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Chemical Syntheses in Electric Discharges

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ABSTRACT

Chemical Syntheses in Electric Discharges

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Several types of radio-frequency, induction-coupled plasma torches have been used for studying gaseous and gas-solid reactions at high temperatures. After a detailed examination of the various parameters which affect the stability of the discharge, design modifications and suggestions concerning the plasma torches, reactors, and traps were made.

These devices have been used for synthesis of nitric oxides and for studies of thermal decomposition of carbonates, chlorination of graphite and oxidation of boron.

ACKNOWLEDGMENTS

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INTRODUCTION

Normally all gases are good electrical insulators, but if a sufficiently high electric field is applied, there is a breakdown of these insulating properties and large currents may be passed through the gas. There are several ways to provide this electric field in order to maintain a gas in a highly ionized state, but for producing essentially equilibrium conditions in plasmas, i.e., temperatures over 5000° K., the most convenient methods are either the arc or electrodeless discharges.

Arc Discharges

At low pressures the formation of a discharge can be separated into several transitions. After the initial breakdown there is the so-called "dark-discharge" if the current is kept sufficiently low ($\sim 10^{-7}$ amperes). As the current is slowly increased there is a drop in the voltage and a glow discharge occurs. This type of discharge continues as the current is increased until the voltage sharply increases and reaches a maximum. If the current is further increased, the voltage drops to its lowest value and the arc discharge begins. No stable form of arc discharge can occur until this arc form is reached and, in fact, the necessary condition for the development of a plasma in any discharge is that the rate of generation of charged particles is sufficient to produce a potential maximum in the discharge container.

Usually arc discharges are classified as either low or high intensity arcs. The low intensity arc has three distinguishable regions--the plasma gas region with the voltage drop across the plasma region accounting for approximately 70% of the arc voltage, and the anode and cathode fall spaces caused by space charge accumulations associated with the conditions required for the transfer of charges across the boundary between a solid and gaseous conductor. In the case of the low intensity arc, increasing the current does not cause an appreciable increase in the current density because the volume of the arc also increases. Since temperature increases with increasing current density, this type of arc is not useful for metallurgical work or for the production of very high temperatures, but it is very suitable for spectral work.

High intensity arcs are formed when the anode is heated to the boiling point and issues a long gaseous stream whose length and intensity vary directly with the current. The temperature of the plasma in a high intensity arc can reach approximately 10,000° K., whereas in a low intensity arc the temperature is usually of the order of 5000-6000° K.

In trying to improve the high intensity arc Gerdien and Lotz (1) discovered that the arc could be constricted and thereby intensified by cooling its periphery with water. This thermal pinch produced very high current densities in the arc and is the basis of modern plasma jets. The present d.c. plasma torch is capable of producing quite high temperatures (up to $\sim$ 50,000° K.) and has been used for welding and cutting as well as spheroidizing and spraying of metals.

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Applications in chemical syntheses have been limited mainly because many reactive gases, especially oxidizing agents, cannot be used in forming the plasma, but must be added downstream from the torch. Even with the use of inert gases such as argon or helium there is still substantial electrode erosion and hence contamination of the product.

Electrodeless Discharges

The principal electrodeless arc used for the creation of high temperatures in gases at pressures near one atmosphere is the r.f. induction heated plasma torch. This type of torch utilizes a radio-frequency electromagnetic field to maintain a thermal plasma and there is no contamination of the product from the electrodes although the walls may be attacked by reactive discharge species. The first electrodeless discharges at atmospheric pressure can be traced to Babat (2), but he made no effort to flow gas through the discharge in order to make a plasma torch. Reed (3) fabricated a plasma torch based on inductive coupling to an ionized gas and studied some of the parameters which affect the stability of the discharge.
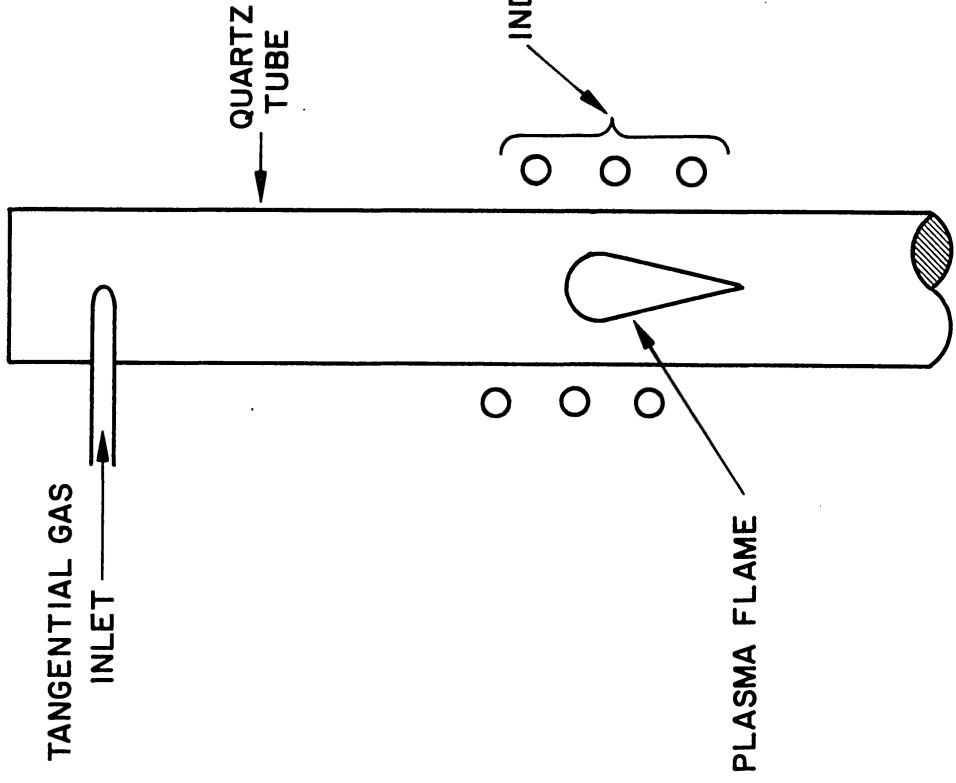
The development and widespread availability of efficient high frequency power sources have stimulated research in electrodeless discharges and, to some extent, decreased the interest in arc discharges. Not only does the electrodeless discharge produce a purer product, it also allows a much simpler construction of the discharge tube and reactor.

Radiofrequency energy can be transferred into a discharge tube either by capacitive coupling where the electrodes are placed on the outside of the tube or, more commonly, by inductive coupling where the discharge tube is placed inside a metal water-cooled solenoid. Both methods of coupling utilize a radiofrequency field which interacts with the ionized gaseous particles (molecule ions, atomic ions, and electrons) and maintains the high degree of dissociation necessary for a thermal plasma. Actually there is nothing extraordinary in the heating of gases by induction for, after the initial ionization of the plasma gas, this method in principle becomes similar to the general heating of a resistor coupled by induction. There is one special point to observe, however; the plasma "resistor" has a negative temperature coefficient and becomes a better conductor the higher the temperature. Thus, a plasma arc tends to get hotter and hotter until something regulates it, or the circuit is broken.

Merely supplying enough energy for the continued dissociation of the plasma gas is not sifficient for the maintenance of the discharge. Unless some method of stabilization is used, the plasma will either destroy the discharge tube or be extinguished. Reed (3), (4) has described the two most commonly used methods of stabilization (vortex and sheath stabilization) for an induction-coupled plasma torch. Vortex stabilization (Figure 1-a) is most useful when only gases are to be fed into the plasma torch. The reactant gases are introduced tangentially and as they spiral down the walls of the discharge tube, they tend to center the plasma and keep it off of the walls of the tube. This helical gas flow also produces a low

FIGURE 1

(a) Vortex-stabilized discharge tube.

(b) Sheath-stabilized discharge tube.

CONNECTION TO POWDER FEEDER

POWDER FALLS
THROUGH CENTRAL
TUBE

(b)

GAS
INLET

QUARTZ
TUBES

INDUCTION COIL

PLASMA FLAME

QUARTZ
TUBE

TANGENTIAL GAS
INLET

PLASMA FLAME

(a)
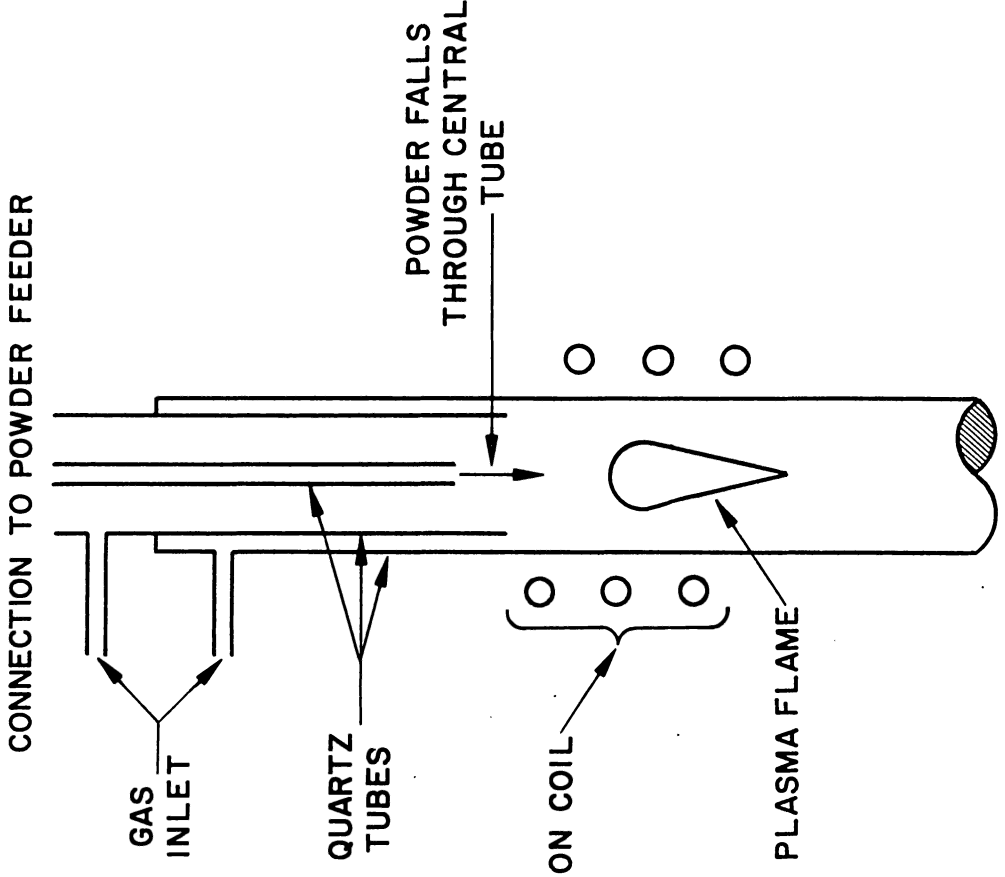
pressure area in the center of the discharge tube which forces some
of the plasma to flow up the tube counter-current to the main gas
flow and it is this feed-back which allows continued coupling between
the induction coil and the plasma gas.

The sheath-stabilized induction plasma torch basically consists
of three concentric tubes with three independent gas flows. As shown
in Figure 1-b, the two outer tubes are quite close together and they
create a high velocity gas flow which keeps the plasma centered in
the torch without extinguishing the discharge. Sheath stabilization
can often be used when vortex stabilization is inapplicable. For
example, the feeding of powders into a discharge tube for solid-gas
reactions or Verneuil crystal growth is not possible with a vortex-
stabilized torch because the powder cannot be kept in the plasma, but
is instead swept along the cool walls of the tube. With sheath stabi-
lization the powder can be kept in the center of the discharge tube
where it can interact with the hot plasma gas.

As shown above, the method of stabilization which is chosen for
a particular experiment is solely determined by the type of reactants
that are to be fed into the plasma torch for either method offers
fairly effective stabilization by the formation of reverse eddy cur-
rents that recirculate a portion of the hot plasma gas (5).

Certain aspects concerning the initiation and stabilization of
an r.f. induction coupled discharge will be discussed in greater
detail later when the problem of designing suitable plasma torches
and reactors is encountered. For further information concerning arc
and electrodeless discharges and the various chemical reactions in
these discharges, see "Chemical Reactions in Electric Discharges" (6).

CHEMICAL SYNTHESES

Vortex-Stabilized Gaseous Reactions

It has been shown in several recent publications that d.c. plasma torches can be used to produce a variety of endothermic species and that these can combine to form metastable or thermodynamically stable molecules, e.g., nitric oxide, acetylene, hydrogen cyanide, and cyanogen (7),(8),(9),(10),(11). Other syntheses have recently been performed at high temperatures in high intensity arcs (12),(13),(14),(15),(16).

During the last three years some papers have been devoted to the design of the r.f. plasma torch (3),(17),(18),(19),(20),(21), to its applications (4),(22),(23),(24), and to the related theory (25), but only a few describe chemical syntheses (26),(27).

Design of the Plasma Torch

The r.f. plasma torches described in the literature (3),(19), (21), generally include a discharge tube of Vycor connected to a metallic head through which the plasma gas and the graphite rod (used to initiate the discharge) are introduced (Figure 2-a). In this work, the design has been simplified by using a Vycor tube with a sealed tangential gas inlet. If the discharge is started with a Tesla-coil, one end of the tube may be sealed (Figure 2-c) or closed by a rubber stopper, or it may be closed by a stopcock if the discharge is initiated with a tungsten wire (Figure 2-b). In the latter
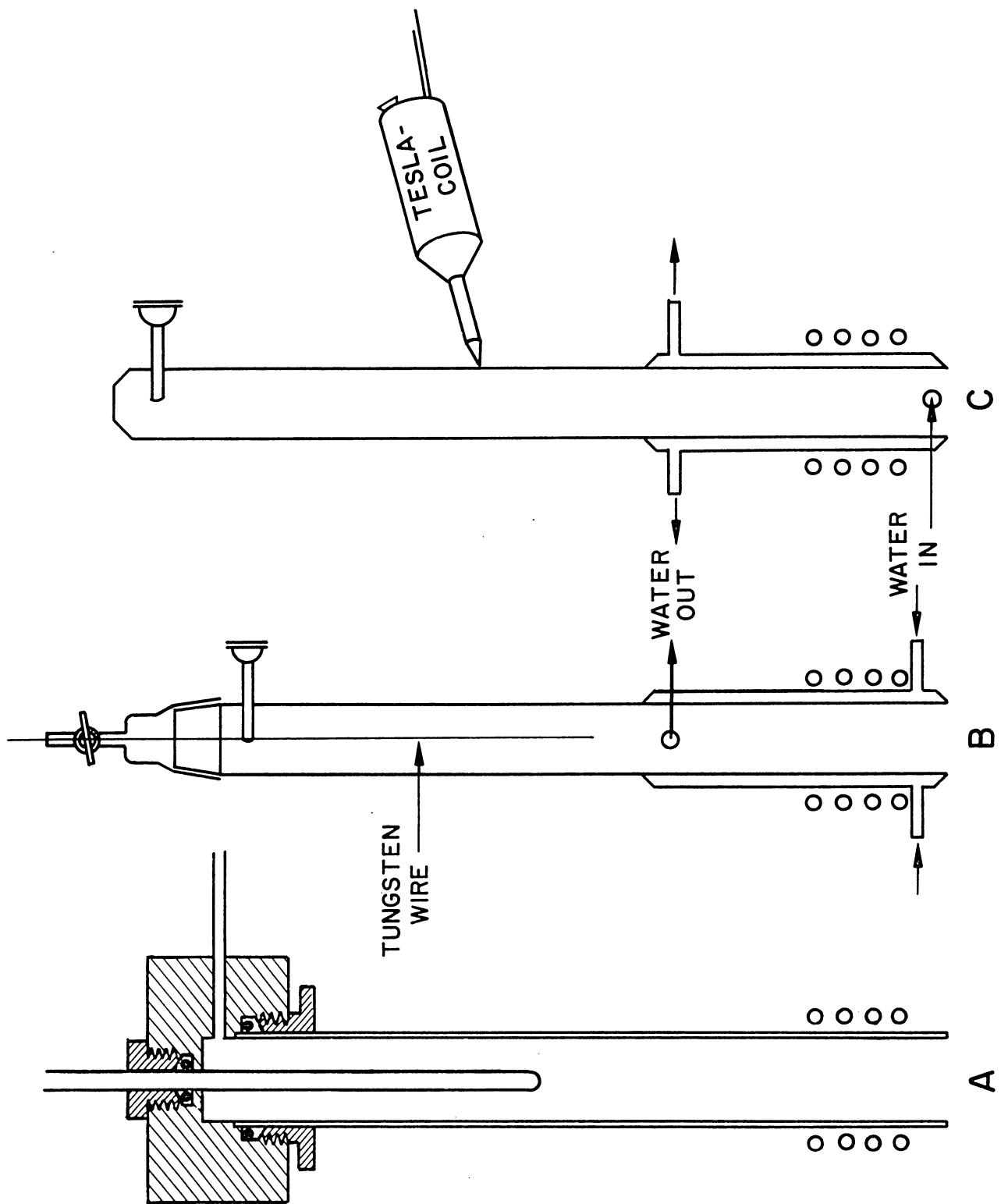
FIGURE 2

Radiofrequency plasma torches showing

3 different types of initiation:

      A - With a carbon rod

      B - With a tungsten wire

      C - With a Tesla-coil.

TESLA-COIL

TUNGSTEN WIRE

WATER OUT

WATER IN

A

B

C

case the tip of the wire is placed $\sim$ 1" from the top turn of the

coil; the wire is pulled out as soon as the discharge is started.

These two systems eliminate sparking between the metallic head and

the discharge region as well as contamination by graphite, and also

have the advantage of being gas-tight.

Diameter of the Tube

To protect the tube, its diameter should be larger than that of

the discharge (20). The difference depends on the enthalpy of the

gas, its flow rate, the kind of stabilization and the way in which

the walls are cooled. For high power densities, a tube with a diam-

eter close to that of the discharge can be used. Depending on the

power input, the tube may be cooled by air jets or water jacketed

(see Figures 2-b and 2-c). For very high power densities a split

metal tube can be used (28). In these cases essentially the whole

section of the gas flow is brought to a high temperature and the

radial gradient of temperature is very high. Vycor tubes, 1" in

diameter, have been used to heat oxygen, nitrogen, and argon at a

frequency of approximately 5 Mc.

Tubes appreciably larger than the discharge can be used when

instabilities are expected, e.g., when caused by the introduction of

a powder or a solid rod in the discharge, by the presence of a reac-

tor, or to facilitate the transition from one gas to another, e.g.,

replacement of argon with oxygen and/or nitrogen (see next para-

graph). It would be wrong to think that a real doughnut discharge

is formed as soon as the skin depth is smaller than the diameter of

the tube. For example, a vortex-stabilized discharge can easily be

maintained on the axis of the tube even if the diameter of the latter

is much greater than the skin depth of the plasma gas. Figure 3 shows

an argon plasma with a visible diameter of 35 mm "burning" in a Vycor

tube of 60 mm diameter. The temperature of such a plasma is probably

more uniform than in the case of a small tube and no darker spot can

be seen on the axis of the tube. Because the wall is only under

slight thermal stress when a large tube is used, the synthesis of

nitric oxide was performed in a 50 mm diameter tube which gave a good

margin of security.

Initiation of the Discharge

The discharge may be initiated in argon with a Tesla-coil (19).

If a plasma in a diatomic gas is desired (e.g., O_2 or N_2), it is

slowly added to the argon and the power increased simultaneously.

After the desired flow rate is reached, the flow rate of argon is

slowly decreased with a further increase in power.

Plasmas of diatomic gases need more power than argon plasmas

and, therefore, when one of these gases is added to the argon, the

power must be increased. For a given composition and flow rate, the

diameter of the plasma increases with power, but because of their

thermal conductivity, diatomic gas plasmas tend to be more contracted

than argon plasmas. Thus, the discharge can usually be kept at a

reasonable distance from the wall if the addition of power and the

increase in flow rate of diatomic gas are synchronized. Too fast

an increase of diatomic gas concentration leads to the extinction of

the discharge while too fast an increase in power can cause destruc-

tion of the tube. Thus, as already mentioned in the previous

FIGURE 3

Argon plasma "burning" in a Vycor tube. Diameter of the
tube is at least 50 times as large as the skin depth.
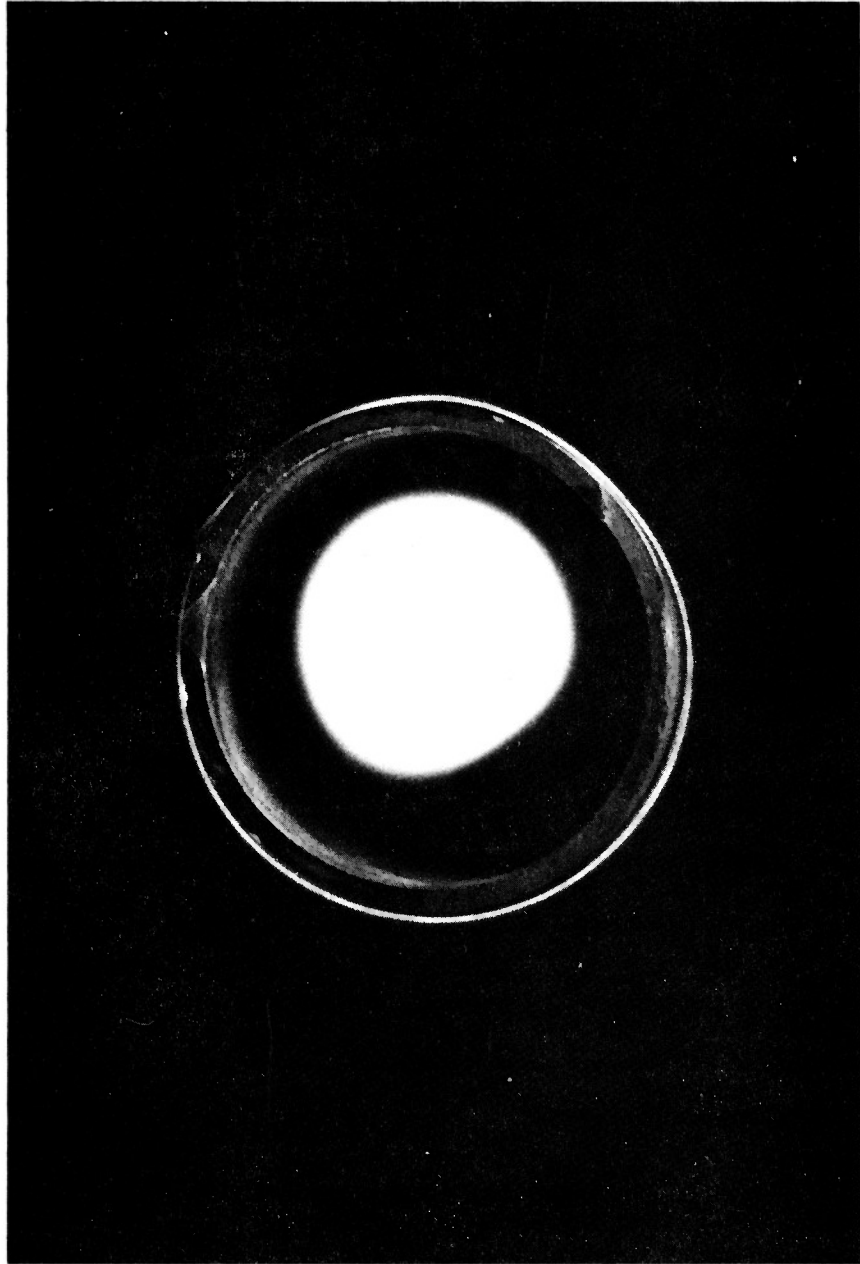
paragraph, the transition from argon to a diatomic gas is more difficult in a tube of small diameter.

The Generator and its Match with the Load

The generator used in this work was a Lepel dual-frequency generator, Model T 15-3-DF (15 kw output) with two outlets, one for frequencies between 2 and 10 Mc/sec and the other for frequencies between 10 and 25 Mc/sec. The tank-circuit corresponding to the low-frequency range is composed of a coil with four taps of maximum inductance $L_t = 2\mu H$ and a bank of capacitors whose total capacitance C_t can be varied between 50 and 500 pF. The grid can be excited by means of a tickler-coil which can also be tapped at different positions. The power is regulated by means of a saturable reactor.

The best match of the load with the generator can be found empirically by varying C_t, L_t, and the inductance L_c of the load coil. The effectiveness in matching the impedances is estimated by measuring the power conversion as explained in the next paragraph. Tap 4 (corresponding to the smallest possible inductance of the tank coil), $C_t = 150$ pF and a load coil of 5 closely spaced turns of copper tubing (I.D. = 2.5") have been used in this work giving an oscillator frequency between 5 and 7 Mc. As seen in Table I, power conversions of the order of 60% have been obtained, which can be considered satisfactory.

TABLE I

Power Balance for the Generator and Loads

$I_p \cdot V_p$	P_{tube}	P_{tank}	P_{load} calc.	P_{load} exp.	DC-power conversion	Error
Kcal/s	Kcal/s	Kcal/s	Kcal/s	Kcal/s	%	%
0.789	0.388	0	0.401	0.335	42.5	19.7
2.105	0.749	0.082	1.274	1.112	52.8	14.6
2.694	0.888	0.106	1.700	1.586	58.9	7.2
2.698	0.842	0.102	1.754	1.615	59.9	8.6

<u>Measurement</u> <u>of</u> <u>the</u> <u>Power</u> <u>Delivered</u> <u>to</u> <u>the</u> <u>Plasma</u>

The power delivered by the rectifier system can be estimated by the product $I_p \cdot V_p$ of the plate voltage and the plate current which can be read directly on the instrument panel. This power is dissipated in the oscillator tube, tank system, and load, plus radiation and heating losses in adjacent metal parts. Since the oscillator tube as well as some parts of the tank circuit are water-cooled, the power dissipated in them can be estimated calorimetrically.

The difference between $I_p \cdot V_p$ and these two last power losses gives an estimate of the power in the load. The accuracy of this estimate has been checked by heating a water-cooled iron tube and measuring the power dissipated in it. Table I gives the power balance as well as the error in the determination of the power absorbed by the load for different arrangements of the tank system.

The power dissipated in the generator is always underestimated, <u>i.e.</u>, the calculated power in the load is greater than that measured experimentally. As the match of the generator with the load (evaluated from the percentage of d.c. power conversion) improves, the error decreases. In the nitric oxide synthesis power conversions higher than 55% were obtained, and, therefore, the accuracy of the power determinations should be better than 10% in these cases.

In order to estimate the enthalpy and the average temperature of the gas flow leaving the discharge region, the power dissipated by radiation and by conduction to the walls of the discharge tube must be measured. This has been done by Reed (3) who determined the partition of the lost power among radiation, convection, and conduction.

For example, Reed found that with an argon plasma (9.4 1/min) and a
total power input of 1.63 kw that 0.54 kw was lost by radiation and
0.74 kw was lost by convection and conduction to the walls, thereby
leaving 0.35 kw power transferred to the gas.

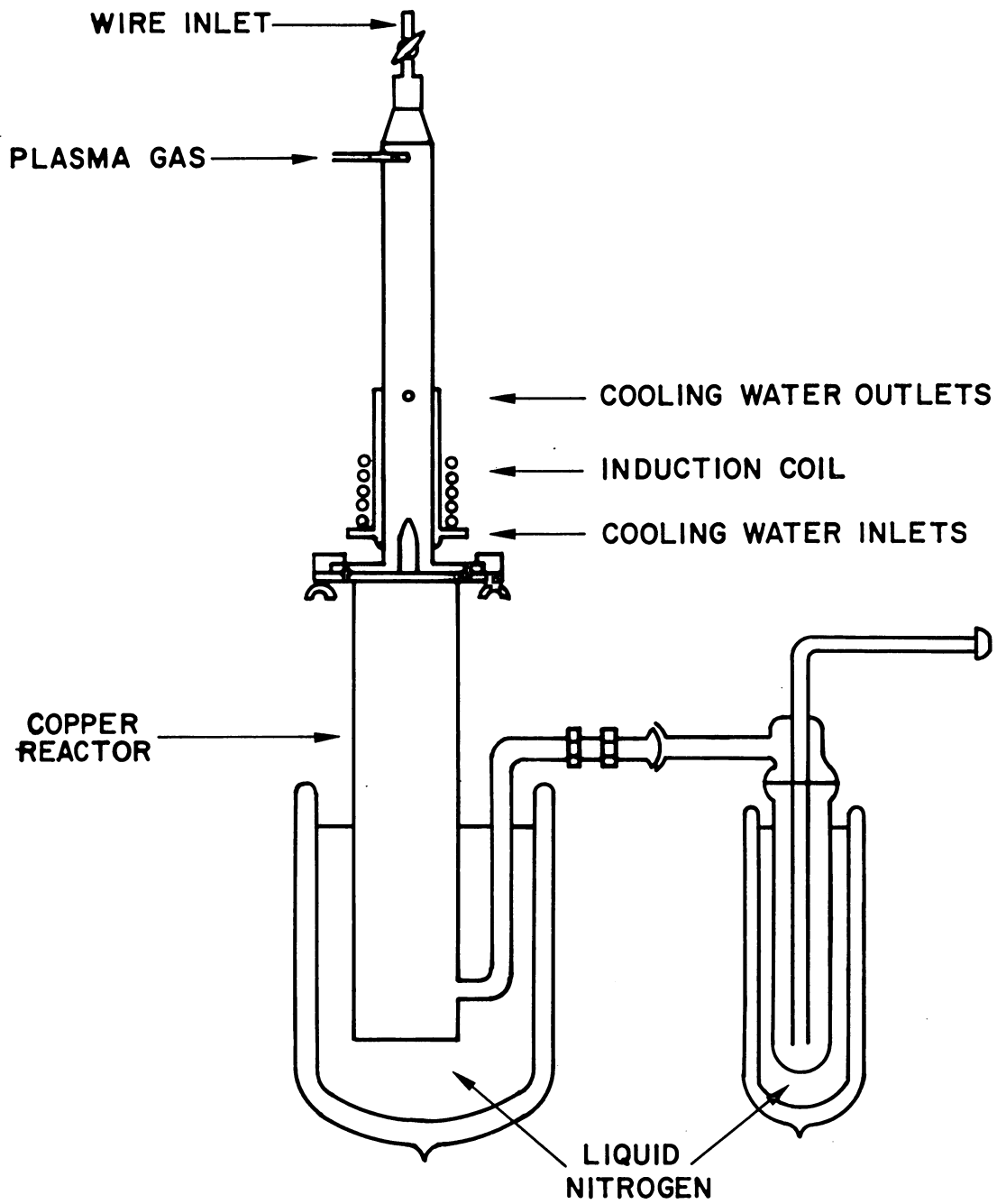## Synthesis of Nitric Oxide (29)

Design of the Plasma Reactor

The ideal plasma reactor should be built to allow a stable dis-
charge and a fast quenching of the exit gases. In the torches
described in most publications (3),(17),(18),(19),(20),(21), the dis-
charge tube is open immediately below the level of the lowest turn
of the induction coil, with part of the visible plasma flame outside
the tube. Difficulties arise when the flame is entirely enclosed,
as in any apparatus used for chemical synthesis.

The initial experiments were made with an arrangement similar to
that seen in Figure 4, where the plasma flame enters into a copper
trap cooled by liquid nitrogen. In such an apparatus a fast cooling
rate should be attained but, unfortunately, even when the trap is
electrically floating, a discharge is created between the trap and
the plasma region. As a consequence the plasma flame is usually dis-
placed toward the wall and can break the Vycor or quartz tube or in
some cases the discharge between the plasma region and the trap is
able to kill the discharge completely. For this reason, the initial
design was abandoned for one in which the tube immediately following
the discharge is made out of Vycor.

FIGURE 4

First reactor used to perform the NO synthesis.

WIRE INLET

PLASMA GAS

COOLING WATER OUTLETS

INDUCTION COIL

COOLING WATER INLETS

COPPER REACTOR

LIQUID NITROGEN

When the discharge tube is in line with a vertical trap, it is sometimes impossible to stabilize the plasma because standing waves similar to those created in organ pipes are built up in the discharge tube. This phenomenon can be well demonstrated with the arrangement seen in Figure 5 where, for certain positions of the piston, the main discharge disappears and is replaced by a low power discharge. As soon as the piston is removed from the critical position, the normal discharge resumes. This problem is eliminated by choosing the right distance between the discharge and the bottom of the trap or by covering the latter with glass wool. As a general rule it has been observed that it is easier to work with a system of low flow resistance, i.e., with traps and outlets of large dimensions.

The final form of the reactor used for nitrogen fixation is seen in Figure 6. For descriptive purposes, the Vycor discharge tube can be divided into two parts: a lower section with a length of 17" and a diameter of 2" and an upper section with a length of 11" and a diameter of 4". It is connected to a water-cooled copper vessel with two outlets each joined to two large Pyrex traps (inlet tube, O.D. = 2"; central tube, O.D. = 2.5"; and outside tube, O.D. = 3.5"). The surface of the tube surrounding the discharge region is cooled by two air jets. The reaction has been operated for periods of up to 20 minutes and longer heating periods could be used without overheating of the tube.

Procedure

Before the experiment was started, the system was purged with nitrogen and the Dewars filled with liquid nitrogen. After nitrogen

FIGURE 5

Arrangement used to demonstrate the existence of standing waves when the plasma is "burning."

Stopper

Gas Inlet

Induction Coil

Vycor Tube

Gas Outlet

Pyrex tube closed
at one end and
acting as a piston
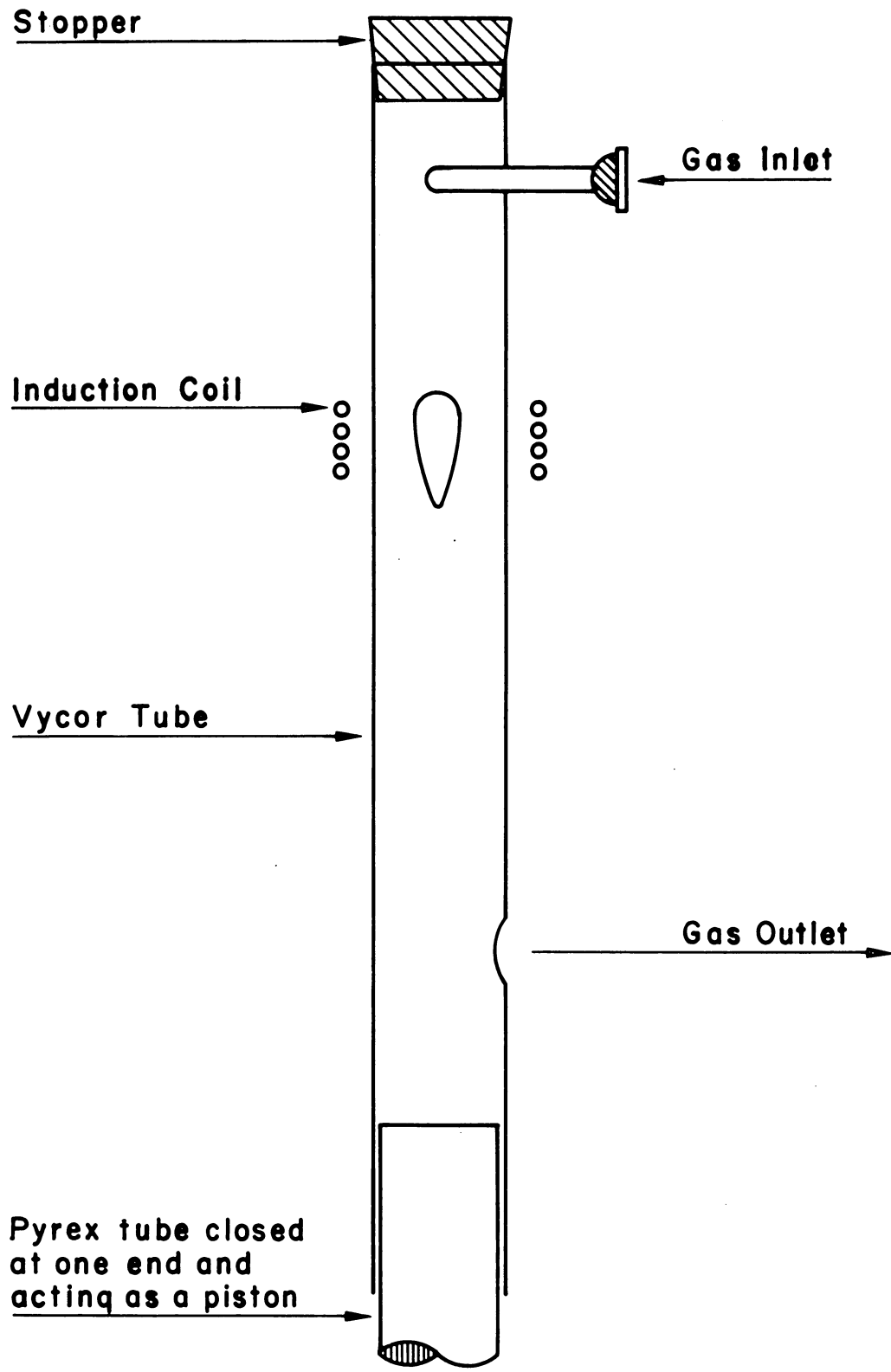
FIGURE 6

Final form of the reactor for NO synthesis.

LIQUID NITROGEN

LIQUID NITROGEN

WATER OUTLET

WATER INLET

COMPRESSED AIR

VYCOR TUBE

PLASMA GAS

COMPRESSED AIR

INDUCTION COIL

LIQUID NITROGEN
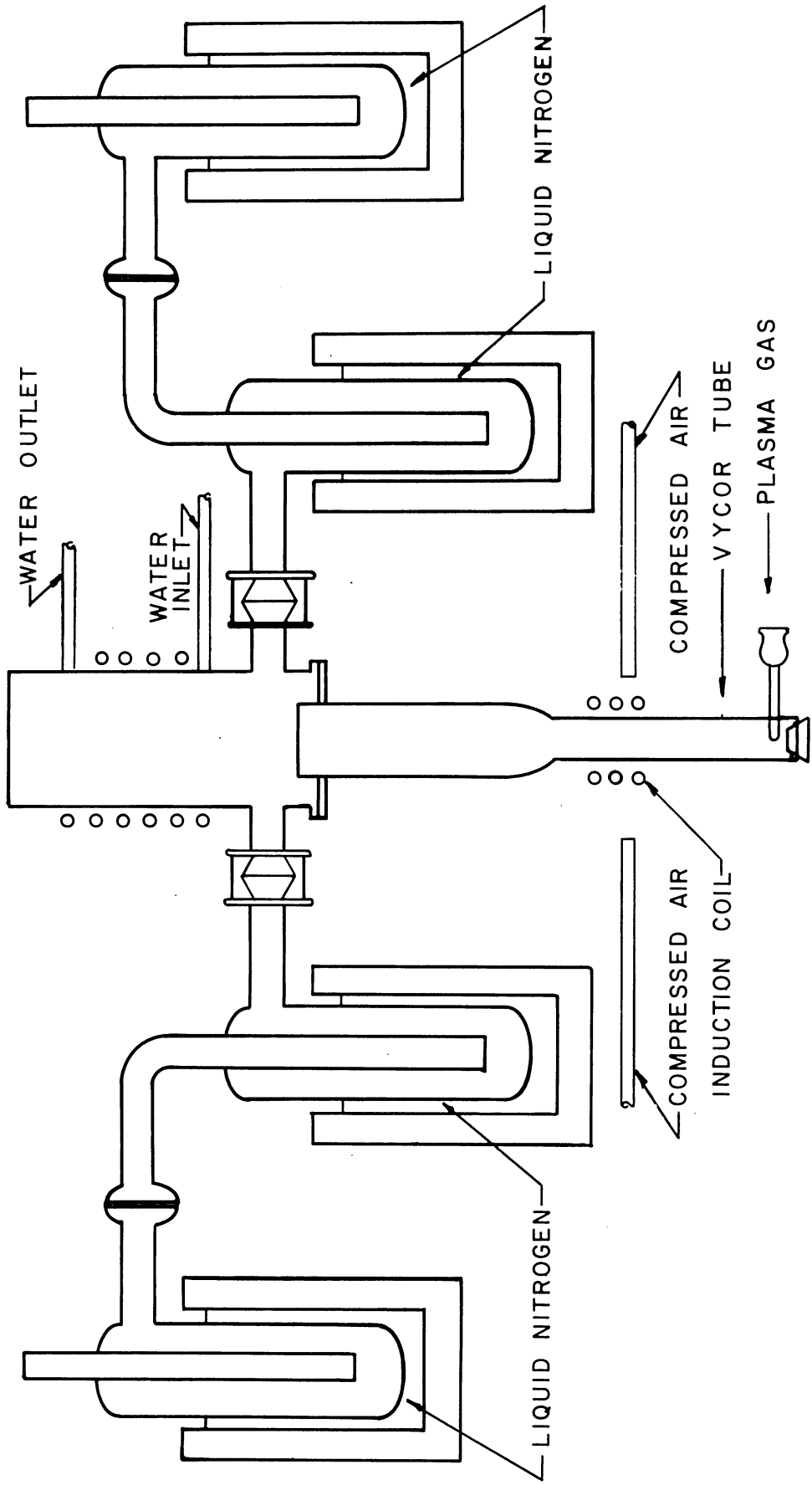
was replaced by argon and the discharge initiated in this gas with a Tesla-coil, oxygen was gradually added until the correct flow rate was reached. At this moment, considered as the starting time, nitrogen was introduced into the discharge and adjusted to its required flow rate ($N_2:O_2 = 1$) in approximately ten seconds. The flow rate of argon was then decreased to zero in a period of approximately twenty seconds. Sometimes the start failed because of a lack of synchronization between the power increase and addition of nitrogen gas. In this case, the discharge was initiated again and the time devoted to the "mistrial" added to the starting time. In order to minimize the starting time, during which the running conditions were variable, the total duration of each experiment exceeded the starting time by a factor of ten or more. The products were condensed in four traps as solids along with small amounts of liquid argon and larger amounts of liquid oxygen. Table II indicates the conditions and results of three of these experiments.

Analysis

The amount of nitrogen fixed has been determined by the method of Johnson (30) in which a mixture of NO and NO_2 is converted to nitric acid by shaking it with a solution of hydrogen peroxide. The nitric acid is then titrated with one normal NaOH to a methyl-red end point.

The technique has been tested by filling a calibrated glass-sphere with pure NO (Matheson 99%) under a pressure of approximately 0.5 atm. A peroxide solution was drawn into the spherical vessel until the pressure reached approximately one atmosphere. The vessel

TABLE II

Expt. No.	N$_2$ Flow	O$_2$ Flow	Starting Time	Total Time	Total N$_2$	Total N$_2$ Fixed	Yield of NO	Total DC Power	Tube Power	Tank Power	Plasma Power	DC Power Conversion
	m/min	m/min	min	min	moles	moles	%	kw	kw	kw	kw	%
1	0.62	0.52	1.08	10.48	6.49	0.113	1.75	16.2	5.4	1.1	9.5	58.6
22	0.74	0.61	1.73	13.22	9.78	0.178	1.82	16.7	5.0	1.3	10.2	61.4
3	0.79	0.64	1.50	22.14	17.49	0.372	2.12	17.2	6.0	1.4	9.8	56.6

was then placed in an ice bath and shaken frequently for one hour.
Next, the solution was poured into an Erlenmeyer flask and titrated
as described above. Typical results are given in Table III.

Conclusions

1. A gaseous mixture of N_2 and O_2 can be heated to high temper-
atures with an induction-heated plasma torch and the products trapped
without major difficulties.

2. The same arrangement should be satisfactory for other homo-
geneous gas reactions at high temperature for it provides a stable
plasma for long periods of operation without overheating of the walls
and without contamination of the reactions, and there is a fast
quenching rate for the product gases.

3. Grosse (31) and his collaborators have performed nitrogen
fixation by injecting oxygen into a stream of hot nitrogen leaving a
d.c. plasma torch. The results and conditions of his experiment are
compared with Experiment No. 3 of this study in Table IV.

The nitrogen fixed is approximately the same in both cases. The
total power to the r.f. generator was not determined, but it appears
that the amount of fixed nitrogen per kwh is at least comparable to
that obtained by Grosse and coworkers.

4. Shortening of the 4" diameter Vycor tube which is part of
the reactor would bring an improvement in the quenching rate and
might increase the yield of nitrogen fixed.

5. This work has been performed with an all Vycor torch. Prob-
ably higher power densities and yields of fixation could be obtained
with a split-metal tube.

TABLE III

Analysis of NO

Volume	Pressure	Temperature	NO Quantity	NO Quantity Found	Error
liters	atm.	°C	m-moles	m-moles	%
1.063^6	0.542	25	22.6	21.9	-3.1
1.063^6	0.525	25.5	22.8	22.3	-2.2
1.063^6	0.538	25.7	23.3	22.3	-4.3

TABLE IV

Comparison Between the Nitrogen Fixation Yields

Obtained with DC and RF Plasma Torches

Authors	N_2	O_2	DC Power	Nitrogen Conversion
	Flow rate L/min	Flow rate L/min	kw	%
Grosse	5.5	5.5	15	2.03
This work	17.7	14.3	17.2	2.12

Reaction of Carbon with a Chlorine Plasma

The synthesis of hexachlorobenzene has been performed by reacting CCl_4 in a hot argon plasma (32). Since the formation of C_6Cl_6 from CCl_4 could be explained by a free radical mechanism in which the parent molecule was stripped of some of its chlorine atoms stepwise to yield CCl_2 and CCl, and these fragments then polymerized to give C_6Cl_6, it was postulated that hexachlorobenzene might also be formed by the reaction of an argon-chlorine plasma with a graphite rod.

Equipment

The plasma torch used in the nitric oxide synthesis was altered slightly to allow a 3/8 x 12" graphite rod to be inserted along the axis of the torch. With this one exception the apparatus (torch, reactor, and traps) was identical to that used in the NO synthesis.

Procedure

As in the preceding experiment, the system was purged with nitrogen and the Dewars filled with liquid nitrogen. Nitrogen was then replaced with argon and the discharge was initiated by either allowing the graphite rod (special spectroscopic grade electrode, National Carbon Co.) to couple with the r.f. field and heat the gas to its ionization temperature or by using a Tesla-coil. Chlorine gas (Matheson, 99.5% min.) was next introduced into the system and its flow was regulated to allow maximum constriction around the axial graphite rod.

After the torch was run several minutes, the chlorine was turned off and then the discharge was stopped. The liquid nitrogen Dewars were then taken from the traps and they were allowed to warm up gradually to room temperature. The unreacted chlorine was removed from the traps with a stream of argon gas and bubbled through an aqueous alkaline solution (NaOH) to remove any chlorine.

Conclusions

1. No residue was ever found in the traps once they were at room temperature and thus no stable carbon-chlorine compounds were apparently made, with the possible exception of dichloroacetylene which would have volatilized away.

2. The lack of any carbon-chlorine product is apparently the result of inefficient heating of the rod and thus of the low concentration of carbon in the vapor phase. If the bar were heated to a higher temperature or if carbon powder were dropped through a sheath-stabilized chlorine-argon plasma, it should be possible to form perchloro-carbon compounds as was previously observed for plasmas fed CCl_4 directly.

Sheath-Stabilized Gas-Solid Reactions

The melting of powders in an r.f. heated gas stream is possible because the hot gas usually flows at a relatively low velocity in the discharge tube, whereas the plasma gas leaves the nozzle of an arc plasma jet at near sonic velocities. This "slow" heating can be used to either melt the powder for operations such as Verneuil crystal growth, or for superficial melting of larger particles as in spheroidization processes, or for complete vaporization of a powder to obtain an ultra fine product.

Because both the temperature and residence time of solid particles passing through the discharge are variable, it is possible to react solid powders with a reactive plasma gas such as oxygen or nitrogen. Metal halides have been reacted with oxygen in a sheath-stabilized discharge and the corresponding metallic oxide can be obtained (33), e.g., titanium tetrachloride in an oxygen plasma yields titanium dioxide (34). By carefully controlling the possible variables in a gas-solid reaction, there should be a large number of possible reactions worthy of study.

Design of the Powder Feeder

Most powder feeding devices utilize a vibrating screen in order to shake powders into a gas stream which then carries this powder through a tube and into a hot plasma gas (4),(33).

The powder feeder (Figure 7) used in this laboratory has been designed to be as versatile as possible so that many operations can be done without extensive changes in the apparatus. The housing of the powder feeder has been fabricated entirely from free-machining brass and contains a tool steel screw. This powder feeder incorporates the following features:

1. The vibratory screen used in conventional powder feeding devices has been replaced with a screw feeder which is capable of handling powders of various particle size without any alteration of the powder feeder.

2. The powder feed rate can be varied over a considerable range by utilizing a variable speed drive motor. To insure reproducible powder flow rates, an over-sized drive motor (1/8 h.p., shunt wound, variable speed motor capable of delivering 27 in. lbs. of torque at 125 r.p.m. with a gear ratio of 40 to 1) powers the feeder.

3. To minimize arcing, the apparatus has been designed so that it is electrically floating. The drive motor and feeder are mounted on a nonconducting (wood) platform and are connected by a hard rubber chuck.

4. The feeder incorporates a tangential gas inlet so that either vortex or sheath-stabilized discharges can be obtained.

5. A solid Teflon plug over the axis of the discharge tube can be unscrewed and replaced with a similar plug which has a hole through its center. By making this alteration, it is possible to initiate the discharge with either a tungsten wire or a Tesla-coil.

FIGURE 7

Powder feeder for sheath-stabilized gas-solid reactions.
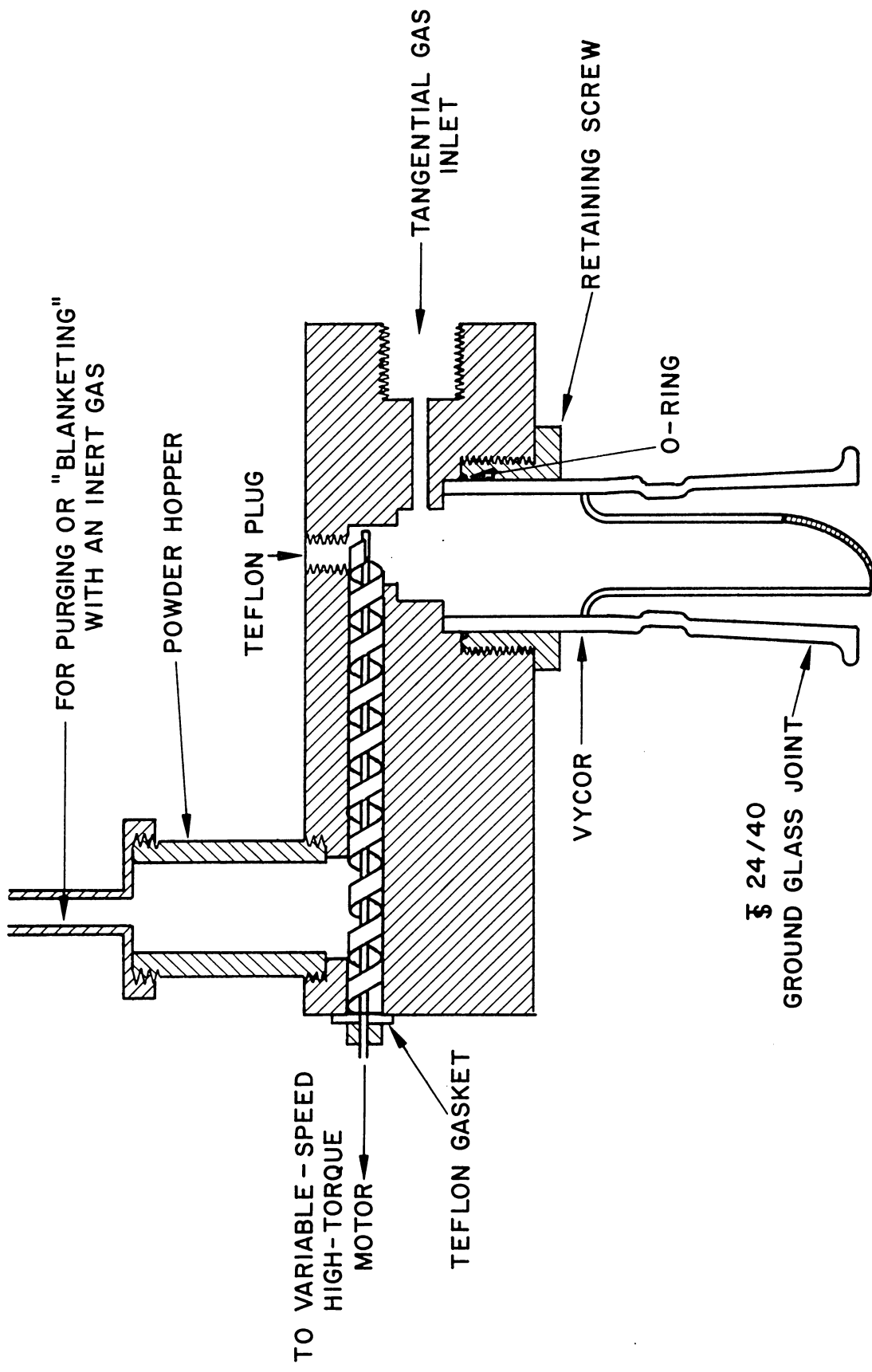
FOR PURGING OR "BLANKETING" WITH AN INERT GAS

POWDER HOPPER

TEFLON PLUG

TANGENTIAL GAS INLET

RETAINING SCREW

O-RING

VYCOR

$\bar{S}$ 24/40 GROUND GLASS JOINT

TO VARIABLE-SPEED HIGH-TORQUE MOTOR

TEFLON GASKET

6. Reactive powders can be used in this powder feeder since the top of the powder hopper contains a gas inlet which can be used to "blanket" the reactive powder with an inert gas.

7. The discharge tube can be coupled to the powder feeder by either using the ground glass joint with a central feeding tube (see Figure 7), or by direct connection to the powder feeder.

Design of the Plasma Torch

The plasma torch used in the following experiments has been patterned after conventional designs (4) and consists of either two or three concentric Vycor tubes (see Figure 1-b). The outer tube is 36" x 1-3/8" (I.D.) and the inner tube is 24" x 1" (I.D.), both having a gas inlet 3" from the top of their respective tubes. In order to center the inner tube precisely, so that the plasma flame is not directed to one side of the outer wall, three Vycor beads are joined to the inner tube at equidistant intervals around the tube. A $ 24/40 male Vycor joint is connected to the inner tube which can then accommodate a central feeding tube as shown in Figure 7. The generator settings for this torch were the same as those of the NO-synthesis, and a 1-1/2" load coil was used in place of the 2-1/2" coil previously used.

Operation of a Sheath-Stabilized Discharge

Many of the details concerning the operation of a vortex-stabilized discharge, e.g., initiation, diameter of the tube, etc., are certainly applicable to sheath-stabilized discharges, but since they have already been dealt with at length previously, they will not be considered again.

Assuming that the generator has been set at its optimum imped-
ance and frequency for a given gas(es) and discharge tube by the
methods presented earlier, the only problem which remains is the
stabilization of the plasma with respect to the various gas veloc-
ities in the discharge tube at a given power level. A power level
sufficient to sustain ionization in the discharge is in itself not
enough to assure a stable plasma, for if the stream of gas along the
outer wall is not fast enough, the discharge will destroy the tube,
whereas too high a flow rate will extinguish the plasma. By manip-
ulation of the flow rate of the outer gas stream, it is possible to
find an optimum velocity with respect to the slower inner gas stream,
and thereby stabilize the plasma. The ratio of the two gas flows
for optimum conditions is not constant, but varies for different
gases, flow rates, and power levels. Thus, for the present, only
trial and error methods will determine the best flow conditions,
but quite often this procedure is not as difficult as it might seem
and a stable discharge can be conveniently obtained.

The Reactions of Boron and Boric Anhydride with Oxygen

Several solid boron compounds, notably the metal borides, have
been exposed to an arc discharge (35),(36), but there has been no
attempt to react boron or its oxides in an r.f. discharge. The argon
matrix infrared spectrum of condensed boron dioxide, BO_2, has been
observed (37). B_2O (38) and also BO_2 (39) have been synthesized
under high pressures. It was felt that it might also be possible to
synthesize these or other new boron oxides by dropping B or B_2O_3
through an oxygen plasma.

Procedure

The powder feeder and discharge tube (without the central feed-
ing tube) were set up as previously described. The discharge was
initiated in pure argon with a Tesla-coil and then oxygen was added
to the plasma. Ratios of argon to oxygen varied from 4 to 1 to
approximately 2 to 1 in these powder feeding experiments. After the
discharge was stabilized at a given concentration of oxygen, the
powder was dropped through the discharge and then quenched in a Dewar
containing liquid nitrogen and oxygen, or oxygen alone. The product
was removed from the Dewar by boiling off the liquified gas and
examined spectroscopically (IR, KBr disc technique) to determine its
composition. The results are tabulated in Table V.

Conclusions

The anticipated product could not be detected and no other
product except the simple oxidation product of B to B_2O_3 was obtained.
It might be possible (see Suggested Design Improvements . . .) to
synthesize BO_2 if the falling powder could be kept in the hot plasma
zone for a longer period of time, for it appears that these experi-
ments only succeeded in superficially heating the falling powder.

The Reaction of Sodium Carbonate with Oxygen

At the temperatures found in an r.f. discharge at one atmosphere,
sodium carbonate readily decomposes to the oxide. Since metallic
sodium can be burned in an oxygen atmosphere to give the peroxide,
Na_2O_2 (40),(41), the reaction of Na_2CO_3 in an oxygen plasma seemed
likely to give Na_2O_2 also.

TABLE V

Results of Boron and Boron Anhydride-Oxygen Experiments

Powder	Quench	Product
B_2O_3	liquid N_2+O_2	B_2O_3
B_2O_3	liquid O_2	B_2O_3
B	liquid N_2+O_2	B_2O_3+B
B	liquid O_2	B_2O_3+B

Procedure

The apparatus and method of initiation in an argon atmosphere were the same as in the preceding powder feeding experiment. After initiation oxygen was slowly added to the discharge until the ratio of oxygen to argon was approximately 1:4. Powdered sodium carbonate (Baker, reagent grade) was then dropped through the discharge and collected in a Dewar containing liquid oxygen (see Figure 8). After ten minutes the discharge was extinguished, the liquid oxygen was decanted, and the product collected. It was difficult to exclude all moisture from the powder since the reaction was not run in a closed system, but this did not seem to affect the product.

Analysis

The product from the powder feeding experiment was dissolved in a 10% (by volume) H_2SO_4 solution and after the reaction of unreacted carbonate was complete (as detected by the evolution of CO_2), the solution was tested for oxidizing properties by adding KI (Baker, reagent grade).

A common test for peroxide ion, O_2^{-2}, is the oxidation of PbS to $PbSO_4$ (42). This test on the product gave a negative result so a more sensitive test, the coloration of $Ti(SO_4)_2$ by peroxide ion was tried (43), this also giving a negative test.

Infrared analysis (KBr disc technique) showed a spectrum of only the starting material, but there are no characteristic sharp bands for peroxide ion (the ion is thought to be homopolar and so its vibrations are infrared inactive) (44).

FIGURE 8

Oxygen-argon sheath-stabilized discharge.

Sodium carbonate dropping through an oxygen-
argon sheath-stabilized discharge.
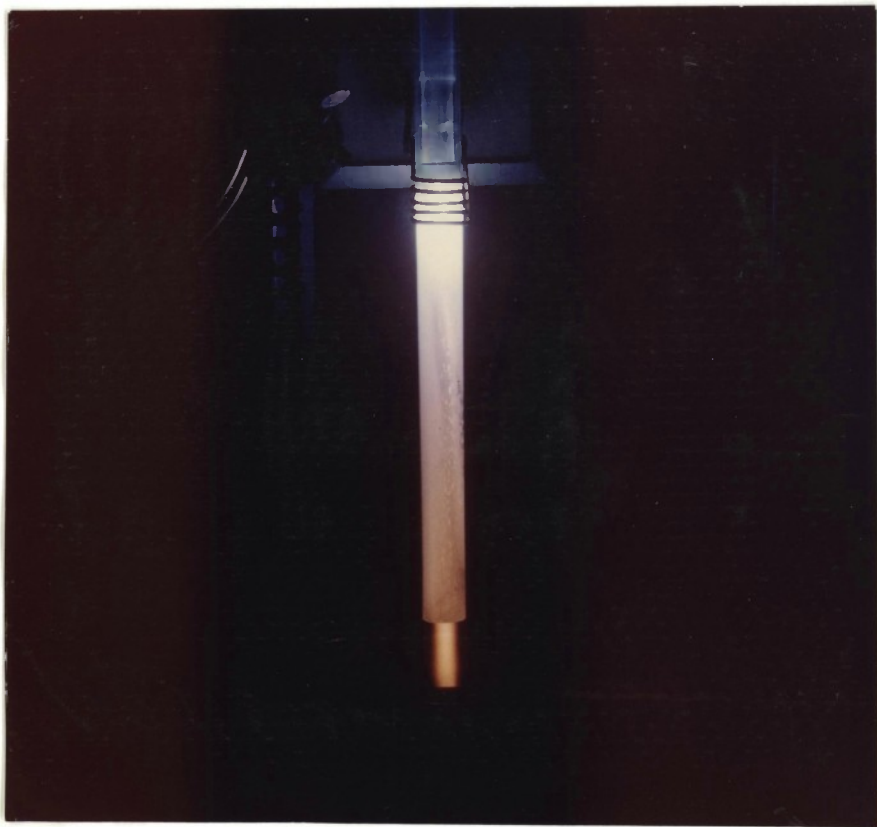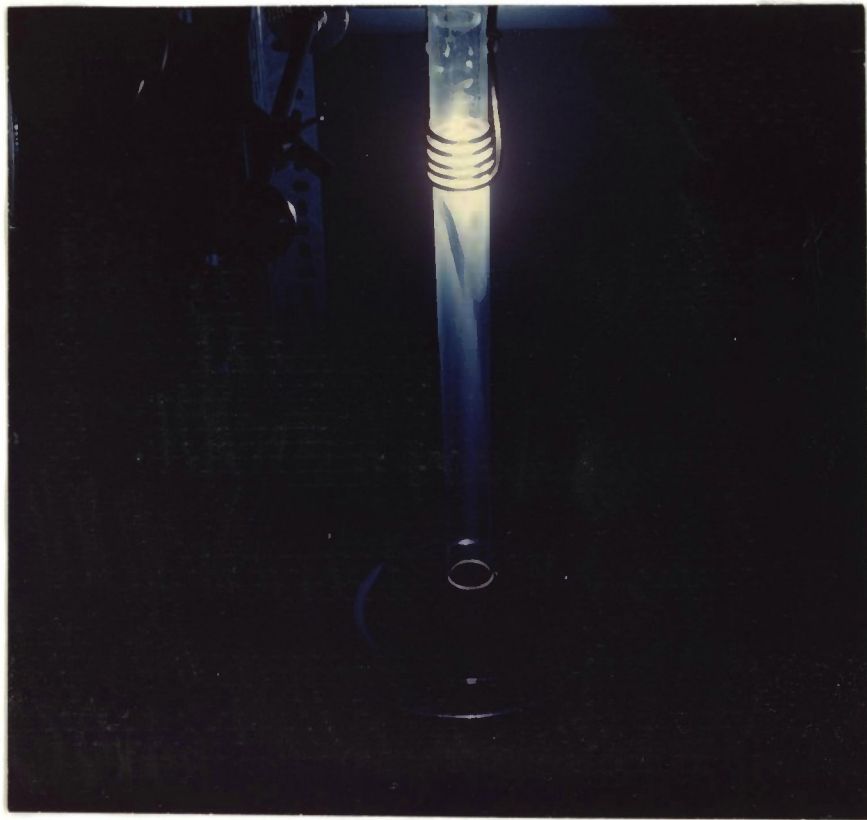
An X-ray powder diffraction pattern showed the product to be only $Na_2CO_3 \cdot H_2O$, but since the instrument could not detect the presence of a compound with less than 4% concentration, this just set an upper limit on the concentration of the oxidizing species present in the $Na_2CO_3 \cdot H_2O$.

Since the discharge was run in an open system, the possibility of a nitrate existed and its presence was tested in the following manner: Metallic zinc (powdered) will reduce a nitrate to nitrite in neutral or acid solution, and the presence of nitrites can be shown with Griess reagent (sulfanilic acid plus 1-naphthylamine) (45). This test is quite selective and when the product was tested for a nitrate, a positive test was obtained.

Results

The product revealed absolutely no trace of peroxide ion, but contained the hydrated starting material $Na_2CO_3 \cdot H_2O$ plus a small percentage ($<$ 4%) of sodium nitrate.

Conclusions

As in earlier powder feeding experiments, the powder's residence time in the hot plasma is too short to allow adequate heating. Since so much carbonate was recovered from the product, there is no doubt that the heating time of the powder must be increased, and once the necessary modifications to increase the residence time have been completed, it might be interesting to repeat this experiment. Only when the carbonate can be decomposed, can one even hope to obtain a product different than the starting material.

The Reaction of Lithium Carbonate with Oxygen

It might be thought that the preparation of Li_2O_2 would be quite similar to the synthesis of Na_2O_2, but in fact Li_2O_2 cannot be formed by the simple oxidation of lithium in air, nor can the oxide be oxidized further by heating in air. These methods of oxidation do not work because at atmospheric pressure lithium peroxide decomposes over the temperature range of 285°-315° C (46). Since rapid quenching methods are used in these powder feeding experiments, there was a greater probability of forming lithium peroxide than in the earlier attempts when the oxide was simply heated in air (47).

Procedure and Results

The laboratory set-up and operating conditions were the same as those in the Na_2CO_3-O_2 experiment (see Figure 9). The product was also tested in a similar manner, and as before, only the carbonate and nitrate were found, with X-ray diffraction techniques again setting an upper limit on the nitrate concentration ($< 4\%$).

The poor heating of the carbonate is again believed to be the main reason why the starting material was recovered unreacted.

FIGURE 9

Two views of lithium carbonate dropping through

an oxygen-argon sheath-stabilized discharge.
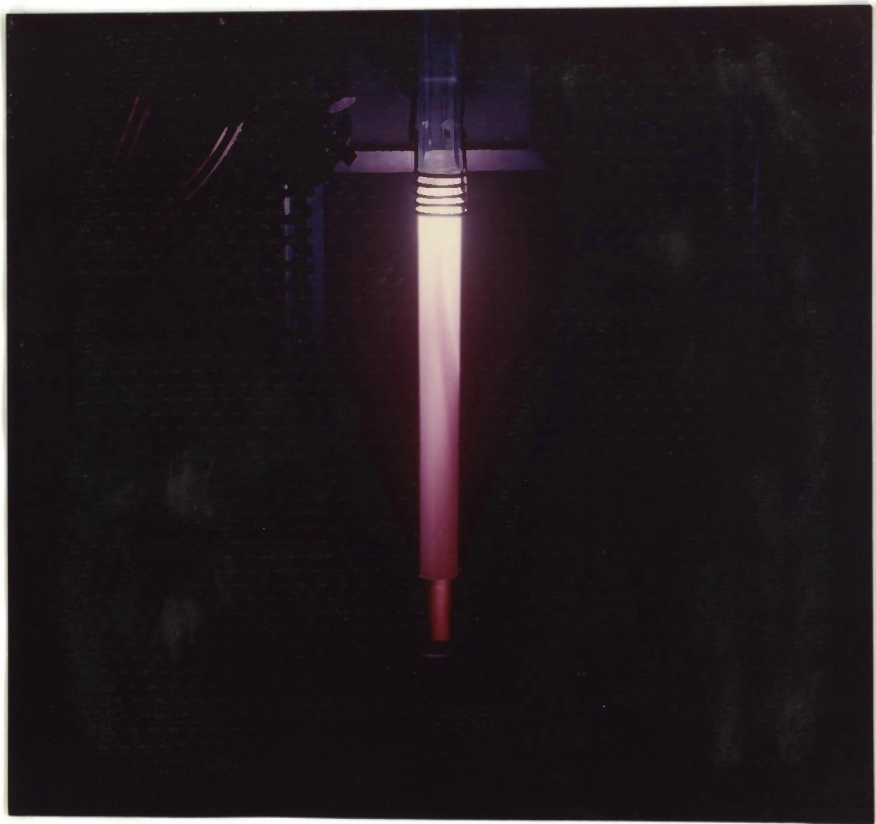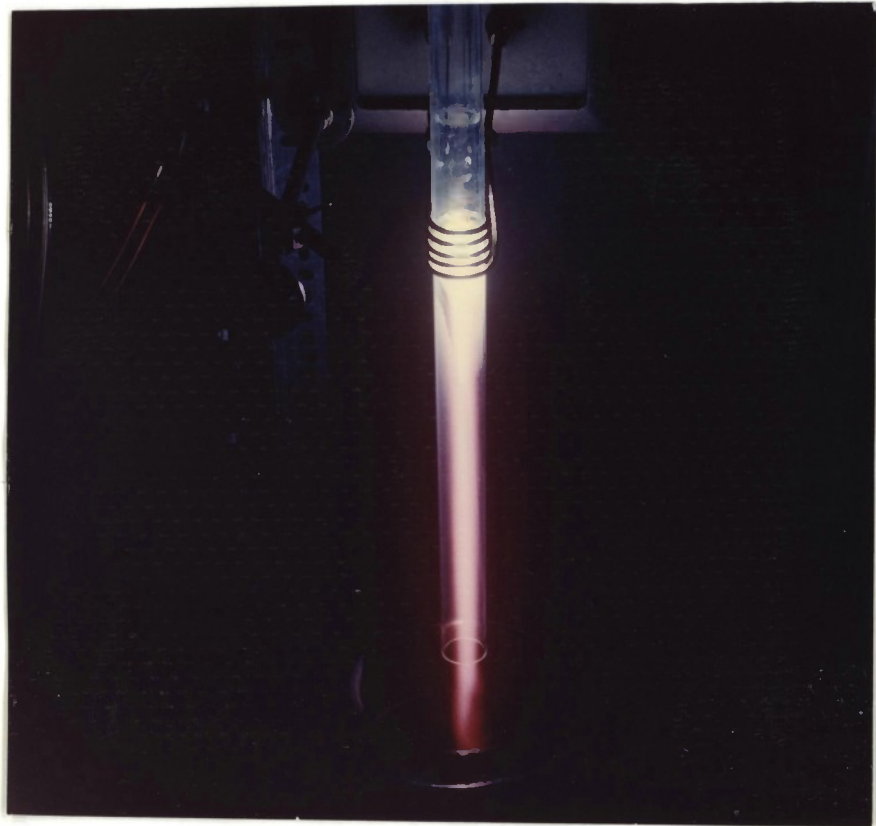
SUGGESTED DESIGN IMPROVEMENTS FOR THE

SHEATH-STABILIZED DISCHARGE

There are two areas which need immediate improvement in order
to run gas-solid reactions in a sheath-stabilized discharge--the
design and fabrication of a reactor which can be connected to traps,
and the development of an improved method for feeding powders so
that their residence time can be increased.

Figure 10 shows the design of a sheath-stabilized torch which
can be connected to a copper reactor by means of a $\mathbb{T}$ 45/50 ground
glass Vycor joint. The joint is attached to a brass plate by means
of Sauereisen (No. 78), and then this connection is covered on the
outside with an epoxy resin so that a completely gas-tight seal is
made. Traps can be connected, thus completing the "closed" system
and excluding both moisture and air. Once air has been excluded,
there should no longer be the problem of the formation of nitrates
as seen earlier and this gas-tight system should also allow the
study of reactions with more reactive gases such as fluorine or SiF_4.

Figure 11 suggests one possible method for increasing the
residence time of falling powders in the plasma. The sheath-stabi-
lized torch is inverted in a manner similar to that of the torch in
the nitric oxide synthesis. As powder falls from above, it will now
be falling against the plasma gas stream and not be propelled by it.
Any powder which is vaporized or reacts to form gaseous products
will be collected in traps, whereas any solid particles will fall

FIGURE 10

Closed system for sheath-stabilized discharge

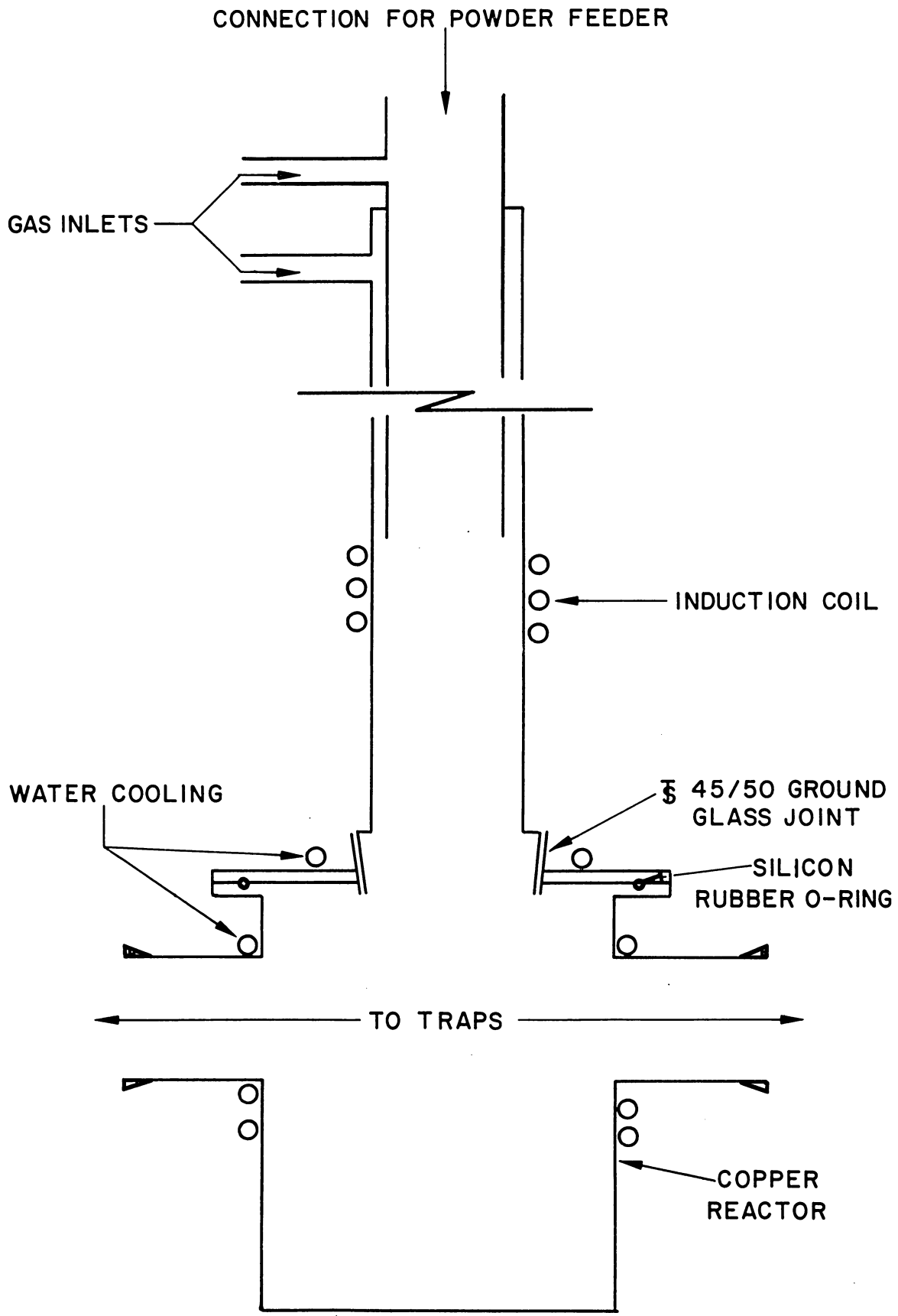showing plasma torch and reactor.

CONNECTION FOR POWDER FEEDER

GAS INLETS

INDUCTION COIL

WATER COOLING

⊥ 45/50 GROUND
S GLASS JOINT

SILICON
RUBBER O-RING

TO TRAPS

COPPER
REACTOR

FIGURE 11

Apparatus for increasing residence

time of falling powders.

CONNECTION FOR POWDER FEEDER

WATER COOLING

TO TRAPS ←

→ TO TRAPS

SILICON RUBBER O-RING

WATER COOLING

CONNECTION FOR PLASMA TORCH

GROUND GLASS JOINT ($ 45/50) (VYCOR)
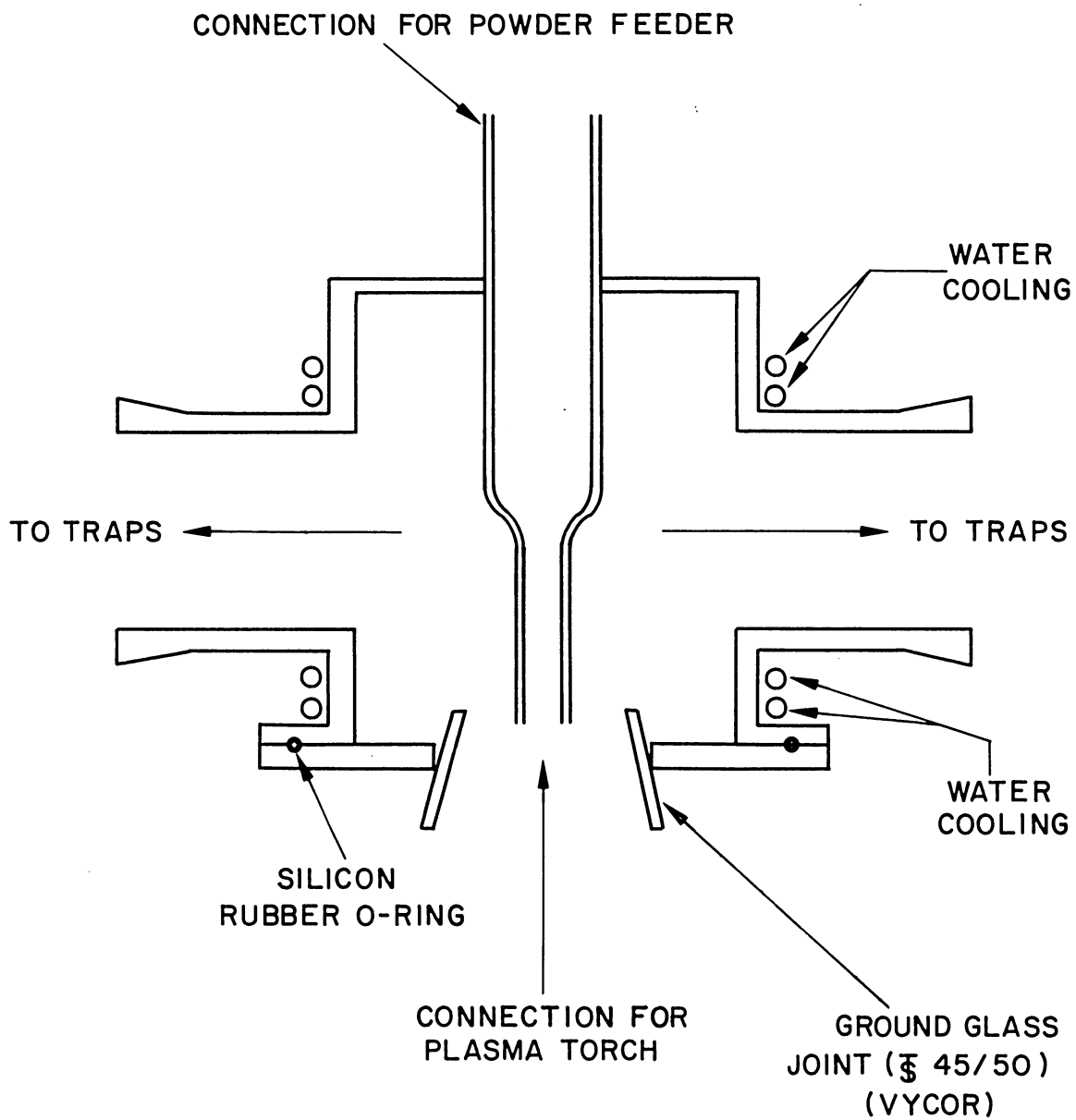
through the plasma and be collected at the bottom of the discharge tube.

In principle, this system can be extended to a fluidized-bed operation in which the powder floats in the gas stream at the level of the plasma blob and is thoroughly heated and reacted before falling into the collection trap.

REFERENCES

1. H. Gerdien and A. Lotz, Z. Tech. Physik, 4, 157 (1923).

2. G.I. Babat, J. Inst. Elec. Engrs. (London), 94, Part III, 27 (1947).

3. T.B. Reed, J. Appl. Phys., 32, 821 (1961).

4. Ibid., p. 2534.

5. C.W. Marynowski, Proceedings of International Symposium on High Temperature Technology, Asilomar, California, p. 71 (Butterworths, Washington, 1964).

6. A.S. Kana'an and J.L. Margrave, Advances in Inorganic Chemistry and Radiochemistry, Vol. 6, H.J. Emeleus and A.G. Sharpe, eds., pp. 143-206 (Academic Press, New York, 1964).

7. J.E. Anderson and L.K. Case, Ind. Eng. Chem., Process Design and Development, 1, 161 (1962).

8. H.W. Leutner, Ind. Eng. Chem., Process Design and Development, 2, 315 (1963).

9. H.W. Leutner and C.S. Stokes, Ind. Eng. Chem., 53, 341 (1961).

10. H.W. Leutner, Ind. Eng. Chem., Process Design and Development, 1, 166 (1962).

11. C.S. Stokes and W.W. Knipe, Ind. Eng. Chem., 52, 287 (1960).

12. R.F. Baddour and J.L. Blanchet, Ind. Eng. Chem., Process Design and Development, 3, 258 (1964).

13. R.F. Baddour and J.M. Iwasyk, Ind. Eng. Chem., Process Design and Development, 1, 169 (1962).

14. R.F. Baddour and B.R. Bronfin, Ind. Eng. Chem., Process Design and Development, 4, 162 (1965).

15. J.O. Gibson and R. Weidman, Chem. Eng. Prog., 59, 53 (1963).

16. C. Sheer, S. Korman, and collaborators, Arcs in Inert Atmospheres and Vacuum, W.E. Kuhn, ed., pp. 149-188 (Wiley and Sons, Inc., New York, 1956).

17. R. Collongues and F. Leprince-Ringuet, Bull. Soc. Chim. France, 1962, 522 (1962).

18. F. Galtier, F. Leprince-Ringuet, J. Reboux, R. Collongues, and G. Chaudron, Compt. Rend., 255, 2539 (1962).

19. C.W. Marynowski, Proceedings of International Symposium on High Temperature Technology, Asilomar, California, p. 67 (Butterworths, Washington, 1964).

20. J. Reboux, "Chalumeau a plasma haute frequences et hautes temperatures," Procede S.T.E.L.-C.N.R.S. (Vitry) (1962).

21. T.B. Reed, Intl. Sci. Tech., No. 6, 42 (1962).

22. R. Collongues, Chimie Moderne, IX, 3 (1964).

23. H.J. Hedger and A.R. Hall, Powder Metallurgy, No. 8, 65 (1961).

24. A.G. Monroe, Proceedings of International Symposium on High Temperature Technology, Asilomar, California, p. 77 (Butterworths, Washington, 1964).

25. A. Mironer and F. Hushfar, AIAA Electric Propulsion Conference, Colorado Springs, Colorado, March 11-13 (1963).

26. K. Johnson and M.S. Bloom, British Patent No. 915,771 assigned
    to Imperial Chemical Industries (1963).

27. F. Leprince-Ringuet, A.M. Lejus, and R. Collongues, Compt.
    Rend., 258, 221 (1964).

28. See Proceedings of International Symposium on High Temperature
    Technology, Session I, p. 525 (Butterworths, Washington,
    1964).

29. C.P. Beguin, D.G. Vickroy, and J.L. Margrave, "Chemical
    Syntheses in Radio-frequency Plasma Torches," to be published.

30. C.L. Johnson, Anal. Chem., 24, 1572 (1952).

31. A.V. Grosse, H.W. Leutner, and C.S. Stokes, First Annual Report
    "Plasma Jet Chemistry," December 31, 1961, The Research
    Institute of Temple University, Philadelphia (1961).

32. A.S. Kana'an and J.L. Margrave, Int. Sci. Tech., No. 8, 75
    (1962).

33. A.G. Monroe, Proceedings of International Symposium on High
    Temperature Technology, Asilomar, California, pp. 81-83
    (Butterworths, Washington, 1964).

34. C.M. Olson and J.M. Tully, British Patent No. 926,716 and
    U.S. Patent No. 2,915,367 assigned to DuPont, Wilmington,
    Delaware (1959).

35. S. Aleonard, Compt. Rend., 253, 1213 (1961).

36. J.A. Kahlswa, British Patent No. 790,938 (1958); Chem. Abstr.
    52, 12628e (1958).

37. A. Sommer, D. White, M.J. Linevsky, and D.E. Mann, J. Chem.
    Phys., 38, 87-98 (1963).

38. H.T. Hall and L.A. Compton, Inorg. Chem., $\underline{4}$, 1213-1216 (1965).

39. C.H. Chang and J.L. Margrave, unpublished work (1965).

40. L.G. Gay-Lussac and L.J. Thenard, Reserches phys. chim., Paris, $\underline{1}$, 154 (1811).

41. H. Davy, Phil. Trans., $\underline{100}$, 16 (1810).

42. F. Feigl, Spot Tests, Vol. I, Inorganic Applications, pp. 325-326 (Elsevier, New York, 1954).

43. Ibid., p. 186.

44. E.G. Brame, Jr., S. Cohen, J.L. Margrave, and V.W. Meloche, J. Inorg. Nucl. Chem., $\underline{4}$., 91 (1957).

45. J. Blom, Ber., $\underline{59}$, 121 (1926).

46. T.V. Rode and T.A. Dobrynina, Proc. Acad, Sci., USSR, $\underline{91}$, 125 (1953).

47. J. Milbauer, Chem. Z., $\underline{40}$, 587 (1916).