the formation of heavy metal borides from their oxides.

Aleonard (*5*) reported the formation of two new manganese borides in an electric arc.

4. Other Boron Compounds in Electric Discharges

A mixture of boron trichloride and carbon monoxide, when subjected to the action of an ozonizer-type discharge, produced an apparently polymeric solid possessing properties not commonly associated with boron compounds. The discharge, as well as the properties of the product, are described by Wartik and Rosenberg (*235*). The polymer deposit was a transparent light-yellow film on the walls of the discharge tube and had a cedarlike odor. The authors suggested the formula $BCl_3 \cdot 2CO$. A similar film was obtained by repeating the experiment, using BF_3 in a mixture with CO. Other discharge-induced reactions of boron halides with nonmetallic oxides are discussed by Rosenberg (*178*).

Pure carbides and nitrides of boron, along with other elements of Groups IV–VI such as Si and Ti, have been produced by mixing a volatile boron compound with a source of carbon or nitrogen and passing a high-frequency electric discharge through the mixture. Sucket (*209*) described an apparatus for mixing, electrical treatment, and disposal of the by-products of the reaction between BCl_3 and propane. A fine hard black product, B_4C, with some free carbon impurity was obtained. The pure nitride was similarly produced by replacing the hydrocarbon by hydrogen and nitrogen. Williams *et al.* (*239*) reported the formation of unidentified compounds in an electric discharge through pentaborane and acetylene. The carbon-boron compounds from this reaction were referred to as carboranes.

A high purity boron was obtained by passing a mixture of BCl_3 and hydrogen (optimum ratio 1:5) through an electric discharge. Markovskii *et al.* (*147*) carried out the process in the pressure range 30–200 mm Hg, and reported a boron purity of 99.9%.

B. SILICON AND ITS COMPOUNDS

1. Silicon-Nitrogen Compounds

Tris(trichlorosilyl)amine $(SiCl_3)_3N$ was formed by passing an equimolar mixture of $SiCl_4$ and nitrogen at reduced pressure (0.2–0.8 mm Hg) through a glow discharge, similar to the one shown in Fig. 14. Pflugmacher and Dahmen (*169*) reported that vacuum distillation of the reaction product yielded a crystalline solid which was collected at 1–20°C, along with a colorless oil collected in the boiling range 170–250°C and a yellow-brown resinous residue. Fractional distillation of the crystalline product gave $(SiCl_3)_3N$ and $(Si_2NCl_5)_n$. On ice-water cooling of $(SiCl_3)_3N$ vapor, lardlike crystals (m.p. 44–48°) were obtained. It changed, probably to a monoclinic form (m.p. 78°), on condensation at room temperature. At temperatures

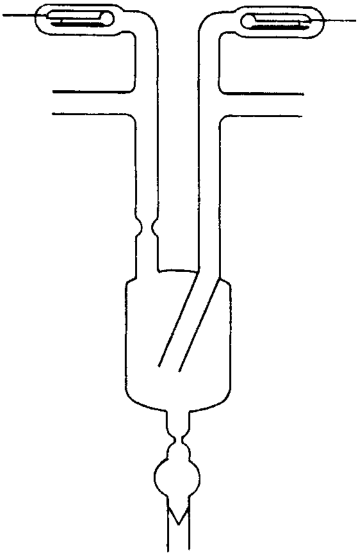


FIG. 14. Pflugmacher and Dahmen discharge tube (*169*).

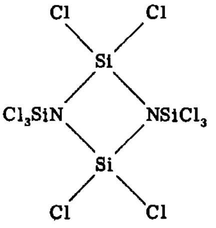
higher than its boiling point in vacuum (135°) it decomposed to $SiCl_4$, Si, and a white solid of lower silicon and chlorine content. The authors (*169*) suggested a cyclic chain-like structure for the discharge products, according to a mechanism which involved the initial formation of $(SiCl_3)_3N$. Subsequently,

$$2(SiCl_3)_3N \rightarrow 2SiCl_4 + (Si_2NCl_5)_2,$$

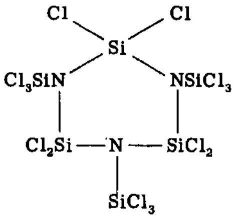
$(Si_2NCl_5)_2$ is probably the only product collected in the temperature range 170–250°C, but at higher temperatures,

$$3(SiCl_3)_3N \rightarrow 3SiCl_4 + (Si_2NCl_5)_3$$
$$4(SiCl_3)_3N \rightarrow 4SiCl_4 + (Si_2NCl_5)_4.$$

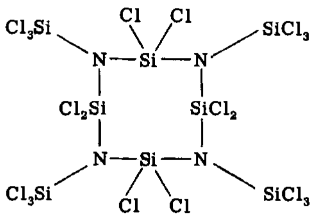
The proposed structural formulas are:



$(Si_2NCl_5)_2$



$(Si_2NCl_5)_3$



$(Si_2NCl_5)_4$

2. Organosilicon Compounds

Organosilicon compounds, useful in the preparation of polymers, were reported by Akerlof (*2–4*) to be obtained in a continuous process when mixtures of hydrocarbons or their halogenated derivatives and $SiCl_4$ react in the vapor phase in the presence of an electric discharge. A dry mixture of $SiCl_4$ and CH_4 in a mole ratio 5:1 was passed through an electrodeless discharge operated at 14.5 kv, 120 ma, and 800 cycles/sec, as shown in Fig. 15, and gave organosilanes, which were liquids over large temperature ranges with boiling points in the neighborhood of 400°C. The reaction product was assumed to contain CH_3SiCl_3 and a smaller amount of $(CH_3)_2SiCl_2$.

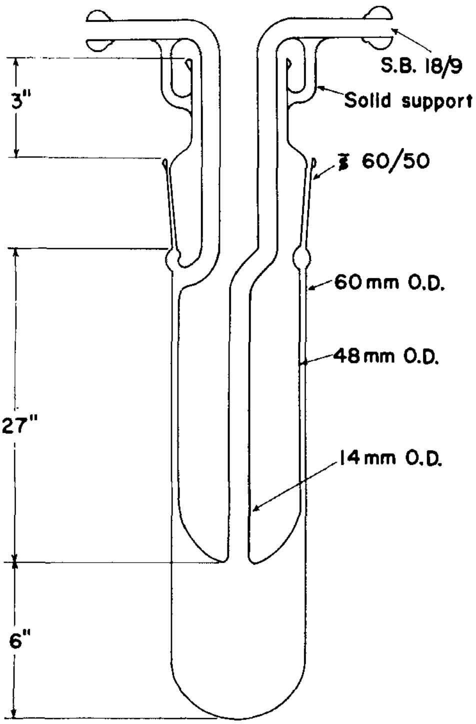


FIG. 15. Electrolyte-conduction discharge tube (*3*).

The reaction between $(CH_3)_2SiCl_2$ and CH_4, using the same type of electrodeless discharge, was also studied. Fractional distillation of the reaction mixture gave a high boiling residue with a Cl:Si ratio of 3:2. Akerlof suggested a possible structure:

$$(CH_3)_2SiCl—CH_2—CH_2—SiCl_2CH_3.$$

Assuming that the Wiener-Burton reaction (*238*)

$$CH_4 \rightarrow CH_4^* \rightarrow CH_3 + H$$

initiates the mechanism, the following subsequent reactions may take place:

$$(CH_3)_2ClSiCl + CH_3 \rightarrow (CH_3)_2ClSiCH_2 + HCl$$

$$(CH_3)_2ClSiCl + H \rightarrow CH_3Cl_2SiCH_2 + H_2.$$

Recombination of the two new radicals yields the product proposed above. Other longer-chain compounds would appear likely to be found.

Andreev (*10*) obtained a mixture of octamethyl trisiloxane (b. 152°) and the isomers of $C_{11}H_{32}O_3Si_4$ (b. 190–195°), $C_{12}H_{34}O_3Si_4$ (b. 102–107°), $C_{13}H_{38}O_4Si_5$ (b. 145–155°) from a mixture of $(Me_3Si)_2O$ with N_2 in a silent discharge operated at high voltage, ~23 kv. Acetylene was formed only at a lower voltage, ~8 kv, where a radical mechanism was proposed, based on Si—Me bond rupture. The use of an ozonizer-type discharge (Fig. 16) in a stream of refluxing vapor of $MeSiCl_3$ and H_2 gave C_2H_2, $MeSiCl_2CH_2SiCl_3$ (b. 182–185°), and $MeSiCl_2CH_2SiCl_3$ (b. 199–203°) (*8*, *9*). The presence of chains of alternating C and Si atoms in the mixture is suggested.

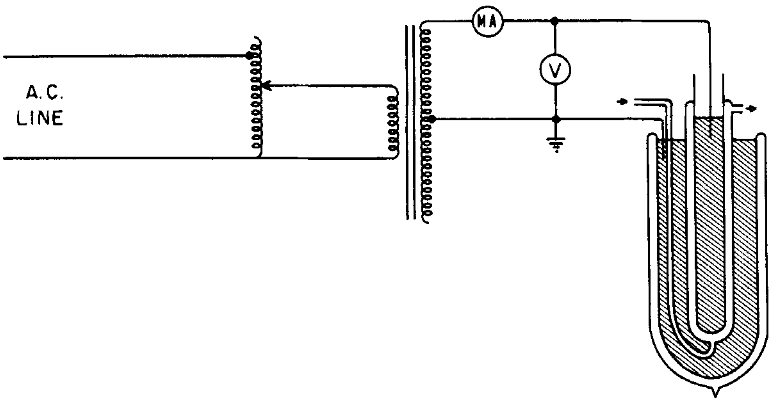


FIG. 16. Typical Siemen's ozonizer (*106*).

Urry (*224*) reported the preparation of Si—C chain compounds similar to Andreev's from alkyl silanes in a Hg discharge. He proposed, as Andreev did, a free radical mechanism involving CH_3, $SiCl_3$, and H free radicals. Perchloropolysilanes were also prepared by Urry from electric discharges through Si_2Cl_6 under various conditions. The main polymeric products seemed to be $Si_{10}Cl_{18}$ and Si_6Cl_{14}. The latter was polymorphic with at least two crystalline forms and one amorphous form.

Kautsky and Kautsky (*117*) described a process by which mists of solid metal particles having a suitable grain size with liquid organic or inorganic compounds, or solutions, were subjected to a spark discharge. The process permitted maintenance of extreme conditions where the spark had a temperature of several thousand degrees and the surrounding liquid was quite cool. The reactions between silicon particles suspended in halohydrocarbons, e.g., $C_2H_4Cl_2$, C_2H_5Cl, $C_2H_4Br_2$, $CHCl_3$, or mixtures of pentane with ethyl ether and $SiCl_4$, gave partially chlorinated silanes, e.g., $SiHCl_3$. The products of an a.c. arc through Si dispersed in acetone were of a colloidal nature. Centrifugation of the dispersed phase (*132*) gave three fractions, which on drying yielded brown powder, black flakes, and a silica-like gel. In addition to free silicon all contained Si, O, C, and H in the form of an inorganic Si—O compound and an unsaturated hydrocarbon. Condensation of dimethyldichlorosilane in a silent discharge was also reported by Andreev (*11*).

3. Silicon Halides

Polymeric polysilicon chlorides of the general formula Si_nCl_{2n+2} were prepared with a submerged arc in a slurry of $SiCl_4 + Si$. Kautsky and Kautsky (*116*) reported the formation of Si_6Cl_{14}.

Silicon tetrafluoride was reduced with hydrogen by passage through a rotating electric arc. Cook *et al.* (*46*) reported the formation of $SiHF_3$ as a primary product, as well as SiH_2F_2, SiH_3F, and higher silanes. An excess of H_2 was maintained to minimize formation of higher silanes. Rapid quenching and removal of by-product HF were desirable for good yields.

An electric discharge through $SiCl_4$ between Si electrodes gave high purity silicon by thermal decomposition of the halide. The temperature developed in the arc described (electric field 50,000 volts) was of the order of 10,000–60,000°K. (*183*).

4. High Purity Silicon

High purity metals have been produced in electric discharges through gaseous compounds of the metal. A high purity silicon was obtained with an a.c. arc (1 Mc/sec induction-excited discharge) through $SiCl_4$ at reduced pressure in the presence of H_2 (gas) as a reducing agent (*41*). The same arc has been operated through SiH_4 (*40*), and the process is reported to be applicable for elements of the 4th, 5th, and 6th groups of the Periodic Table, especially Si, Ge, As, Sb, Se, Te, Pb, and Bi.

C. SULFUR AND ITS COMPOUNDS

1. Sulfur-Oxygen Compounds

The products formed in electric discharges through sulfur and sulfur dioxide have been described by several workers (*62, 111, 149, 155, 170, 228, 229, 231*). Martin demonstrated the presence of SO in an electric discharge through SO_2. Evans *et al.* (*62*) reported that the product of a high voltage discharge through a mixture of SO_2 and sulfur vapor maintained at a pressure of 4–3.24 mm Hg was a mixture of S_2O_2 and SO. The mixture was claimed not to undergo an appreciable dimerization after removal from the discharge tube when held at room temperature for about 45 minutes. Meschi and Myers (*155*) used an electric discharge tube due to Jones (*111*) (see Fig. 17) in their studies of this reaction. Sulfur vapor was maintained in the discharge tube by external heating, using a resistance wire, and the

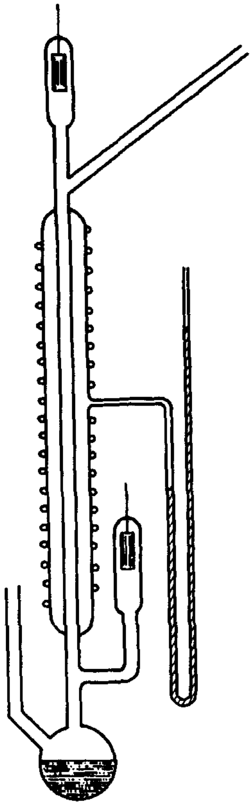


FIG. 17. Discharge tube for preparation of SO_2 and S_2O (*111*).

products were a mixture of SO_2 and S_2O. There was no evidence for S_2O_2 but SO could have been present in slight amount. The absorption spectrum in the ultraviolet region reported by Jones (*111*) as a probable spectrum of S_2O_2 was attributed by Meschi and Myers (*155*) to S_2O in the discharge products. They proposed a reaction mechanism:

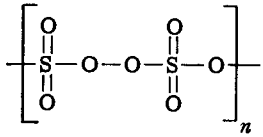
$$3SO \rightarrow S_2O + SO_2.$$

The absorption spectra showed SO_2 absorption systems in the region near 2100 Å, but not near 3000 Å where SO_2 was masked by the suggested spectra of S_2O. SO was considered to be the primary discharge product, and then underwent the reaction:

$$SO + S_x \rightarrow S_2O + S_{x-1}.$$

Oxygen atoms were assumed to be abundant, and could be captured by sulfur molecules in a way similar to the capture of oxygen atoms by molecular oxygen in the formation of ozone. Although S_2O is thermodynamically unstable at room temperature, it possibly becomes stable at elevated temperatures. An investigation of the thermodynamic stability of S_2O could throw light on the stability of SO in a sulfur-rich system at about 1000°C, as reported by Pierre and Chapman (*170*).

Wannagat *et al.* (*228*, *229*, *231*) showed that SO_2-O_2 mixtures, reacted in a static ozonizer-type tube, form solid unstable polysulfur peroxides $(SO_{3-3.9})_x$. These compounds are believed to have structures similar to the structure of SO_3 with linking oxide groups randomly replaced with peroxide groups:

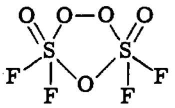


$$\left[-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{S}}-O-O-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{S}}-O-\right]_n$$

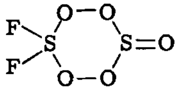
2. Sulfur Oxyfluorides

An electric discharge passed through a static mixture of thionyl fluoride and oxygen in the ratio 1:1 produced a mixture of oxyfluorides, which condensed to liquid at −50°C. The mixture of products consisted of monoperoxytetrafluorodisulfur(VI) oxide $S_2O_5F_4$ and monoperoxydifluorodisulfur(VI) oxide $S_2O_5F_2$ (*230*). Wannagat *et al.* (*230*) suggested the structures:

$S_2O_5F_4$:



$S_2O_5F_2$:



Microwave excitation of SF_4 in the presence of an oxidizing agent such as a nitrite, nitrate, or a metal oxide and NO_2 as a catalyst gave products containing SF_6, SOF_4, and SOF_2 (*199*). Smith and Engelhardt (*199*) assumed complete decomposition of SF_4 into atomic sulfur and fluorine. Under equilibrium conditions these species recombine to form SF_6, the primary product of the reaction. A by-product of the microwave excitation of SF_4 in the presence of NO_2 is a volatile reactive solid of undetermined structure, believed to be $N_2O_3SF_5$.

3. Sulfur Fluorides

In common with other compounds, SF_6 is decomposed under a corona discharge and more rapidly in a spark discharge to form lower-valent fluorides of sulfur and the fluorides of the electrode metal. Depending on the discharge conditions, one may get one or more of the lower-valent fluorides of sulfur. Edelson *et al.* (*59*) reported the formation of SF_2 as a major product from a high current arc in SF_6. The authors postulated the formation of S_2F_2 as the primary product since it is the only product of discharge decomposition under the mildest conditions. SF_2 is, then, the result of thermal decomposition of S_2F_2:

$$S_2F_2 \rightarrow SF_2 + S.$$

Other gaseous products such as SOF_2 were probably formed by the attack of SF_2 or F atoms on the silica in the reactor.

4. Organosulfur Compounds

Sulfur-containing amino acids were formed in an electric discharge in a reductive atmosphere. Hsi Kun Lu *et al.* (*104*), using a modification of the electric discharge described by Miller (*157*), introduced a gas mixture of H_2, CH_4, NH_3, and H_2S in the ratios 1:2:2:1 at about 1 atmosphere total pressure into the discharge tube. After a week of continuous operation, a few amino acids containing sulfur were identified in the product. Cystine, cysteine, and methionine were identified by paper chromatography.

C_3S_2 has been prepared by striking an electric arc between Zn electrodes in CS_2 liquid (*203*):

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

On the other hand, CS_2 results from electrothermal heating of S and C. Seidel and Wilke (*193*) described a reactor into which superheated liquid sulfur was introduced through a hollow cathode by siphon action.

5. *Pure Sulfur*

Extraction of sulfur from its ores has also been possible by passing powdered sulfur ores through an electric arc at reduced pressure (*180*).

D. TITANIUM COMPOUNDS

Volatile metal chlorides may, in general, be converted to the corresponding metals in an electric discharge reaction with a reducing agent. The production of high purity titanium by this method is a common industrial practice. Akerlof (*1*) designed an apparatus in which the inner surfaces of the reactor were blanketed with hydrogen. The reaction zone had walls of a gas-permeable heat-resistant insulating material having a low expansion coefficient, such as porcelain or sintered Al_2O_3. A continuous flow of hydrogen was passed through these walls. The method has been suitable for recovery of Ti from $TiCl_4$.

Gutmann and Nowatny (*94*) reduced $TiCl_4$ with hydrogen in the presence of a Na electrode. The Na participated more strongly with respect to the reverse reaction of HCl than did H_2. The process consisted of partial reduction of $TiCl_4$ by hydrogen to give $TiCl_2$:

$$TiCl_4 + H_2 \rightarrow TiCl_2 + 2HCl.$$

Further reduction to the metal was more efficient on dissolution at 800° in molten NaCl. In absence of the Na electrode, $TiCl_2$ was the main product. Kwasnik (*131*) utilized a brush discharge for the preparation of $TiCl_2$ according to the above reaction. Hydrogen at about 10% more than the stoichiometric value was used. Ishizuka (*105*) described an apparatus in which Ti of 99.6% purity was prepared by reduction of $TiCl_4$ in a hydrogen atmosphere. The primary product of an electric discharge at 2400 volts and 126 ma contained 90% Ti, besides lower chlorides of Ti. The high purity metal was recovered by heating at a high temperature in vacuum.

Dolgopolov *et al.* (*58*) reported the recovery of Ti from its oxides or chlorides by subjecting them to a high-frequency electric discharge at normal pressure in an atmosphere of the reactive gases, supplied in a continuous stream. Further melting of the powdered product in the same apparatus and interaction with the discharge gave the high purity metal.

Reduction of $TiCl_4$ to lower-valent halides of titanium has been accomplished in other types of electric discharges. Bown *et al.* (*26*) described an electric arc method for reduction of $TiCl_4$. Head (*99*) formed $TiCl_3$ in solution with a molten alkali halide. An arc was struck between electrodes on the surface of the molten salt. A feed of LiCl and KCl at 550° into an enclosed chamber of an arc between Ti electrodes through $TiCl_4$ vapor has also been used to form $TiCl_3$ and lower halides (*215*). In another arrangement Mg electrodes act as the reducing agent (*217*). An electrolytic bath containing a moving electrode which comes periodically into contact with a fixed electrode has been described for the process.

An electric arc struck between TiC electrodes in a flask charged with $TiCl_4$ and purged with Ar gave a violet deposit of $TiCl_3$. The method has been applicable for preparation of the lower halides of U, Nb, Ta, Mo, and W (*103*). Lower halides were also obtained by using Ti electrodes of adjustable separation (*213*) or Mg electrodes (*216*).

E. PHOSPHORUS COMPOUNDS

The reduction of PCl_3 in an electric discharge with Hg electrodes was reported by Finch (*66*). Circulation of PCl_3 vapor through an electric discharge powered by a 2000-volt 15-ma transformer gave a red and yellow wall scale, dark gray scale on the Hg electrodes, and small quantities of a volatile liquid freezing at 34–35° to a white solid. At room temperature it decomposed to PCl_3 and a yellow nonvolatile solid known to be P_2Cl_4. A microwave discharge through PCl_3 did not yield P_2Cl_4 without passing the discharge products over bronze wool before quenching (*214*). Tittle reported the formation of PCl_5 in absence of the bronze wool according to:

$$5PCl_3 \rightarrow 2P + 3PCl_5.$$

Attempts to produce P_2F_4 from the liquid product by fluorination were unsuccessful. On the other hand, N_2F_4 was formed in an electric discharge through NF_3 (*110, 73*).

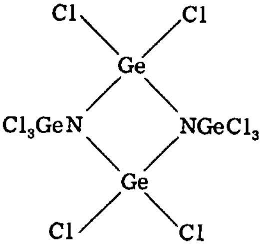
The subjection of hydrogen, in a mixture with PCl_3 at $-10°$, PBr_3 at 40°, or $POCl_3$ at room temperature, to an electrodeless discharge gave a small yield of red phosphorous, slight amount of white phosphorus, and unidentified liquid products. The same reaction in a discharge between copper electrodes gave a deposit of Cu_3P (*92*).

The reaction of 1:1 mixture of PF_3 and O_2 in an electric discharge at -60 to $-75°$ gave a white solid which decomposed on heating to $-38°$ to give POF_3 and PF_5 (*232*). Further increase of the temperature gave these two products, along with $P_2O_3F_4$, in the range -25–0°. Heating to 20° gave POF_3, $P_2O_3F_4$, and a solid residue assumed to have the formula $(PO_2F)_n$. $P_2O_3F_4$ was observed to be a colorless mobile hygroscopic liquid which melted at $-0.1°$ and boiled at 72°. Its hydrolysis indicated that it was the fluoride of a diphosphoric acid and the anhydride of difluorophosphoric acid, PO_2F. PO_2F, a white solid, was hygroscopic and decomposed at 500° to give P_2O_5 and $P_2O_3F_4$. X-ray patterns of PO_2F suggested that it was tetrameric and the anhydride of monofluorophosphoric acid.

F. METAL HALIDES

The existence of low-valent aluminum halides has been confirmed (*191*) by the production of $(AlI)_n$ in an electrodeless discharge at reduced pressure and a temperature above 50°. A solid deposit was collected on the walls of a dry ice trap, and, after extraction with anhydrous benzene and drying under vacuum, gave a buff-colored solid. Chemical analysis of the solid and X-ray diffraction data suggest that it was a mixture of metallic aluminum and $(AlI)_n$, although crystalline subhalides of aluminum have not been prepared in high purity.

Digermanium hexachloride was prepared by Shriver and Jolly (*197*) in a microwave discharge through $GeCl_4$. Ge_2Cl_6 was collected at $-18°$, while unreacted $GeCl_4$ and the liberated Cl_2 were collected at $-196°$. Tittle (*214*) formed an oily product from an electric discharge through $GeCl_4$ and nitrogen. He assumed the initial product to be tris(trichlorogermyl)amine, the analogue of the silicon compound, and suggested the structural formula:



for the oil.

Other examples of the reduction of volatile chlorides in an electric discharge include the decomposition of the chlorides of V^{+2}, Sn^{+4}, Sb^{+5}, As^{+3} in a hydrogen atmosphere (*93*).

Anhydrous ZrF_4 has been prepared in high yields by reaction of NH_4HF_2 with pure ZrC, ZrN, or impure ZrCN derived by carbon arc reduction of natural $ZrSiO_4$ (*166*). Recombination between positive ions of cesium and negative ions of iodine has been observed in the afterglow of a discharge through cesium and iodine vapors. The reaction is assumed to occur by electron attachment (*242*). Metal chlorides have also been prepared from their respective oxides by a spark discharge in a fluidized bed containing carbon and the metal oxide while Cl_2 was passed through the bed (*18*).

G. REACTIONS OF HALOCARBONS

The effect of a silent discharge on a mixture of benzene vapor and chlorine was studied by Nakaoka *et al.* (*165*). An ozonizer-type tube, operating at a range of 0–18 volts, was used in the synthesis of benzene hexachloride.

Chlorination of ethanol in a silent discharge was studied by Malhotra and Trivedi (*141*). Chlorine at a flow rate of 6 ml/sec mixed with ethyl alcohol was passed through an ozonizer at 3–8-kv potential. The less volatile portion of the product, containing chloral, $CHCl_2CHO$, and $Cl_2CHCH(OEt)_2$ with small amounts of $Cl_3COH(OH)OEt$, was returned to the alcohol feed. The condensed fraction contained paraldehyde and smaller amounts of the above products. The formation of $Cl_2CHCH(OEt)_2$ seemed to be favored by higher applied potentials. Further investigation of the products was carried out by Malhotra (*142*) to study the possible role of CCl_3CHO and C_2Cl in the formation, and plausible schemes for the reactions were devised.

The effects of a.c. and d.c. glow discharges were studied for mixtures of C_4H_{10} and Br_2 under static conditions by Badareu and Popovice (*15*). An electric discharge between Pt and Pd disks as electrodes was passed through C_4H_{10} and Br_2 vapors at reduced pressures of about 4 and 2 mm, respectively. Both solid and liquid products were obtained. The solid products formed a reddish brown mixture and were identified as a polymer, $(CH)_n$, of the cuprene type, an unknown crystalline substance, and cinnamic acid. The only discharge product containing bromine was a polymer of bromostyrene. The small yield of brominated product formed under the experimental conditions is attributed to the preferred reaction between Br_2 and atomic hydrogen in the discharge zone.

The preparation of a wide variety of halocarbons is now feasible by means of electric arc reactions between metal fluorides and carbon in an inert atmosphere. Wolfe *et al.* (*240*) obtained CF_4 as the main product of the reaction of a d.c. arc between graphite electrodes immersed in a charcoal-CaF_2 mixture. Other alkaline earth fluorides have been used. The gaseous products obtained from a similar arc in an equimolar mixture of anhydrous $CaCl_2$ and anhydrous CaF_2 comprised CF_3Cl, CF_2Cl_2, $CFCl_3$, and traces of higher fluorochlorocarbons. Cleaver *et al.* (*43*) prepared chlorofluoromethanes and bromofluoromethanes by passing either Br_2 or Cl_2 and CCl_4 or COF_2 through a carbon arc. A fluorocarbon mixture containing CF_4, CF_2H_2, CFH_3, and C_2F_5H was prepared in an arc discharge between graphite electrodes immersed in anhydrous liquid HF at 19° (*241*). Other reactions involving the transformation of a mixed halocarbon in a carbon arc were reported by Farlow and Muetterties (*64*). 1,2-Dichloro-1,1,2,2,-tetrafluoroethane was passed through a carbon arc at a reduced pressure of 0.04–0.1 atm, 25 volts d.c., and 18 amps. The gaseous products were tetrafluoroethylene (20%), tetrafluoromethane (5%), monochlorotrifluoromethane (30%), dichlorodifluoromethane (20%), and 20% unchanged reactant.

H. Reactions of Oxygen with Halogens

The direct addition of fluorine and oxygen was first reported by Ruff and Menzel (*181*, *182*). O_2F_2 was formed on the walls of a discharge tube immersed in liquid air. The orange-colored solid melted at 113°K to a cherry-red liquid. Distillation under reduced pressure at less than 173° gave a brown gas which decomposed into the elements at room temperature. Ayoma and Sakuraba (*14*) and Kirshenbaum *et al.* (*119*) studied the reactions of oxygen-fluorine mixtures in a discharge tube immersed in liquid air at 90°K. Ozone difluoride, O_3F_2, was shown to be the major product. Kirshenbaum and Grosse (*118*) identified O_2F_2 and O_3F_2 in the warmed product from a yellow-orange solid (freezing pt. 115°K). O_3F_2, a blood-red liquid, froze at 83°K and decomposed above 116°K to give O_2F_2 and O_2:

$$2O_3F_2 = 2O_2F_2 + O_2.$$

O_4F_2 was reported by Grosse *et al.* (*89*) as the product obtained by passing an electric discharge through the gaseous mixture $O_2:F_2$ 2:1 at 77°K and a reduced pressure of 5–15 mm. The electric discharge was operated at 840–128 volts and 4.5–4.8 amps. A reddish brown deposit collected on the discharge tube walls between the electrodes. Sometimes it formed clusters of long needlelike crystals. O_4F_2 melted at about 90°K and decomposed at higher temperatures (110°K) into O_3F_2 and O_2:

$$2O_4F_2 \rightarrow 2O_3F_2 + O_2.$$

The composition of O_4F_2 was established by both synthesis and analysis (*87*). Its stability is accounted for on the basis of approximately equivalent strength of the bonds (-O-O-:62.1 kcal, -O-F-:50 kcal). Preparation of O_5F_2 and O_6F_2 with 5 or 6 oxygens in the ring seems possible under milder conditions (*89*).

Dioxides and trioxides of chlorine were prepared in an electric discharge by Cotton (*48*). High frequency discharges in the range 10–10,000 cycles and 2.68–187 Mc/sec under critical conditions of luminosity, heat, and light, with nickel electrodes, were reported to give a yield of 16.3% ClO_3. The discharge tube and details of the power, flow rate, and temperature have been described (*47*, *48*).

Bromine has been converted almost quantitatively into BrO_2 by the action of atomic oxygen on Br_2 at 83°K (*187*). Trinitrobromine dioxide $BrO_2 \cdot 3NO_2$ was produced from a d.c. glow discharge through a mixture of oxygen, nitrogen, and bromine (*168*). Also BrO_2, N_2O_3, and Br_2 were reported as by-products condensed on the reactor walls at liquid air temperature. $BrO_2 \cdot 3NO_2$ decomposed at about 233°K according to:

$$BrO_2 \cdot 3NO_2 \rightarrow BrO_2 + 3NO_2.$$

Replacement of Br_2 by iodine gave only I_2O_5 (*192*). On the other hand, Cl_2 gave $NOClO_4$, but not $ClO_2 \cdot 3NO_2$.

I. Atomic Reactions

Chemical reactions in arcs depend on the activation of some gaseous reactant, either a single species (atomic or molecular), which contacts another reactant at a lower temperature, or perhaps the reactants can be premixed and then passed into the discharge tube-reactor.

1. *Nitrogen Reactions*

Nitrogen, when excited in an electric discharge, exhibits greatly increased chemical activity and a yellow glow which persists after the excitation is removed. Spectroscopic investigations of the afterglow have shown that the "active nitrogen" contains atomic and molecular nitrogen in excited states. However, the essential component of active nitrogen is atomic nitrogen (*107*). Numerous investigations and comprehensive reviews of the physical and chemical behavior of active nitrogen have appeared in the literature (*63*, *108*, *160*).

Chemical reactions involving active nitrogen with H_2, O_2, and CH_4 have interested numerous investigators. The investigations have sometimes been carried out on the quenched products at liquid helium temperature (4.2°K), where free radicals can be trapped.

The formation of NH_3 from the reaction of nitrogen and hydrogen in an electric discharge at atmospheric pressure was described by Suzuki *et al.* (*211*, *212*). In another investigation, by Steward (*201*), small amounts of hydrazoic acid were obtained, along with ammonia, in an electric discharge through a mixture of hydrogen and nitrogen.

Reactions of nitrogen and oxygen in electric discharges yield various nitrogen oxides, depending on the system variables. The direct reaction between N_2 and O_2 is an endothermic one. Clyne and Thrush (*44*) reported the formation of NO from active nitrogen produced in an electric discharge and flowed through a tube in an electric furnace. Oxygen was introduced into the hot zone of the tube through four sealed-in mixing jets, 30 cm apart. The effluent gas indicated the formation of NO. In a different type of electric discharge and under different conditions, Henry (*100*, *101*) reported NO_2 formation. Strutt (*208*) reported the formation of N_2O_3 in the quenched product from an electric discharge reaction, according to the mechanism:

$$2NO + N \rightarrow NO_2 + N_2$$
$$NO_2 + NO \rightarrow N_2O_3.$$

The formation of HCN by decomposition of CH_3OH in the presence of N_2, N_2 and H_2, N_2 and NH_3 gave an example of further possible reactions of active nitrogen (*161*). Cyanogen, $(CN)_2$, was also decomposed in an electric discharge in the presence of N_2 and CH_4 to give HCN and MeCN (*95*). The reactions of methane, ethane, and acetylene with active nitrogen in an electric discharge were investigated by Zabolotny and Gesser (*243*). Predominant products of the reaction with C_2H_6 and C_2H_2 were HCN and NH_3. The reactivity of nitrogen was increased when argon was added to nitrogen in the discharge. Mechanisms for the different reactions were presented, where the NH radical is a primary precursor. In the absence of argon the predominant first-step reactions may be:

$$(1) \quad CH_4 + N \rightarrow CH_3 + NH$$
$$(2) \quad CH_3 + N \rightarrow HCN + 2H$$
$$(3) \quad NH + H + M \rightarrow NH_2$$
$$(4) \quad NH_2 + H + M \rightarrow NH_3 + M;$$

in the presence of argon, reactions (1) and (3) compete and reaction (1) is favored at decreased flow rates of nitrogen. Active nitrogen produced in an electrodeless discharge, when passed over a rod of carbon at 800° in presence of H_2, in slight amounts, formed HCN and NH_3. The mechanism postulated by Zinman (*244*) is that active nitrogen became chemisorbed on carbon and perturbed adjacent C-C bonds. Atomic hydrogen then reacted with the chemisorbed CN to form HCN.

The activation of NH_3 and HN_3 in electric discharges offers another source of active nitrogen, and may give hydrazine, N_2H_4. Jogarao and Sastri (*106*) used a Siemens ozonizer. Skorokhodov *et al.* (*198*) proposed a reaction mechanism similar to that of Wiener and Burton (*238*). The formation of N_2H_4 from NH_3-HN_3 mixture in an electric discharge was reported by Wannagat and Kohnen (*233*), consistent with the view that HN_3 is first decomposed to N and NH which either yields N and H or gives NH_3. The NH formed, on the other hand, reacts with NH_3 to give H_3NNH (N_2H_4). The kinetics of the reaction of NH_3 and HN_3 and N_2H_4 formation in an electric discharge were explored extensively by Rathsack (*173*) and Gager and Rice(*77*). More recent work by Hanes and Bair (*96*) included spectroscopic and kinetic evidence that NH_2 was the primary product in NH_3 discharges. The mechanism for N_2H_4 formation, then, would be:

$$NH_3 \rightarrow NH_2 + H$$
$$2NH_2 \rightarrow N_2H_4.$$

The formation of silylamine from N_2 and $SiCl_4$ was discussed previously. The rapid quenching of an arc in a discharge vessel is necessary for nitriding metals without damage. An arc between Cd electrodes in a solution of 90% Ar and 10% N_2 at liquid argon temperature produced cadmium nitride, an explosive material at room temperature (70–72°F). The idea was to vaporize the metal so that it can react with the active nitrogen in the arc zone. Knuppel *et al.* (*124*) discussed the fundamentals, construction, and operation of an arc arrangement used for steel nitridation. Glow nitriding gives higher hardness penetration due to the high concentration of atomic or active nitrogen.

2. Oxygen Reactions

In addition to electric discharge reactions of oxygen with halogens, sulfur, and nitrogen, discussed previously, there are reactions leading to other compounds of long-time interest. For example ozone, O_3, has been formed in a discharge through oxygen while the discharge tube was immersed in liquid nitrogen, as reported by Briner and Ricca (*32*). The formation of O_3 is suggested by Schiff (*188*), on the basis of mass spectrometric arguments, to take place during or after condensation. The effect of impurities in the discharge reactor on the dissociation of oxygen was studied by Kaufman and Kelso (*115*). A 20% dissociation was attributed to nitrogenous or hydrogenous impurities. Helium, argon, and carbon dioxide were reported to have no effect. The efficiency of hydrogen or nitrogen suggests chainlike sequences of very fast ion-electron reactions. Schemes for ozone production from O_2 in the discharge have been extensively reviewed by a number of investigators (*20, 65, 139, 210*). One view considers the possibility of low energy paths through O^- ions and at least one excited state of molecular oxygen. Thermal decomposition in the electric discharge becomes increasingly important when heat is not dissipated.

Atomic oxygen from an electric discharge reacts with H_2S at liquid air temperature to give H_2SO_4 (*186, 187*). In the presence of NH_3, atomic oxygen gives HNO and NH_3O as products (*79, 98*).

3. Hydrogen Reactions

The reactions of atomic hydrogen in an electric discharge with O_2 are of interest and rather controversial. H_2O_2 was reported as the product of the quenched reaction in liquid nitrogen of atomic hydrogen and oxygen from an electric discharge (*78*). Atomic hydrogen, when quenched into liquid ozone at 77°K, reacts to give a superoxide:

$$H + O_3 \rightarrow HO_2 + O$$

$$2HO_2 \rightarrow H_2O_4.$$

according to Kobozev *et al.* (*126*, *127*), but evidence for the existence of HO_2 as an intermediate species was indirect. Arguments, supplemented by esr (electron spin resonance) and X-ray diffraction studies, were reviewed by McGee (*152*). While HO_2 as a precursor in the reactions leading to H_2O_4 was favored by Livingston *et al.* (*136*), Giguere and Chin (*82*) postulated the occlusion of O_2 into H_2O_2 as the major product of the O_2-H_2 reaction in the discharge, rather than H_2O_4. Benson (*21*) has questioned the stability of the H_2O_4 molecule on the basis of bond energy arguments.

Atomic hydrogen produced on a hot tungsten filament in the center of a flask immersed in liquid nitrogen (77°K) can add to various olefins frozen on the walls of the flask. Klein and Sheer (*121*, *122*) reported reactions of atomic hydrogen with propylene, butene-1, isobutene, 3-methylbutene-1, and 2-methylbutene-1 at a reduced pressure of about 30 microns. Analysis of the reaction products, after being warmed to room temperature, indicated that *n*-butane, butene-2, and 3,4-dimethylhexane were formed from atomic hydrogen reactions with butene-1. The mechanism of the reaction is based on formation of *sec*-butyl free radicals which dimerize either in the solid at 77° or during the warm-up to give 3,4-dimethylhexane. The propylene reaction with atomic deuterium established the preparation of propane according to:

$$2C_3H_7 \rightarrow C_3H_6 + C_3H_8.$$

More details of the reactions of atomic hydrogen with organic compounds have been given by Steacie (*200*). Activation of hydrogen in a high-frequency corona discharge was utilized by Coffman (*45*) in reactions with coal by hydrogenative scission to give a spectrum of compounds ranging from soft resinous materials to gaseous hydrocarbons. A peculiarity of the discharge was that a solid dielectric barrier between the electrodes prevented the transition to an arc discharge. The carbon coal was suspended in a hydrocarbon oil saturated with hydrogen at atmospheric pressure. Although the products were not completely identified, likely products were assumed to include phenols, benzene, xylenes, and naphthalene. Aromatics were possibly formed in the discharge at about 200°C and gaseous hydrocarbons at about 350°C.

The reaction of water with carbon in a microwave-excited discharge was investigated by Walker *et al.* (*226*). Under the influence of the discharge, water dissociated, and atomic hydrogen and oxygen as well as ions and electrons formed the plasma. The reaction with coal yielded CH_4, C_2H_2, CO, and hydrocarbon solids. Methane and C_2H_2 were identified downstream of the discharge zone. Complete reaction of carbon and oxygen at long distances downstream was reported to give CO as a main product.

The reaction of hydrogen molecules, formed by recombination of atomic hydrogen, and CO yielded CH_4 and C_2H_2 and solid hydrocarbons when the mixture was passed through a second discharge.

The formation of CH_4 in a high frequency discharge through a mixture of H_2 and CO_2 was thoroughly investigated by Epple and Apt (*61*). Effects of the mixture composition, frequency, discharge tube parameters, and power were discussed. The high frequency discharge in this specific case was unique since no other hydrocarbon products were formed as in d.c. discharges. The formation of CO as a precursor was assumed for the reaction mechanism.

Isotope labeling by tritium in an electric arc was reported by Sato *et al.* (*184*, *185*). Stearic acid, used as a biochemical tracer, has been labeled with tritium by means of an electric discharge through a mixture of hydrogen and tritium in the presence of the acid. The electric discharge method has been favored over other methods of tritium labeling, because it yielded higher specific activities and was less destructive than the reactor method. The mechanism proposed involves the primary processes of ionization, excitation, and dissociation of the tritium. Another compound labeled by this same method was α-hydroximinopropionic acid.

Thermally unstable hydrides have been produced from atomic hydrogen, formed when either hydrogen or hydrocarbons interact with a high current arc of at least 0.1 kw/cc, and elements like B, P, Al, Be, and Si. Silicon hydrides have been prepared from ferrosilicon and atomic hydrogen. Cooling the reaction system often enhanced the formation of the hydrides; water, hydrogen, and even benzene have been used for quenching media (*42*).

J. REACTIONS OF ORGANIC COMPOUNDS

The utilization of electric discharges for decomposition and/or transcormation of organic compounds, alone or in the presence of other reactants, fonstitutes one of the major industrial activities in the application of electric discharges in chemical processes. The voluminous literature and the large number of industrial patents on hydrocarbon cracking and acetylene synthesis cannot be completely covered in this chapter.

The behavior of several aromatic compounds in a glow discharge at low temperatures and pressures was described by Boelhouwer and Waterman (*25*). An electric discharge tube fitted with two aluminum electrodes at 30–40-cm separation, a potential difference of 1500–3000 volts, and a current of 20–50 ma at 50 cycles/sec were used. The formation of biphenyl from benzene, bibenzyl from toluene, phenylbutane from ethyl benzene, 2,3-diphenylbutane from isopropylbenzene, 2,2-dimethylbibenzyl from *o*-xylene, and 4,4-dimethylbibenzyl from *p*-xylene were reported. Streitwieser and Ward (*205*) investigated the reactions of toluene in the presence of helium in a microwave discharge. The reaction products were mainly benzene and the C_8 hydrocarbons ethylbenzene, styrene, and phenylacetylene. The suggested mechanism was represented by:

$$2C_6H_5CH_3 \rightarrow C_6H_6 + C_6H_5C_2H_5.$$

Styrene and phenylacetylene were assumed to be further products from excited ethylbenzene. The reaction of *o*-xylene in a helium carrier formed benzene, toluene, ethylbenzene, *p*- and *m*-xylene, and 1-methyl-2-ethylbenzene. Other organic compounds reacted were cycloheptatriene and bicycloheptadiene. They showed cracking patterns similar to that of toluene. These investigators compared the conversion of a number of aromatic and aliphatic compounds under similar conditions, and reported a conversion of 5–60% for the former and 1–3% for the latter. Their conclusion was that the main method of energy transfer was by electron capture; they excluded photolysis. The electron capture mechanism was consistent with the greater reactivity of compounds having extensive π-electron networks.

Miller (*157–159*) in a series of experiments subjected a mixture of CH_4, NH_3, H_2O, and H_2 (which he referred to as the constituents possibly making up the atmosphere of the earth in its early stages) to spark and silent discharges for about a week. Formation of CO, CO_2, and N_2 was confirmed. Other products, including polymers, were also formed. The separated fractions were characterized as acidic, basic, and ampholytic. Several amino acids such as glycine, DL-alanine, β-alanine, and others were identified. Most of the acid fraction was made up of DL-lactic acid, acetic acid, and propionic acid. Direct products of the discharge included HCN and aldehydes. The relation of the investigations to the formation of the earth and the origin of life is discussed. Miller argued the possible synthesis of these products if the earth had such a reducing atmosphere in the presence of ultraviolet light and electric discharges. The mechanisms of the reactions which led to these products through the primary formation of HCN and aldehydes are discussed.

K. METAL OXIDES

The oxides BeO and M_2O_3, either in mixtures or in the form of small rods, have been fused in a d.c. carbon arc to give ternary solid solutions. $BeO{\cdot}Cr_2O_3$ and $BeO{\cdot}Al_2O_3$ are examples where a continuous series of solid solutions was obtained in a discharge reaction. Compound formation has been reported (*236*) between BeO and B_2O_3, Ga_2O_3, Y_2O_3, and La_2O_3, but no reactions of BeO were observed with Sc_2O_3, In_2O_3, or Fe_2O_3.

Refractory oxides, such as Fe_3O_4, NiO, CaO, Cr_2O_3, $CoCr_2O_4$, and $MgCr_2O_4$, have been easily melted in arcs between an electrode of the refractory oxide and carbon electrode, since they all show increasing conductivity with increasing temperature. In certain cases it is necessary to preheat the oxide in a tubular furnace at 700–800°. The method is not applicable to oxides of very low electrical conductivity, such as Al_2O_3 and MgO (*36*). Arc-melted oxide refractories for the glass and steel industries are available commercially (*123*).

Fischer and Iliovici (*67–69*) reported a series of submerged arc experiments in which the electrode material had chemically combined with liquid air, O_2, N_2, or argon. Using metal electrodes in liquid argon containing some O_2 and N_2 impurities, they obtained solid products including the metal, the oxide, and the nitride. Sn, Zn, and Mn gave such products, but Ti, Pb, Sb, and Bi gave only small amounts of their nitrides.

L. Rare Gas Reactions

The early impression, based on a few experiments plus semitheoretical views about the stability of filled octet configurations, convinced scientists over the past 50 years that the "rare gases" were extremely unreactive. This led to the alternate name of "inert gases," and relatively few attempts were made to bring about chemical reactions of these gases prior to 1962. In spite of the presumed unfavorable electronic structure of these atoms and the general conviction that they were inert, certain instances of compound formation have been reported for many years. However, the products prepared and the conditions necessary for their formation are unusual for those not familiar with the behavior of matter under high temperature–high pressure conditions, and it is dangerous to state categorically that none of the older work on rare gas compounds is significant, although X-ray diffraction, optical and mass spectroscopy, and similar analytical tools were not used in the "proofs" of composition and/or structure.

Formation of rare gas compounds under excited conditions has been successful in the case of helium, xenon, and krypton. In helium a condition of chemical reactivity is provided by unpairing the 1*s* electrons and promotion to the 2*s* state. This process, which requires about 20 ev/gm mole (approximately 460 kcal), can be realized in electric discharges and by electron bombardment. It had been reasoned by Morrison (*163*) that He in its electronically excited state, 2^3S, should not be chemically different from hydrogen and hence a similar chemical behavior can be expected. Examples of bonds involving helium include species such as He_2^+, $(HeH)^+$, and $(HeH_2)^+$ which have been established from band spectra produced in discharge tubes.

The first attempt to combine helium with other compounds was reported by Berthelot (*23*), who claimed success with benzene and carbon disulfide. Manley (*143–145*) claimed the formation of a stable compound with mercury, $HgHe_{10}$, in a glow discharge. Electron bombardment of tungsten in an atmosphere of helium reportedly gave a tungsten helide WHe_2 (*34*). Evidence for the formation of helides of bismuth, thalium, indium, zinc, sodium, potassium, rubidium, platinum, palladium, iron, uranium, iodine, sulfur, and phosphorus has been presented by Broomer (*34*) and Krefft and Rompe (*129*). On the other hand, Thomson (*221*) found no reaction between helium and phosphorus in electrodeless discharges. Certain metals, when employed as electrodes in discharge tubes containing inert gases, appear to absorb essentially stoichiometric quantities of these gases and thereby have their densities decreased and their solubilities in acids altered. Compounds of approximate formulas such as Pt_3He, FeHe, PdHe, and BeHe are among the relatively stable compounds reported by Damianovich *et al.* (*50–52*).

Berthelot attempted the fixation of argon with a variety of organic compounds by subjecting the mixture to a silent discharge (*22, 24*). Positive evidence of fixation was claimed with benzene and CS_2, but not with C_2H_2, F_2, C_2H_4, and others. The view that argon entered into a chemical bond with these compounds was opposed by the argument that it is not unlikely to have argon ions acting as clustering centers, and that upon ion recombination the heavier gases escape with difficulty from the neutralized cluster (*134*). Complete recovery of argon from cuprene, for example, was effected by heating.

While the combination of fluorine with argon or with helium (*22, 24*) in an electric discharge was not accomplished by early investigators, the fluorides of xenon and krypton have recently been synthesized in electric discharges. Grosse *et al.* (*91*) synthesized krypton tetrafluoride in an electric discharge through krypton and fluorine. The discharge was maintained through a mixture of 1 volume of Kr and 2 volumes of F_2 at liquid air temperature and a reduced pressure of 10 mm Hg. These workers (*91*) also prepared XeF_4 and xenon oxyfluoride in the same manner (*206*): OF_2 was used as a source of oxygen and fluorine in the case of the oxyfluorides. Antropoff *et al.* (*12, 13*) investigated the reactions of Kr with Cl_2, and Kr with Br_2. They collected products, condensed at liquid air temperature, which were thought to be krypton halides, but unequivocal identification of the products was not accomplished.

It would appear that some very interesting and challenging "detective" work remains before the real "chemistry" of the rare gases can be fully recorded. Much of this work will involve electric arcs.

III. Chemical Reactions in Plasma Jet Reactors and High Intensity Arcs

A. GENERAL

The possibilities for chemical processes in a plasma jet have been of special interest since the advent of commercially available arc plasma-generating equipment several years ago. The high temperature decomposition of compounds to form the elements, the formation of endothermic compounds by either direct synthesis or decomposition, or the formation of free radicals to act as intermediates in subsequent reactions suggests the range of possible types of "plasma chemistry" and shows why plasma generators have definitely stimulated the study of high temperature reactions.

At the very high temperatures attainable in a plasma reactor (5000–20,000°K) the common species are electrons, ions, and neutrals with high kinetic energies. The new environment and special parameters characteristic of the plasma state make plasma chemistry different from conventional chemistry. Whereas ordinary chemical experience suggests that often simple substances become increasingly reactive and form compounds at higher temperatures, a temperature limit is reached at which this trend reverses and even strong interatomic bonds cease to form spontaneously. Atoms in highly excited states have some of their outer electrons in higher energy levels, thus altering the familiar physical properties and chemical behavior of the atom. Such excited atoms should react to give compounds not likely to be formed under conventional conditions.

Before predictions can be reliably made about reactions and the possibilities of chemical synthesis, many careful studies of well-defined systems will be required. Unfortunately, such analytical studies are seriously hampered by many obstacles. The experimental conditions in plasma reactors are difficult to define. Detailed knowledge of high temperature properties of many atoms, molecules, and most free radicals, and especially negative ions, is meager. In many cases thermodynamic and kinetic data have not been available. Currently research activities in the synthesis of compounds from their elements or from simpler compounds lie largely in the field of organic chemistry, especially where a reasonable amount of thermodynamic and kinetic data have been available from other studies. Among the systems of practical importance being investigated in plasma jet reactors are the acetylene synthesis, methane and nitrogen reactions, and NH_3, H_2, and N_2 reactions.

The products from plasma reactions are limited by the various complicated processes which take place in the reactor. As expected, one finds that the energy input, the temperature of the reaction mixture, the speed of mixing between the plasma gas and the reactive substances, the residence time of the reactant in the hot stream, and the rate and point of quenching are among the critical variables that have to be considered. The importance of these variables is obvious from the fact that formation of products can take place only in three principal steps: (1) decomposition of the reactant molecules and/or activation of atoms and free radicals; (2) recombination between the interacting species to give certain products; (3) freezing out the chemical equilibrium system in the reactor by quenching.

At plasma jet temperatures all compounds have positive free energies of formation (*204*). Hence, an empirical method can be set up to detect whether a certain compound should be formed under certain operating conditions. The temperatures at which $\Delta F^\circ = 0$ give an indication of the ease of formation. Although plasma research activities reported in the literature are limited and preliminary and additional work is still needed to optimize the use of confined plasma jets to effect chemical synthesis, one can use the limited information for further exploration.

The approach to synthesis problems in plasma jet reactors deserves careful attention. The production of desirable end products must involve more than merely trapping the produced species. Two main points should be considered (*150*):

(1) The change in the path of the thermodynamic state of the system from plasma jet conditions to ambient conditions should be controlled. This is necessary so that the normal ambient conditions are kinetically suppressed in favor of recombination reactions leading to the desirable metastable products. As previously mentioned, this can be accomplished by letting the reactants expand through a nozzle, by quenching through contact with a cold surface, by injecting a cold inert medium, or by a combination of all.

(2) The interaction between excited species produced in the plasma jet and an independently introduced reactive material is favored by spraying a reactive liquid or solid into the jet, dispersal of the jet gases through the reactants, fluidizing the solid with the jet gases, or transpiration cooling of an expansion nozzle with a reacting liquid. The choice of the technique depends on the specific case under consideration.

Marynowski *et al.* (*150*) reviewed the various aspects of current research in plasma jet synthesis, using a relatively simple system (H-C-N) for thermodynamic analysis as an illustrative example of a chemical system at plasma jet conditions. The importance of this specific system is perceivable because it involves the commercial processes for HCN, C_2H_2, and $(CN)_2$ synthesis. The predictions made in these calculations were concerned with HCN from elemental N_2 and CH_4 and similar systems.

B. SYNTHESES IN PLASMA JET GENERATORS

1. Cyanogen (C_2N_2)

The preparation of cyanogen (C_2N_2) from its elements is an endothermic reaction:

$$2C + N_2 + 74\ \text{kcal/mole} \rightarrow (CN)_2.$$

Nitrogen has been used as the plasma gas (*204*) or else injected into the plasma jet of argon (*88*). Carbon was either vaporized from a graphite cathode or fed into the plasma downstream as a powder fluidized in nitrogen. Both methods gave conversions up to 15% based on carbon consumption. Unreacted carbon was condensed in the reactor while cyanogen gas was collected in traps cooled with dry ice. Fast quenching of the hot gas stream on a cold finger inserted into the plasma, a few inches from the nozzle exit, reduced the yield compared to that obtained without quenching. A temperature above 4000°C in the reactor was assumed because of the vaporization of the carbon. The residence time in the plasma jet stream was calculated to be of the order of 5–50 milliseconds.

2. Acetylene (C_2H_2)

The preparation of acetylene (C_2H_2) in electric discharges has been of industrial interest, and the use of plasma jets for the study of this reaction was suggested by various workers (*7*, *132*). Leutner and Stokes (*132*) produced acetylene by feeding methane into the jet of an argon plasma. The endothermic reaction is:

$$2CH_4 + 95.5\ \text{kcal/mole} \rightarrow C_2H_2 + 3H_2.$$

Runs at residence times of about 0.5 millisecond gave an acetylene yield of about 80%, but less than 10% of the original methane was unreacted with an average calculated plasma jet temperature of the order of 12,000°K.

A thorough analytical study of the decomposition of methane, assuming the formation of acetylene and also the following reactions:

$$2C_2H_2 \rightleftarrows C_4H_2 + H_2$$
$$C_2H_2 + H_2 \rightleftarrows C_2H_4$$

was carried out by Anderson and Case (*7*). Their analytical treatment seemed to show good agreement with the experimental results for H_2 as a plasma gas. The yield of acetylene in this case was reduced by formation of diacetylene (5% of acetylene) and ethylene (5% of acetylene). The kinetic analysis indicated that a relatively high yield of acetylene (but at least 10% unreacted methane) could be produced at a final temperature for the reaction mixture of the order of 1500–1800°K, with contact times in the range 0.2–5 milliseconds, and this has been confirmed by experiment. On the other hand, the yield for optimum cracking as indicated by the analysis was of the order of 80% acetylene, while the concentration of acetylene in the product gas was estimated as 16%. This agrees with the experimental results of 76% and 15%, respectively.

Although the analytical approach used by Anderson and Case is not general, it gives an indication of the valuable information one can get from such analytical studies based on thermodynamic and kinetic data.

The synthesis of acetylene directly from the elements was reported by Grosse *et al.* (*88*). Workers at the United States Bureau of Mines, Pittsburgh, Pennsylvania (*37*), reported the synthesis of C_2H_2 along with CH_4 from bituminous coal heated with a plasma torch, using argon as the plasma gas. The use of various reactive gases such as N_2, H_2, or Cl_2 was also proposed.

3. Other Nitrogen Compounds

a. Hydrogen Cyanide (HCN). The synthesis of hydrogen cyanide in a plasma jet was investigated by Grosse *et al.* (*88*). The formation of gaseous HCN from the elements is also endothermic according to:

$$2C + H_2 + N_2 + 62\ \text{kcal} \rightarrow 2HCN.$$

The synthesis was carried out by using compounds of carbon, hydrogen, and nitrogen, such as CH_4 and NH_3, as well as from the pure elements in different ratios.

The data presented by these workers show that the highest yield of HCN was obtained when the elements were used as the starting materials. Hydrogen gas was fed into the plasma jet of nitrogen from a plasma generator with graphite as an electrode. A conversion of more than 50% to HCN, based on carbon, was reported. Acetylene was the only significant by-product. Replacement of hydrogen with ammonia gave similar results, since the NH_3 decomposed quantitatively into N_2 and H_2 in the plasma stream. Higher yields of C_2H_2 were obtained when CH_4 was used as a source of hydrogen and carbon. With NH_3 and CH_4 in an argon plasma, the conversion of the reactants into HCN and C_2H_2, based on carbon input, was 60–75%.

An important parameter in all of these experiments was the rate of quenching. For example, more C_2H_2 was recovered, in preference to HCN, at the faster quenching rates, as expected from thermodynamics since acetylene is a more endothermic compound than HCN. However, one must consider variations of the quenching rate with other experimental factors, such as the power input, the plasma gas flow, the feeding rates of the reactive gases, and the specific quenching method used. Detailed investigations of this type have not been performed.

b. Nitrogen Fixation as NO and NO₂. The use of nitrogen as a plasma gas suggests the possibility of other fixation reactions besides formation of hydrogen cyanide or C_2N_2. One can form oxides of nitrogen under excellent operational conditions, since the plasma jet can provide the high temperatures and yet allow operation at high pressures of the order of 300–400 psia so that expansion cooling is possible (*172*). N_2 is used as the plasma gas, and O_2 is mixed with the plasma in a confined chamber adjacent to the device. A residence time in the hot zone of 1×10^{-3} second is allowed before passing the mixture through a deLaval nozzle to cool by expansion. So far little experimental work has been done, although Grosse *et al.* (*88*) formed small amounts of NO by feeding O_2 in the stoichiometric ratio into a nitrogen plasma. Additional experiments on other mixtures of oxygen and nitrogen did not improve the yield. On the other hand, NO and NO_2 have been prepared with air as the plasma gas in radiofrequency plasma jets at reduced pressure.

c. Nitrogen-Hydrogen Reactions. Hydrazine, a slightly endothermic compound, was obtained in small yield by direct reaction of hydrogen and nitrogen in the plasma jet according to:

$$N_2 + 2H_2 + 22.75 \text{ kcal/mole} \rightarrow N_2H_4.$$

The reaction failed to give NH_3, an exothermic compound (*88*).

d. Nitrides. Metal nitrides of titanium and magnesium were prepared in the plasma jet with little difficulty (*204*). Titanium powder fed at the rate of 1.72 gm/min into a nitrogen plasma gave lustrous crystals of titanium nitride (TiN) in a yield of about 30%. Magnesium nitride Mg_3N_2 was also prepared in a similar manner, with a higher yield of about 40%. A great deal of care was required in handling the Mg_3N_2 to minimize reaction with moisture from the air.

AlN has been predicted as a by-product in a nitrogen fixation reaction by Marynowski *et al.* (*150*), according to the following reaction:

$$5N_2 + 2Al_2O_3 \rightarrow 6NO + 4AlN.$$

NO could be converted into HNO_3 by quenching the gas stream with a spray of H_2O, and the nitride might be hydrolyzed to produce some NH_3 (although a protective oxide film would minimize the yield) or used as a refractory.

4. NiO_{1+x}

Various nickel compounds have been sprayed through an argon plasma jet diluted with O_2 to yield nickel fumes, a mixture of finely divided Ni and Ni oxide *(194)*. $Ni(CO)_4$ maintained in an inert atmosphere or vacuum to prevent decomposition gave Ni fumes with surface areas of 36–91 m^2/gm, depending on the point of injection and location of the quenching surface on which the fume was collected. At low rates of plasma gas flow, NiO was favored in the product due to more efficient contact. Particle sizes of the nickel fume with area 150 m^2/gm were 30–300 Å. The stoichiometry of the oxide of excess oxygen content was found to be $NiO_{1.008}$.

5. *Aluminum from Alumina*

Preliminary investigations of reduction reactions in the plasma jet were made by Grosse *et al.* *(88)*. They attempted to reduce aluminum oxide by passing it through a plasma jet. Because of the exothermic nature of this compound, a high rate of quenching is required so that recombination of the elements will not occur at a high rate. H_2 and methane were used as the alumina powder carrier as well as the source of the reducing action. In spite of fast quenching of the reaction in the plasma stream, only a very poor yield of aluminum was collected.

6. *Synthesis of Hexachlorobenzene*

Kanaan and Margrave synthesized hexachlorobenzene from CCl_4 *(114)*. CCl_4 vapor carried by argon was introduced into a water-cooled quartz reactor confining a plasma jet. The plasma stream at the nozzle exit was at an estimated temperature of 6000°K. CCl_4 under the influence of the hot gas stream and intense radiation from the plasma jet suffered decomposition into transient species, which on cooling gave rise to a yellow-brown deposit on the reactor walls. Along with this deposit, chlorine gas was liberated as identified by its odor in the exhaust gas. The brown deposit was soluble in CCl_4. Vacuum distillation and sublimation of the residue gave colorless needlelike crystals. Elemental analysis, X-ray powder pattern, infrared spectrum, and melting point (226–228°C) of this crystalline product confirmed its identity as hexachlorobenzene (C_6Cl_6). The formation of hexachlorobenzene from CCl_4 may be explained by a free radical mechanism, in which the parent compound is assumed to be stripped of its chlorine atoms, stepwise, and then the fragments (CCl, CCl_2) undergo dimerization and polymerization. There is also evidence for C_2Cl_4 formation in a radiofrequency plasma device.

C. CHEMICAL PROCESSES IN THE HIGH INTENSITY ARC

The unique property of the high intensity arc is the rapid and efficient vaporization of the electrode material, which makes it possible to process refractories and ores incorporated into a matrix with a reducing agent and used as a consumable electrode. An advantage of this technique is that reactions can be performed without contacting any furnace or reactor walls. Reduction in an inert atmosphere or in a vacuum, halogenation, and oxidation are possible applications. At the high temperatures developed in the arc plasma, the reactions occur in the gas phase even with the most refractory materials, and an ideal configuration for quick quenching, to freeze an equilibrium which may be favorable at high temperatures, is provided in the tail flame of the arc. Most applications of this type of arc at present are for metallurgical processes on account of the high power requirements, but the potentiality of this tool in chemical synthesis should not be overlooked. A few examples of the reported work in this area are summarized here.

Fine fumes of silica (SiO_2) (30–40 mμ in diameter) were formed from silica incorporated in a carbon anode (80% silica and 20% carbon). The ions in the vapor provide high efficiency centers for nucleation (*225*).

Separation of various constituents of an ore has been possible, where the volatilities of the various constituents were different. Phosphorus and selenium have been distilled from their ores by vaporization and interposition of a dust filter in the arc effluent stream at a point where the temperature in the tail flame was below that of the condensation point for the more refractory constituent, but still high enough to maintain phosphorus or selenium in the vapor. The latter were then condensed at lower temperatures downstream (*225*).

Decomposition of complex oxides into simpler oxides by sublimation in the arc was reported by workers at the Vitro Laboratories (*225*). For example, metal silicates, $MeSiO_3$, were decomposed in the arc open to air into the metal oxide and silica:

$$MeSiO_3 \rightleftarrows MeO + SiO_2.$$

By rapid condensation the two oxides had not time to recombine and form the original ternary oxide. Decomposition of rhodonite to give MnO and SiO_2 was reported by Harris *et al.* (*97*).

If the arc is run in a reactive atmosphere, chlorine for example, a metal oxide may react to form the metal halide and CO;

$$MeO + Cl_2 + C \rightleftarrows MeCl_2 + CO.$$

Vapor phase reduction of MgO with carbon in the tail flame of the intensity arc has been reported by Korman and Sheer (*120*). Thermodynamic calculations showed that the reduction should be complete at temperatures above 1800°C, and the lowest recorded temperature in the tail flame, about 2000°C, favors such a reaction. Removal of oxygen by carbon is also favored by the formation of the very stable CO at the high temperature in the tail. The main problem of carbothermic reduction is to conduct the reaction at a sufficiently high temperature to allow reduction to proceed to a favorable equilibrium point, and then to inhibit or at least minimize back-reaction by providing appropriate conditions of cooling.

Acetylene was synthesized in a high intensity arc from carbon and H_2 and from methane; Baddour and Iwasyk (*16*) obtained a yield of 25.5% from the first reactants and a yield of 52% from methane. Conversion of CF_4 into C_2F_4 and other by-products, such as C_2F_6 and C_3F_6, was also reported in a high intensity arc. The proposed mechanism involves formation of C_2F_2 as an intermediate, which reacts with free fluorine atoms to give C_2F_4. A yield of 64% C_2F_4 was recently reported (*17*) from an arc powered by 25 kw, a reactant flow of 25 cc/sec, and reactor pressure of 0.5 atmosphere.

IV. Miscellaneous Applications of Electric Discharge Devices

The importance of plasma-generating devices in modern technology is not restricted to chemical reactions involving new methods of synthesizing known compounds or unique methods of synthesizing new chemicals, but extends to several other areas of research. For example, several processes that can be performed in an electric furnace, a solar furnace, or a thermite process can be better performed in the plasma jet, where inert gases are used and even higher temperatures and more efficient heat exchange are attained.

A. Purification of Metals

In metallurgy several scarce materials can often be separated from their ores in fairly high purity by means of electric discharge devices, as discussed earlier. Use of a controlled atmosphere permits isolation of even chemically reactive substances. The high temperatures attained in certain plasma-generating devices allow melting of high melting-point refractories. Beall *et al.* (*19*), in a study of melting by the consumable electric arc, reported the melting of Zr. The method involves the compaction, sintering, and/or welding of an electrode of the material to be melted. This electrode serves as the electric conductor from which the arc is struck to additional metal contained in a water-cooled cup or vessel. Molybdenum was fused in both vacuum and argon atmospheres in a.c. and d.c. arcs operated at optimum currents of 1.1–1.3 kiloamperes at 20–35 volts. The metal ore was used as the consumable electrode (*207*). Melting of molybdenum in an arc furnace, without the problem of oxidation which arose when Mo was fused in a ceramic crucible, was described by Stroev *et al.* (*207*). Repeated fusion at reduced pressures was reported to yield the metal with an oxygen content of about 0.001%. A review of arc melting processes for refractory metals is given by Moss (*164*). A further metallurgical application is the alloying of metals in the vapor phase by vaporizing the metals individually and allowing them to condense in appropriate order. Alloys of Ti and of Zr with other metals have been made by using the oxide or carbide of these metals with the carbide or oxide of the alloying agent. Powder of the appropriate composition was pressed into the shape of rods and used in electric furnaces as electrodes. Alloying ingredients specified were Mo, W, Ni, Cr, Al, and Mn (*156*).

B. COATINGS

Coatings of organic and inorganic materials, regardless of their melting point, on substrate materials of various shapes have been successfully applied by arc spraying techniques. For example, coatings applied with plasma jet generators have been used to improve thermal resistance and abrasion resistance and to prevent erosion of the coated piece. The coating material is melted in the jet of the plasma torch and deposited by spraying on the surface to be coated. Usually the coating substance is fed into the plasma stream as a powder, rod, or wire, and impacts in a molten state onto the part to be coated, to form a high-density, uniform, and well-bonded coating. The coating bond is mechanical rather than chemical, and the particle size, gas velocity, melting point and thermodynamic properties of the coating substance are among the variables to be considered for a good coating. In using a mixture of powders, simultaneously applied, the particle sizes should be chosen so that heat capacity per particle is as balanced as possible. Nearly any substance that does not decompose at the high temperature of the plasma jet can be applied. Thermal Dynamics, Inc. has claimed the formation of coatings of a wide variety of pure metallic refractories, chemically inert ceramics, and glass. For example, coatings of tungsten, tantalum, molybdenum, palladium, platinium, aluminum, copper, nickel, chromium, refractory oxides, carbides and borides of niobium, titanium, zirconium, hafnium, and others are mentioned (*222b*). Plasmadyne has claimed the possible application of coatings of low-melting organic materials like penton, nylon, Teflon, and most epoxies by plasma spraying on a base material without the requirement of a furnace curing cycle.

Coatings of materials usually considered stable and resistant to chemical reactions were found to undergo unexpected changes when a plasma jet was used. Davis (*56*) reported that a coating of BeO applied with a nitrogen plasma contained 15% BeN and a complex Be-O-N compound. Carbides of refractory metals required certain depositing conditions, and analysis revealed less free carbon than in the sprayed powder. Coatings of thickness 0.001–0.375 inch were obtained. Use of surfacing alloys in powder form furnishes a means of altering the composition of alloy coatings to suit certain requirements without restriction to the form in which the material is available.

For fabricating simple shapes from the most refractory materials, one can spray powdered tungsten, molybdenum, hafnium oxides, hafnium carbide, etc. onto a mandrel of the desired configuration. Levinstein *et al.* (*133*) reported coatings of wall thickness of 0.01–0.06 inch as compared with 0.125 inch by other processes. A discussion of this application of plasma jet devices is presented by Walton (*227*). Pyrographite was deposited in this manner by passing heated methane or propane from a plasma reactor over a hot mandrel of the desired shape (*222a*). As the gas broke down the carbon was deposited on the hot mandrel surface and the hydrogen passed off, as illustrated in Fig. 18.

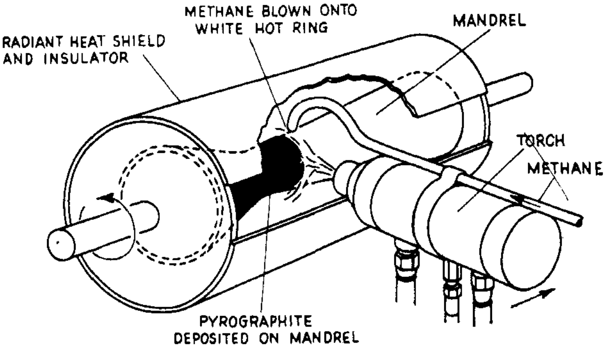


FIG. 18. Pyrographite coating by a plasma jet (*218*).

C. Crystal Growth

The induction-coupled plasma torch has a number of desirable features for growing crystals. For example, the torch may be operated with inert, oxidizing, or reducing atmospheres. Sapphire crystals were grown by Reed (*176*) in an argon plasma. Reed was also able to grow single crystals of stabilized zirconia for the first time by means of this device. Rubies have been prepared in an electric arc, described by Kuan Hsuing Ch'en (*130*). An electric arc was produced between two horizontally placed graphite electrodes, 0.5 cm in diameter and 20 cm long. A third vertical electrode, 1 cm in diameter and 10 cm long with a central hole 2 mm in diameter, was in contact with one of the two horizontal electrodes. Al_2O_3 powder containing 2.5% Cr_2O_3 was dropped through the hole of the vertical electrode into the arc plasma, and translucent rubies of 1–1.5 carats were obtained.

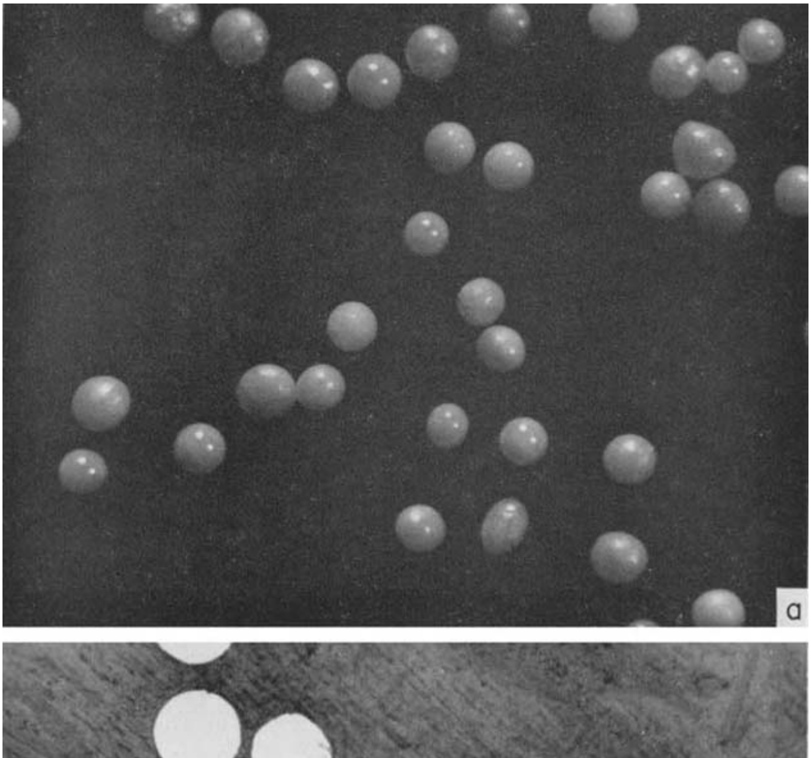


FIG. 19. Particles of zirconia (a) and tungsten (b) spheroidized by the plasma jet processes (*219*).

D. Spheroidizing

Refractories have been spheroidized in the plasma jet into uniform spheres of various sizes. Spheres of refractories (m.p. 2100–3200°C) as small as 100–150 μ in diameter were reported to be formed in a plasma jet operating at temperatures of 16,500–2700°C and a jet velocity of 100–500 ft/sec (*153*). The different sizes and typical uniformity of some of these spheres are shown in Fig. 19.

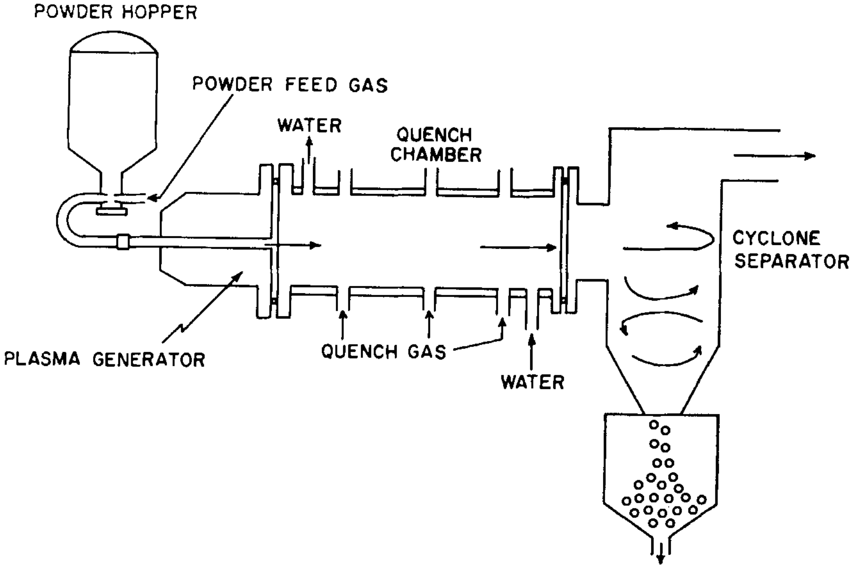


Fig. 20. Spheroidizing process by the plasma jet (*153*).

The equipment required for refractory spheroidization includes a powder feeder chopper, controlled by the rate of gas feed, and a quenching chamber consisting of a water-cooled reaction tube bolted to the plasma

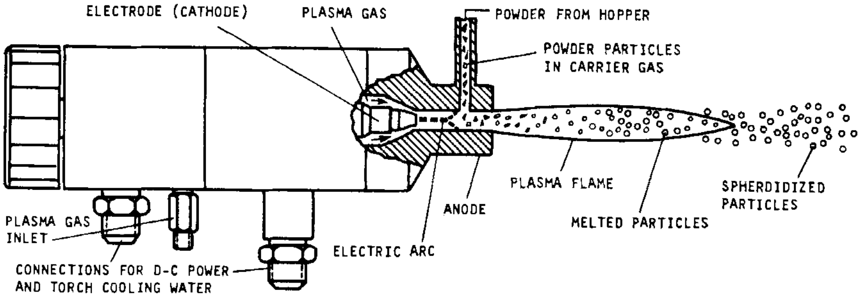


Fig. 21. Spheroidizing apparatus by the plasma jet process (*219*).

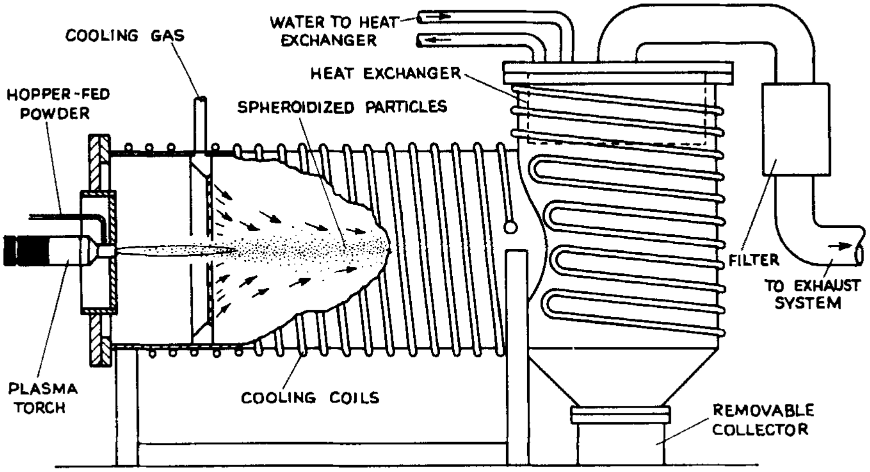


FIG. 22. Spheroidizing apparatus by the plasma jet process (*219*).

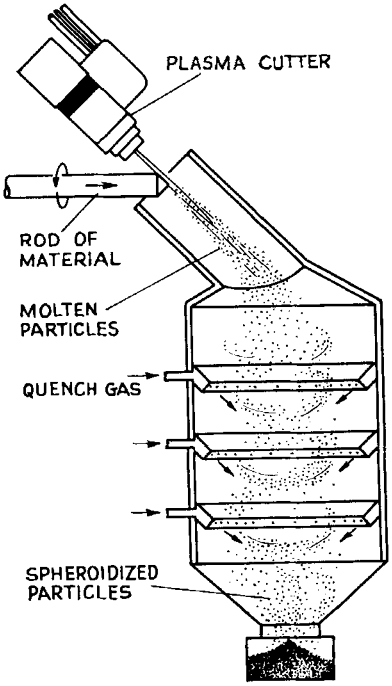


FIG. 23. Spheroidizing apparatus by the plasma jet process (*220*).

generator by means of flanges and joints. The quenching chamber should be gastight and provided with ports for observation and entry of the quenching fluid at different locations along the axis. The spheres formed may be collected and separated into various sizes with a cyclone separator. Figures 20–23 show arrangements for spheroidization marketed by Plasmadyne (*153*) and by Thermal Dynamics, Inc. (*219*, *220*).

E. METAL SUSPENSIONS

The preparation of suspensions of various metals in solutions has been considered as a method for arc utilization in process chemistry. An arc is usually formed by touching two wires of the metal under a liquid and then separating the electrodes slightly to provide the necessary potential drop for a stable arc. An ordinary 110-volt power supply of 10–15 amperes and a resistance of approximately 100 ohms in series form the simple electric circuit for this process. A potential difference of the order of 20–25 volts, depending on the metal of the electrodes, is expected. Quenching of the metal vapor in the liquid results in the formation of the suspension (*49*).

Extreme reaction conditions can possibly be maintained by subjecting to a spark discharge mists of solid particles (metals or nonmetals having suitable grain size and structure) with liquid or molten organic or inorganic compounds, in mixtures or solutions. The high temperature supplied by the discharge and rapid cooling by the surrounding liquid provide quenching in a minimum reaction time. Partially chlorinated silanes were reported to be formed from Si in halohydrocarbon liquids (*117*).

The preparation of cadmium niobate ($Cd_2Nb_2O_7$) is another example of spark synthesis in solutions. An anodic spark of Cd in a niobate solution, after distilling to saturation at 650°C, left crystals of $Cd_2Nb_2O_7$ in the solution (*154*).

F. SPECTROCHEMICAL ANALYSIS

Electric discharge devices have long been used as spectroscopic sources, and there are many textbooks in this area. However, the recent development of the plasma jet requires special attention. The plasma jet has proved to be an energetic source of radiation, which may be utilized for excitation of various substances to high energy states. An interesting application was the excitation of solutions and use of the spectra obtained for accurate quantitative spectral analysis. The conventional plasma torch can be modified for such studies, and examples of these modifications have been reported. To illustrate, Co_2O_3 powder and graphite were fed into a cup-shaped electrode (*125*) in one case. A transfer-type arc with tungsten as an external yet integral cathodic electrode was operated in another case (*167*), where the sample was sprayed into the discharge zone. As the jet emerged from the cathode, it contacted the tungsten rod to which the electric path was transferred. The sample was sprayed into the jet from an atomizer. While helium was used as the plasma gas, argon was used in the atomizer assembly to carry the solution. Precise analyses of various metallic species in solution were obtained by a device described by Margoshes and Scriber (*162*). Their results for the analysis of Cr, Fe, and Ni in stainless steel proved to be more satisfactory than other conventional methods. A detailed description of the structure of the plasma generator is given in the original paper. (See Figure 6.)

G. PHOTOLYSIS STUDIES

The use of electric discharges as radiation sources to induce photochemical reactions is not new, but most types of radiation sources have been limited either in intensity or in the spectral region of radiation. The mercury-arc lamp, Xe-arc lamp, and hydrogen lamp are familiar examples. The spark discharge and the plasma jet have recently been used as radiation sources for photochemical applications. Marcus *et al.* (*148*) reported the use of a spark discharge as a source of monochromatic radiation for photolysis. They described a spark discharge between magnesium electrodes in a low pressure tube. A 10-microfarad capacitor was discharged at 200,000 volts. The characteristic light of the spark emitted intense radiation at 2800 Å. Use of the spark in the photolysis of acetaldehyde was studied and the products (CO, H_2, CH_4, and C_2H_6) were identified. The suggested mechanism involved the formation of CH_3, which dimerized to give C_2H_6 at temperatures above 100°C:

$$
\begin{aligned}
CH_3CHO + h\nu &= CH_4 + CO\\
CH_3CHO + h\nu &= CH_3 + CHO\\
CH_3CHO + CH_3 &= CH_4 + CH_3CO\\
2CH_3 &= C_2H_6\\
2CHO &= C_2H_2O_2\\
\text{(or)}\quad 2CHO &= H_2 + 2CO.
\end{aligned}
$$

The plasma jet was proposed by Damon and White (*55*) to be used to promote photochemical and photosensitized reactions, such as oxidation, reduction, polymerization, decomposition, or combination reactions. The controlled chlorination of CH_4, the oxidation of cyclohexane to nylon intermediates and of acetaldehyde to acetic acid, the reduction of propane to methane, ethane, and ethylene, and the polymerization of ethylene, propylene, etc. to polyolefins are a few examples. Figure 24 (*55*) shows schematically some suggested arrangements for using plasma reactors in photochemical reactions.

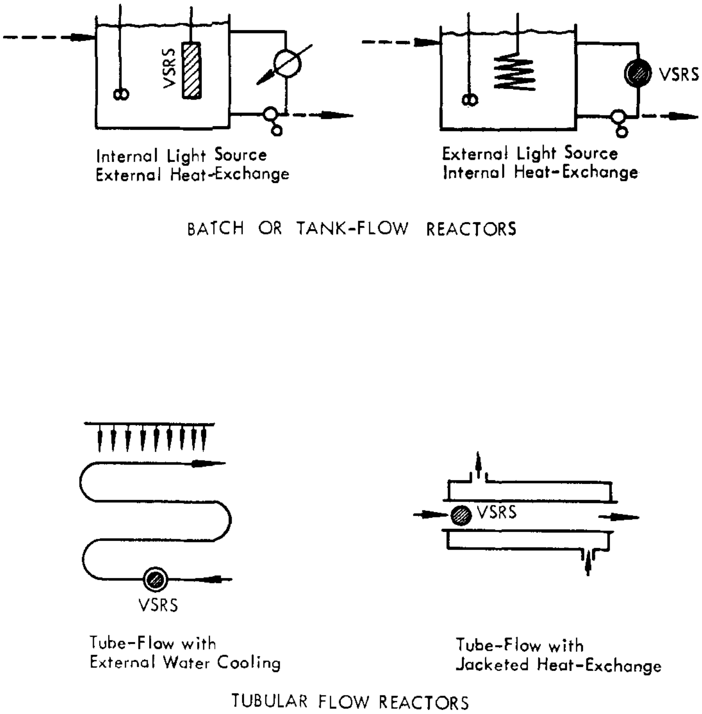


FIG. 24. Schematic illustrations of a few ways to adapt the plasma jet to photolysis reactors (*55*); VSRS = very strong radiation source (plasma jet).

V. Some Proposed Applications of Plasma Devices

Chemical processing in plasma jet reactors is still in its infancy. Few studies of organic and inorganic reactions have been made so far, but the unique potentiality of this device should not be ignored because of the limited work reported. The producers of plasma devices are eager to find and exploit chemical applications. For example, Damon and White (*53*, *54*) have surveyed several potential plasma arc reactions and proposed chemical processes in plasma reactors of interest in inorganic and organic synthesis. The following are but a few of their proposed systems worthy of investigation.

Organic Reactions:

1. Acrylonitrile from C_2H_2 and HCN in one step.
2. Catalytic air oxidation of NH_3 and propylene.
3. Catalytic vapor phase oxidation of naphthalene and *o*-xylene to phthalic anhydride.

4. Air oxidation of benzene to give maleic anhydride. The plasma generator is proposed as a preheater for the reactant.

5. Direct oxidation of benzene in air to phenol and of cyclohexane to adipic acid.

6. The manufacture of C_2H_2 from CH_4 and H_2 preheated in a standard tube furnace to 1000 and 2000°F, respectively, before reaction in the plasma reactor.

Inorganic Reactions:

Reduction of phosphate rock $Ca_3(PO_4)_2$ using CH_4 is feasible in the range 2100–3400°K, if side reactions involving CaO are avoided. This can possibly be performed by feeding the finely powdered ore downstream into the jet. The phosphorus produced need not be quenched as long as it is in a reducing atmosphere.

It is apparent that a great variety of chemical reactions remains to be studied in electric discharges.

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