

# USE OF RADIO-FREQUENCY PLASMA IN CHEMICAL SYNTHESIS

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## I. Introduction

Investigation of chemical reactions in thermal plasma devices operating at atmospheric pressure involves the use of the plasma as an energy source for the activation of endothermic reactions, which can also be carried out by more conventional high-temperature techniques. It is hoped that the use of plasma will result in the formation of either a cheaper product than the conventional route, or one with superior physical or chemical properties.

The first application of a radio-frequency (RF) energy source to sustain a plasma in a flowing stream of argon at atmospheric pressure by Reed (43), triggered a resurgence of interest in plasma chemistry in general. This interest increased rapidly during the 1960s, as evidenced by the large number of articles and patents which have since been published. Several general reviews of the plasma chemistry field have appeared in the last few years. McTaggart (39) reviewed the use of low-pressure microwave discharges in chemical synthesis. The use of arc plasma devices in chemical synthesis was reviewed by Landt (35), and Sayce (45) has described the use of plasma devices in extractive metallurgy. Radio-frequency plasma torches used for chemical syntheses have been mentioned in some review articles (29, 58), but no comprehensive review of chemical syntheses in RF plasmas has as yet been published.

## II. Thermal Decomposition of Gases and Liquids

### A. METHANE

The pyrolysis of methane in an RF plasma discharge was first investigated by Grosse *et al.* (22) using a helium plasma of 0.5-kW power input. They obtained high yields of carbon and hydrogen at high methane concentrations (1:1  $\text{CH}_4/\text{He}$ ), but as the concentration of methane decreased, they were able to obtain 30% conversion to acetylene (1:7  $\text{CH}_4/\text{He}$ ). By extrapolation of these results, Grosse *et al.* predicted that 100% conversion of methane to acetylene would be possible at a  $\text{He}/\text{CH}_4$  ratio of 28:1. They concluded, however, that although the RF plasma was useful for acetylene formation, they obtained better results with a direct-current arc plasma.

Teresawa (49) studied the influence of operating variables, such as argon and methane flow rates and the dimensions of the RF torch, on the conversion of methane to acetylene. He observed that, under certain conditions, methane decomposed completely to 85% acetylene, when passed through the argon plasma. Teresawa also observed that the conversion to acetylene dropped and the level of reaction decreased

when the volume of the reactor was doubled. This was presumably caused either by a lower reaction rate due to decreased energy density in the larger torch or by a residence time effect. Besombes-Vailhé (5) established a relationship between RF torch volume, methane concentration, and input power level in methane pyrolysis. He found that, at power levels between 2 and 5 kW, maximum conversions of methane to acetylene were obtained when a methane concentration of 27% in argon was used and when the contact time of gases in the plasma was  $1.7 \times 10^{-2}$  sec. The minimum power requirement for acetylene production in Besombes-Vailhé's work was given as 23.5 kWh/m<sup>3</sup> C<sub>2</sub>H<sub>2</sub>.

Amouroux and Talbot (1) studied the decomposition of methane to acetylene in an RF plasma employing a fluidized bed of refractory material to quench the reaction products. By using a constant power and constant flow rate argon plasma, they studied the effects of methane flow, fluid bed material, and excess hydrogen on the formation of acetylene. They found that the conversion of methane to acetylene decreased from 50 to 30% when the initial methane concentration was increased from 5 to 25%, and with a fluidized bed of sand at 190°C. Slightly better conversions to acetylene were obtained with graphite as fluidizing material, and Amouroux and Talbot postulated that this was due to the inhibition of carbon formation in the reaction by the partial pressure of carbon already in the graphite bed. By using the graphite fluidized bed and C/H ratios of 0.15:1, they were able to achieve up to 90% conversion of methane to acetylene at power requirements of 28 kWh/m<sup>3</sup> C<sub>2</sub>H<sub>2</sub>.

## B. HIGHER HYDROCARBONS

Nishimura *et al.* (41) studied the pyrolysis of propane in a 15-kW argon induction plasma. They fed in propane countercurrent to the tail of the argon plasma and found that the conversion of propane decreased with increasing distance between plasma and feed point. Nishimura *et al.* considered this phenomenon to be due simply to an effective decrease of the reaction temperature. Maximum yields of acetylene (28%) and ethylene (5%) were obtained at a feed distance of 2.5 cm. The yields of acetylene, ethylene, and carbon were found to decrease with increasing propane flow rates, which was considered to be caused by a decreased residence time of the propane in the reaction zone.

Nishimura *et al.* also found that they could successfully inhibit carbon formation by adding hydrogen to the plasma argon. They were thus able to obtain a maximum yield of 40% acetylene while converting

60% of the original propane. This yield, however, was achieved at an extremely high energy consumption of 780 kWh/m<sup>3</sup> C<sub>2</sub>H<sub>2</sub>.

A high surface-area carbon black (90 m<sup>2</sup>/gm) was obtained by Jordan (32) by decomposition of butene-1 in an argon induction plasma. Butene-1 was injected into the plasma at a rate of 0.007 m<sup>3</sup>/hr and after 1 hr operation 15 gm of carbon black was collected. A process for high surface-area carbon black (12) has also been developed in which a carbon feed is vaporized in an RF plasma and the vapor subsequently quenched in a halogen-rich environment.

### C. HALOGEN COMPOUNDS

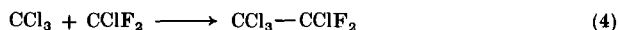
Kana'an and Margrave (33) investigated the decomposition of carbon tetrachloride in an RF plasma and reported the formation of low yields of the benzene derivative, C<sub>6</sub>Cl<sub>6</sub>. Using spectroscopic techniques, Kana'an and Margrave (34) also identified free radicals such as CCl, CF, and CF<sub>2</sub> in a chlorofluorocarbon plasma. They postulated that the C<sub>6</sub>Cl<sub>6</sub> present in the CCl<sub>4</sub> decomposition products was formed by polymerization of reactive species such as CCl<sub>3</sub>, CCl<sub>2</sub>, and CCl.

Bequin *et al.* (4) extended this work and investigated the decomposition of CCl<sub>4</sub>, CCl<sub>3</sub>F, CCl<sub>2</sub>F<sub>2</sub>, and CF<sub>4</sub> in a 10-kW argon RF plasma. They also obtained benzene derivatives such as C<sub>6</sub>Cl<sub>6</sub>, C<sub>6</sub>Cl<sub>5</sub>F, C<sub>6</sub>Cl<sub>4</sub>F<sub>2</sub>, and C<sub>6</sub>Cl<sub>2</sub>F<sub>4</sub> in low yields, together with a variety of chlorofluoroethane and ethylene derivatives. They reported, however, that the major decomposition products were chlorine, fluorine, and carbon.

Bequin *et al.* also identified the molecule CCl<sub>3</sub>—CClF<sub>2</sub> as one of the decomposition products of CClF<sub>3</sub>, and postulated that as there was no CCl<sub>3</sub> present in the reactant, the CCl<sub>3</sub>—CClF<sub>2</sub> must have been formed by recombination of CCl<sub>3</sub>, already formed by recombination of simpler radicals. They suggested the following mechanism for CCl<sub>3</sub> formation:



The radical CClF<sub>2</sub> could have been formed by thermal decomposition of CClF<sub>3</sub> and further reaction could then occur to the ethane derivative as follows:



Bequin *et al.* stated that all identified products could be accounted for by such radical recombination reactions, but produced no other evidence for such mechanisms. They also postulated that, because no acetylene

derivatives were identified as products, it was probable that the benzene derivatives were formed by trimerization of acetylene compounds such as  $C_2Cl_2$ ,  $C_2F_2$ , and  $C_2FCl$ . It is worth noting that the occurrence of such compounds would have represented stronger evidence.

Work carried out on the behavior of boron trichloride in an RF plasma (23) showed that, although it dissociates almost completely when it is passed into the plasma, after it leaves the plasma, complete recombination and charge neutralization of the dissociation products occurs to give  $BCl_3$  again. No dissociation products could be found.

Spectrographic examination of the emission from an argon- $BCl_3$  plasma showed that the main decomposition products of  $BCl_3$  that emit radiation are  $BCl$ ,  $BCl_2$ ,  $B$ ,  $B^+$ ,  $Cl_2$ , and  $Cl_2^+$ . The predominant emitting species was found to be  $BCl$ , which is considered to have been formed by the reaction,



### III. Reduction Reactions

#### A. ALUMINUM OXIDE

Rains and Kadlec (42) injected  $Al_2O_3$  particles into an RF argon plasma and measured the conversions to aluminum under neutral conditions and when  $H_2$ ,  $CH_4$ , and  $CO$  were added to the argon. They found that conversions to aluminum were dependent on parameters such as particle size of  $Al_2O_3$ , power input, type of reducing gas, and the mass flow rate through the plasma. For argon plasmas at 5 kW, a maximum conversion of 30%  $Al_2O_3$  to aluminum was obtained at a feed rate of 6 gm  $Al_2O_3$ /min. As the feed rate was increased to 36 gm/min, the conversion to aluminum dropped rapidly to 2%. Similar conversions and behavior were observed when hydrogen was added to the plasma. However, when carbon monoxide or methane was used as reducing agent, conversions to aluminum of 2 and 4 times that obtained with pure argon or argon-hydrogen mixtures were reported. Rains and Kadlec postulated that this was caused by the presence of carbon vapor in the discharge, which would have a higher affinity for oxygen than for hydrogen.

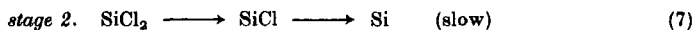
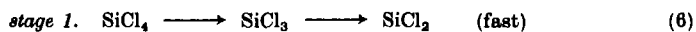
#### B. TITANIUM TETRACHLORIDE

Miller and Ayen (40) investigated the hydrogen reduction of titanium tetrachloride in an RF plasma torch. They obtained conversions of  $TiCl_4$  to  $TiCl_3$  of between 60 and 80%, at feed rates of 1.5

gm/min of  $\text{TiCl}_4$ . They observed that the conversions were independent of  $\text{TiCl}_4$  feed rate and of power input up to 5 kW, as well as of the  $\text{H}_2/\text{TiCl}_4$  ratio when it was greater than stoichiometric. Miller and Ayen injected the  $\text{TiCl}_4$  vapor into an argon plasma but found that the plasma could only tolerate up to 1 mole %  $\text{TiCl}_4$  in the argon at 10 kW, due to low coupling efficiency. They, therefore, measured the coupling efficiency of their plasma induction circuit and found that, although an efficiency of between 60 and 70% was obtained for 2 mole % hydrogen in argon, changeover to 0.15 mole %  $\text{TiCl}_4$  in argon reduced the efficiency to less than 40%. They did not report any attempt to increase the coupling efficiency to  $\text{TiCl}_4$  by better impedance matching of the RF generator. Miller and Ayen also investigated various quenching devices for argon- $\text{TiCl}_4$  plasmas in an attempt to prepare lower titanium chlorides without hydrogen. No significant solid products were obtained under any of the quench conditions, presumably because of extremely rapid recombination and charge neutralization of dissociated species in the plasma tail flame.

### C. SILICON TETRACHLORIDE

Vurzel and Polak (55) carried out extensive kinetic studies of the reduction of silicon tetrachloride to silicon in plasma devices. They first decomposed  $\text{SiCl}_4$  to  $\text{SiCl}_3$  in an adiabatic compression-expansion device and then completed the reduction in an RF plasma. They claimed that the decomposition of  $\text{SiCl}_4$  to silicon proceeded by a two-stage mechanism of chlorine atom removal:



They postulated that the second stage was rate-controlling and determined the rate constants for both stages:

$$k_1 = 5 \times 10^8 \exp(-88,000 \pm 5,000/RT) \text{ sec}^{-1}$$

$$k_2 = 5 \times 10^7 \exp(-126,000 \pm 10,000/RT) \text{ sec}^{-1}$$

From additional calculations of the thermodynamics of the  $\text{SiCl}_4$  decomposition, Vurzel and Polak predicted that the decomposition would be favored by reducing conditions and confirmed this experimentally, obtaining high-purity silicon by use of an RF plasma torch.

### D. BORON TRICHLORIDE

The hydrogen reduction of boron trichloride to boron in an RF plasma has been investigated by Hamblyn *et al.* (25). By use of a special

design of RF reactor system (24), it was found possible to produce up to 0.25 kg/hr of 99% boron at 30 kW. The conversion of  $\text{BCl}_3$  to boron was found to be dependent on parameters such as  $\text{BCl}_3$  concentration in the reaction mixture, residence time of the mixture in the reactor, and the configuration of the reactant feeds to the reactor.

The boron so formed resembled other amorphous borons in appearance and was found to be similar in structure to  $\beta$ -rhombohedral boron. Individual particles were random in shape, consisting mainly of platelets between 200 and 7500 Å in diameter. The presence of regular dodecagonal platelets of boron was also observed, in the product, which had typical diameters of 7000 Å and a unit cell lattice constant of 30 Å. This unit cell dimension is considerably larger than any previously reported form of boron and was considered to be a further modification of known boron structures.

The kinetics of the reduction of  $\text{BCl}_3$  with hydrogen were further studied by Hamblyn (23), and the reaction was found to be approximately first order with respect to  $\text{BCl}_3$  and very low order with respect to hydrogen. The low order for hydrogen suggested that its role in the reaction is merely as a scavenger for chlorine, produced by the dissociation of  $\text{BCl}_3$  in the plasma. Experimental results were interpreted partly by a thermal mechanism involving species such as  $\text{BCl}$ ,  $\text{Cl}$ , and  $\text{BH}$ , and partly in terms of an ionic mechanism.

#### IV. Oxidation Reactions

##### A. MIXED OXIDES

Barry *et al.* (3) injected mixtures of chromium and aluminum chloride vapors and titanium and chromium chloride vapors into RF argon plasmas, and they obtained high yields of the respective oxide mixtures.

McPherson (38), using the same technique, prepared a series of 50–500 Å size range, single and mixed oxides. Spherical, metastable  $\text{Al}_2\text{O}_3$  particles were formed by condensation of molten  $\text{Al}_2\text{O}_3$  droplets in the tail of an oxygen plasma. The  $\text{Al}_2\text{O}_3$  droplets were considered to freeze and undergo nucleation to the  $\gamma$ - $\text{Al}_2\text{O}_3$  form, which on further cooling transformed to stable  $\delta$ - $\text{Al}_2\text{O}_3$ .

By cocondensation of  $\text{Al}_2\text{O}_3$ - $\text{Cr}_2\text{O}_3$  mixtures and  $\text{Al}_2\text{O}_3$ - $\text{TiO}_2$  mixtures, McPherson obtained metastable solid solutions of  $\text{Cr}_2\text{O}_3$  in  $\theta$ - $\text{Al}_2\text{O}_3$  and an  $\text{Al}_2\text{O}_3$ - $\text{TiO}_3$  solid solution in which  $\delta$ - $\text{Al}_2\text{O}_3$  and rutile were present. A third phase was also observed to be present in the latter product, which was tentatively identified as a metastable  $\text{Al}_2\text{O}_3$ - $\text{TiO}_2$  compound.

## B. TITANIUM DIOXIDE

The preparation of a pigmentary  $\text{TiO}_2$  by oxidation of  $\text{TiCl}_4$  in chlorine oxygen and argon RF plasmas is described in two British patents (7, 8). In the former, the use of chlorine as plasma gas enabled a  $\text{TiCl}_4\text{-O}_2$  mixture to be fed into the tail, producing approximately 2.6 kg/hr of pigmentary  $\text{TiO}_2$ . Reduced throughputs of  $\text{TiCl}_4\text{-O}_2$  mixture were necessary when an oxygen plasma was operated because recirculation of  $\text{TiCl}_4$  into the oxygen plasma, where it was oxidized, caused extinction of the plasma. This did not occur in the chlorine plasma. The second patent (8) describes a similar process for the preparation of pigmentary  $\text{TiO}_2$  in an RF plasma. In this process, higher  $\text{TiCl}_4$  throughputs were achieved by use of chlorine as a plasma-stabilizing additive in the  $\text{TiCl}_4$  itself. With an argon plasma and a 5% chlorine in  $\text{TiCl}_4$  mixture, up to 7 kg/hr of pigmentary  $\text{TiO}_2$  could be prepared when quenching was by oxygen or air.

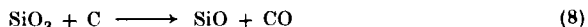
## C. SILICON DIOXIDE

Audsley and Bayliss (2) injected  $\text{SiCl}_4$  vapor into the tail of an RF oxygen plasma and obtained 99% oxidation of the chloride to  $\text{SiO}_2$ . Injection of the  $\text{SiCl}_4$  directly into the oxygen plasma caused plasma extinction in each of four different torches tried, presumably due to the same phenomenon as in the oxidation of  $\text{TiCl}_4$ . However, from experiments with tail feeding of  $\text{SiCl}_4$ , Audsley and Bayliss concluded that the oxidation rate was only limited by kinetics, and they successfully oxidized up to 4 kg/hr of  $\text{SiCl}_4$  to  $\text{SiO}_2$ .

A process for the preparation of high surface-area  $\text{SiO}_2$  by use of an RF plasma is described in a recent patent (13). By the feeding of 200-mesh sand particles into a mixed argon-oxygen plasma, up to 0.25 kg/hr of 260  $\text{m}^2/\text{gm}$  silica could be prepared when the  $\text{SiO}_2$  vapor was quenched with air. When hydrogen was used as quench gas instead of air, an activated silica with hydrophilic properties was prepared. The requirements for the formation of a hydrophilic active silica were that free hydrogen should be present in the quench region during the condensation of the  $\text{SiO}_2$  particles. This condition could be achieved by the inclusion of hydrogen or hydrogen-containing compounds with the plasma gas, so that dissociation to free hydrogen could occur. When the  $\text{SiO}_2$  condensation was carried out in the presence of a hydrogen compound with a hydrophobic group (such as a straight-chain alcohol or a chlorosilane) and the compound was injected into the quench region at a low enough temperature, decomposition of the hydrogen compound did not occur and the activated silica had hydrophobic properties.



Bush and Sterling (15) have extended the foregoing work on activated silica. They developed a rotating RF plasma furnace into which were fed mixtures of sand and carbon in the form of paste or rods. Operating with an argon plasma and speeds of furnace rotation of up to 1000 rpm, they were able to maintain a semiplastic ring of molten silica around the plasma, held in place by centrifugal force. As the reaction of  $\text{SiO}_2$  with carbon occurred,



the melt could be replenished by new material. The SiO was oxidized at the exit of the furnace to give activated silica of high surface area. When operating with an air plasma, Bush and Sterling found it necessary to feed the sand and carbon to the melt in the form of rods, formed by mixing sand with an oil and using a cellulose thickener. This was necessary in order to avoid rapid oxidation of the carbon before reaction with the molten sand could occur. By appropriate control of the composition and feed position of the quench gas, either hydrophilic or hydrophobic activated silica could be prepared.

#### D. OTHER OXIDES

Chase and Potter (18) have carried out extensive investigations of the preparation of high surface area oxides, by oxidation of metal and metal oxide powders. Table I summarizes the experimental conditions and results obtained in this work. The powders were fed to an RF argon plasma in a stream of argon or oxygen, were vaporized in the plasma, and the condensing species oxidized in the plasma tail flame. The condensing vapors were also rapidly quenched in the tail flame to prevent extensive particle growth and to achieve high surface areas. The surface area of  $\text{Sb}_2\text{O}_3$  powder so prepared was found to be greatly influenced by the dilution of the condensing vapors in the gas mixture. For example, a decrease in particle density from  $1.1 \times 10^{-4}$  to  $0.2 \times 10^{-4}$  gm  $\text{Sb}_2\text{O}_3$ /liter gas decreased the average particle diameter of the final product from 820 to 150 Å. The antimony oxide was found to have excellent fire-retarding properties in acrylic fibers and not to decrease the brightness of the fiber to the same extent as normal commercial  $\text{Sb}_2\text{O}_3$ . Zinc oxide so produced was claimed to have an ultraviolet absorption efficiency equivalent to normal commercial UV absorbers when tested in polyurethane film. Films using this zinc oxide also proved more fade-resistant than commercial absorbers when tested in accelerated radiation conditions over 40 hr.

TABLE I  
PREPARATION OF SUBMICRON OXIDES<sup>a</sup>

Feed powder	Feed rate	Argon plasma (kW)	Quench gas	Quench rate (liter/min)	Con-version (%)	Product	Particle size (Å)	Surface area (m <sup>2</sup> /gm)
Zinc dust	0.078 gm/min	1.35	O <sub>2</sub>	280	100	ZnO white	268	40
Antimony (< 44 μm)	0.58 gm/min	1.35	O <sub>2</sub>	280	90	Sb <sub>2</sub> O <sub>3</sub> white	340	—
Antimony 0.15–0.2 μm	0.43 gm/min	1.35	Air	292	100	Sb <sub>2</sub> O <sub>3</sub> white	142	—
WO <sub>3</sub> 0.2–0.4 μm	4 gm/hr	4	Air	425	68	WO <sub>3</sub> light yellow	315	26.6
MoO <sub>3</sub> 5–20 μm	2.7 gm/hr	3	Air	509	100	MoO <sub>3</sub> blue	—	26.5

<sup>a</sup> Data taken from Chase and Potter (18).

## V. Preparation of Refractory Compounds

## A. CARBIDES

A process for the formation of subpigmentary ( $<0.5\ \mu\text{m}$ ) silicon carbide has been described in a recent British patent (9). Silica powder ( $44\text{--}150\ \mu\text{m}$ ) was injected into an argon-methane plasma maintained by a 10-kW RF induction torch. Feed rates of up to 1.5 gm/min silica were used, which yielded a high conversion of micron-sized silicon carbide. An interesting feature of the plasma torch used in this work was the porous plasma-containing wall through which hydrogen was passed, said to prevent carbon building up and to increase plasma enthalpy. Also, the RF coil used had a reverse turn at the lower end to effect magnetic confinement of the plasma tail.

Salinger (44) reported the successful conversion of methyltrichlorosilanes to silicon carbide in a 50-kW RF plasma torch. The liquid methyltrichlorosilanes were fed to the tail flame of various plasmas and the solid products were recovered in an acid-resistant bag filter. Up to 85% recovery of theoretical solid product was reported, which was subsequently heated at  $500^\circ\text{C}$  to remove elemental carbon. Under the best condition (20–25% vol. hydrogen in argon plasma at 36 kW), up to 70% conversion to  $\beta\text{-SiC}$  was obtained with ca. 10% conversion to amorphous SiC. Salinger suggested that the good crystallinity of the  $\beta\text{-SiC}$  so obtained meant that the reaction occurred in a gas temperature range in which  $\beta\text{-SiC}$  was the stable crystalline form (i.e.,  $<2300^\circ\text{C}$ ).

MacKinnon and Wickens (37) have prepared boron carbide in the form of submicron particles by injecting  $\text{BCl}_3$ ,  $\text{H}_2$ , and  $\text{CH}_4$  into the tail of a 20-kW argon RF plasma. A  $3^3$  factorial experiment to study the effect of operating variables was carried out; a preliminary analysis of which gave the following indications:

1. The maximum percentage boron conversion to  $\text{B}_4\text{C}$  (93%) was obtained at a low (20 liters/min)  $\text{BCl}_3$  flow rate, at a relatively high (8:1)  $\text{H}_2/\text{BCl}_3$  ratio, and at a stoichiometric (1:4)  $\text{CH}_4/\text{BCl}_3$  ratio.

2. The complete set of results obtained indicated the presence of interactions among the effects of  $\text{BCl}_3$  flow rate,  $\text{H}_2/\text{BCl}_3$  ratio, and  $\text{CH}_4/\text{BCl}_3$  ratio on the conversions obtained.

Hartl (26) treated vanadium, chromium, and titanium nitrides in argon-5% acetylene RF plasmas. The nitrides were dropped as powders into a vertical plasma torch in which the gas stream was flowing upwards. Product was collected both as wall deposits and as loose powder at the lower end of the torch (i.e., the plasma gas inlet). In the case of vanadium, the products collected were identified by X-ray analysis to be a mixture of vanadium nitride and carbide (VC-VN) with

TABLE II  
PREPARATION OF  $\text{Si}_3\text{N}_4$  AND  $\text{TiN}^a$

RF plasma gas	Flow rate to plasma	$\text{NH}_3$ feed rate	Power (kW)	Conversion to product	Surface area (particle size)
1. $\text{SiCl}_4$	0.5 mole/min	0.65 mole/min	36	65% $\text{Si}_3\text{N}_4$	30.5 $\text{m}^2/\text{gm}$
2. Ar + $\text{SiCl}_4$	25, 0.47 liters/min	0.69 mole/min	26	67% $\text{Si}_3\text{N}_4$	47.5 $\text{m}^2/\text{gm}$
3. Argon	80 liters/min	0.5 liter/min	26.5	70% $\text{TiN}$	0.05–0.4 $\mu\text{m}$
probe $\text{TiCl}_4$	0.25 mole/min	—	—	—	(spherical particles)

<sup>a</sup> Data from British Titan Products (11).

the presence of small amounts of the carbonitride  $\text{VC}_{0.4}\text{N}_{0.4}$ . Chromium nitride ( $\text{CrN}$ ) was converted to the chromium carbide ( $\text{Cr}_3\text{C}_2$ ), and titanium nitride to titanium carbide ( $\text{TiC}$ ).

## B. NITRIDES

Nitridations of silicon, magnesium, and aluminum powder in a 2-kW, 37-MHz argon–nitrogen plasma have been attempted by Fletcher *et al.* (20). Virtually no magnesium or aluminum nitrides were detected in the products. The authors suggested that products had been formed but had been rapidly destroyed by atmospheric hydrolysis. However, 7% nitridation of silicon metal was obtained with 14% nitrogen in argon plasma. Another RF plasma process for the nitridation of metals has also been patented (11). Silicon nitride so produced was described as having an opacity and brightness similar to aluminum silicate when evaluated as a filler and extender in paper. Table II summarizes the reported results from this work. The titanium nitride powder was reported to be in the form of 0.05–0.4  $\mu\text{m}$  spherical particles. This could be possibly due to the use of a relatively low quenching rate, allowing the formation of a liquid TiN phase which, on cooling, formed spheroids.

Hartl (26) reported attempted nitridations of various metal oxides by means of countercurrent feeding of the oxide powders into an RF nitrogen plasma. Although nitrides were identified by X-ray analysis, their separation was not possible. Table III summarizes the resulting oxynitrides obtained for vanadium, titanium, and chromium.

TABLE III  
NITRIDATION OF METAL OXIDES<sup>a</sup>

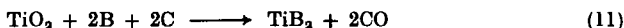
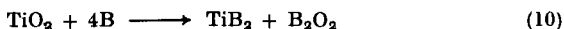
Feed material	Powder product	Torch wall deposit
$\text{V}_2\text{O}_5$	$\text{VO}_{1.4}\text{N}_{0.2}$ ; $\text{VO}_{1.2}\text{N}_{0.1}$	$\text{VN}_{0.7}\text{O}$ ; $\text{VN}_{0.8}\text{O}_{0.1}$
$\text{TiO}_2$	$\text{TiO}_{1.8}\text{N}_{0.1}$ ; $\text{TiO}_{1.8}\text{N}_{0.1}$	$\text{TiO}_{1.5}\text{N}_{0.3}$ ; $\text{TiN}_{0.8}\text{O}_{0.1}$
$\text{Cr}_2\text{O}_3$	$\text{CrO}_{1.4}$ ; $\text{CrO}_{1.5}$	$\text{CrO}_{1.2}\text{N}_{0.2}$ ; $\text{CrN}_{0.7}\text{O}_{0.1}$

<sup>a</sup> Data from Hartl (26).

## C. BORIDES

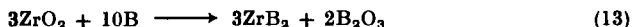
Triché *et al.* (54) reported the successful preparation of titanium diboride in an RF plasma reactor. They exposed compressed pellets of

various combinations of reactants to the tail flame of a 12-kW, 6.3-MHz argon plasma. They carried out the following reactions, in each of which titanium boride was successfully prepared:



The progress of each reaction was followed by spectrographic measurement of the emission of the  $\text{Ti}^+$  ion in the plasma tail flame. Triché *et al.* established that in the reactions involving  $\text{TiO}_2$  as reactant, a maximum in titanium ion emission was reached within 1 min, followed by a rapid decrease to a minimum emission between 2 and 3 min. Thereafter, the emission rose again to an equilibrium value. They postulated that the initial maximum in  $\text{Ti}^+$  emission corresponded to  $\text{TiO}_2$  evaporating from the pellet before reaction commenced, and the minimum in emission to the completion of the reaction. The subsequent increase in  $\text{Ti}^+$  emission was found to correspond to  $\text{Ti}^+$  emission from the tail flame when a  $\text{TiB}_2$  pellet was heated. Times for complete reaction were found to be of the order of 2 min in each case. The progress of one of the reactions, Eq. (10), was followed in more detail by quantitative X-ray analysis of a series of pellets exposed to the plasma for increasing time intervals of up to 3 min. Conversion data obtained correspond approximately to first-order kinetics.

Foex (21) reports the successful formation of borides in a rotating batch melting furnace, fired by an RF induction plasma. An amount of 0.8 kg from a stoichiometric mixture of  $\text{ZrO}_2$  and boron, previously compressed in the rotating vessel to a pressure of 40 kg/cm<sup>2</sup>, is treated by the action of an argon plasma (1 m<sup>3</sup>/hr) for 0.5 hr. Zirconium diboride is formed by the reaction,



which proceeds to about 50% conversion. During the reaction considerable evolution of  $\text{B}_2\text{O}_3$  occurs.

## VI. Nitrogen Fixation

Timmins and Ammann (53) reviewed the application of plasma discharge devices in general to the fixation of atmospheric nitrogen. The bulk of investigations on the preparation of compounds such as nitric oxide, hydrogen cyanide, cyanogen, and hydrazine in plasmas has been carried out in DC devices, either arc torches or glow discharges.

There have been several investigations of nitrogen fixation reactions in RF plasma devices, however, and some patents have been granted protecting processes developed from these investigations.

#### A. NITRIC OXIDE

Table IV summarizes work carried out on nitric oxide preparation in RF plasmas. Two important investigations using DC plasmas have also been included for comparison.

Bequin *et al.* (4) passed nitrogen and oxygen through a 5–7 MHz induced plasma torch and collected nitric oxide, together with trace oxygen and argon, in a series of liquid nitrogen traps. At power inputs to the plasma of 9–10 kW, conversions of nitrogen to nitric oxide of up to 2.12% were obtained. This can be seen from Table IV to be similar to the results obtained by Grosse *et al.* (22) when they quenched a stream of plasma nitrogen from a DC plasma jet with an oxygen stream.

Stokes *et al.* (47) reported similar conversions of oxygen in air to nitrogen oxides in a low-pressure RF plasma. After a run time of 2.5 hr, 0.4 ml of material was collected in liquid nitrogen traps, which on analysis showed a 2% conversion to nitric oxide. LaRoche (36) had previously demonstrated the beneficial effect of quenching the reaction products. In experiments with a low-pressure RF discharge, he obtained an increase in conversion to nitric oxide from 2 to 4% by a rapid quenching technique.

Timmins and Ammann (53) report much higher conversions of oxygen to nitric oxide by use of a DC plasma device, "the constricted arc," in which the anode and cathode are separated by a series of water-cooled segments. A considerably larger plasma zone can be stabilized with this device than with the conventional plasma jet. By operation of this device in air at gas enthalpies greater than 270 cal/gm and with careful control of quench conditions, Timmins and Ammanns were able to obtain up to 7% nitric oxide in the exit gas. This amounts to 30% conversion of oxygen to nitric oxide. Still higher conversions were claimed by Jackson and Bloom (30) using a capacitatively coupled RF plasma, in which conversions of oxygen to nitric oxide of up to 90% were possible.

It would appear from these series of investigations of nitric oxide preparation in plasma devices that, although reasonable conversions of oxygen to nitric oxide can be obtained under conditions of excess nitrogen, the final concentrations and production rates are low. The best conversions quoted in the foregoing are equivalent to approximately 200 kWh/lb nitric oxide produced, which is extremely high. The use of

TABLE IV  
SUMMARY OF NITRIC OXIDE WORK

Plasma device	Reactants	Feed rate (liter/m)		Power (kW)	Percent conversion of $O_2 \rightarrow NO$	NO in product (%)	Reference
		$N_2$	$O_2$				
5-7 MHz RF (atm. pressure)	$N_2 + O_2$	17.7	14.3	10	2.12		Bequin <i>et al.</i> (4)
DC plasma jet	$N_2 + O_2$	5.5	5.5	15	2.03		Grosse <i>et al.</i> (22)
27-MHz low-press. RF plasma	Air		0.1	0.3	2.0		Stokes <i>et al.</i> (47)
RF plasma:							
With quench	Air				20.0	4	LaRoche (36)
Without quench	(low pressure)				10.0	2	
RF plasma	Air		0.5		90.0	17	Jackson and Bloom (30)
(1-2 atm)			10.0		10.0	2	
DC constricted arc	Air	$0.43 \times 10^{-4}$		5.2	30	7	Timmins and Ammann (53)
		(lb/sec)					



higher-power level plasma devices and high surface area plasmas combined with controlled quenching would appear to offer the most promise for commercial processes.

## B. HYDROGEN CYANIDE AND CYANOGEN

There have been two recent investigations of hydrogen cyanide preparation in RF plasma torches. In one investigation carried out at atmospheric pressure in a 1.5-kW nitrogen plasma by Stokes *et al.* (47), conversions of injected methane to HCN of up to 35% were obtained with additional formation of acetylene. The second investigation by Bronfin (14) was carried out mainly at pressures below 460 torr. Injection of  $N_2$  and  $CH_4$  mixtures into a 3.5-kW argon plasma produced conversions of  $N_2$  to HCN of up to 70% at  $CH_4/N_2$  ratios greater than 2:1. These results were reported to be in good agreement with thermodynamic equilibrium conversions. The preparation of HCN from  $CH_4$  and  $N_2$  in a capacitively coupled RF plasma was also carried out by Jackson and Bloom (30). In the exit gases, 0.22 mole% HCN was obtained when  $CH_4$  was added to the tail of a nitrogen plasma. The same workers also claim the successful preparation of hydrazine in this RF plasma torch at atmospheric pressure. Ammonia and nitrogen injected into the torch in various configurations and flow rates produced a maximum yield of 0.02 mole%  $N_2H_4$  in the product gas stream. This yield is slightly better in terms of the mass of hydrazine produced than other work involving low-pressure glow discharges (50). A cheap route to hydrazine would be of great importance in the development of economically viable fuel cells.

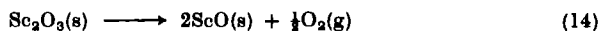
## VII. Heat Treatment of Solids

By injection of refractory powders into RF discharges, it is possible to heat treat the particles. Decomposition, vaporization, melting, or surface modification of particles can be achieved in varying degrees depending on the physical properties of the material, particle residence time, particle surface area, and the enthalpy available in the plasma.

### A. CRYSTAL GROWING

The first reported heat treatment of a solid in an RF plasma was carried out by Reed (43). He injected powders at high velocity through an atmospheric pressure argon plasma and deposited molten powder on a crystal boule in the plasma tail flame. A sapphire polycrystal, some

30 mm long and 10 mm diameter, was grown from sapphire powder by this technique. Zirconium oxide and niobium crystals were also grown in 50% oxygen-argon and 15% helium-argon plasmas, respectively. Reed concluded that the correct particle size range of the powder was crucial for successful crystal growth. Powders that were too fine vaporized and those that were too coarse led to surface bubbling effects on the crystal. Since this early work, many other applications of this technique of crystal growing have been studied and are well reported in other review articles. The most recent application of the technique is probably work carried out by Sienko and Young (46) on the growth of scandium oxide crystals. Scandium sesquioxide ( $\text{Sc}_2\text{O}_3$ ) powder was passed through the axis of a 10-kW RF argon plasma. Crystals of  $\text{Sc}_2\text{O}_3$  were grown on the end of a 5-mm diameter magnesia rod, supported in the plasma tail flame by a boron nitride rod. Crystal boules of up to 12 mm diameter were grown, the lower portions of which were sometimes covered with dendritic and whisker growth extensions. Chemical analysis of the crystals by reoxidation indicated an oxygen deficiency of up to 4% in the crystal. The formation of a substoichiometric scandium oxide,  $\text{Sc}_2\text{O}_{3-x}$  (where  $x = 0.008$  and  $0.115$ ), was explained by the loss of oxygen from the crystal surface according to the reaction,



## B. SPHEROIDIZATION

An extension of the use of RF plasma for particle heating is the spheroidization of solids. By careful control of plasma enthalpy, particle size, feed rate, and feed position, it is possible to melt each particle as it passes through the plasma. The liquid droplet forms a sphere due to surface tension and, on cooling, retains its spherical shape. Spheroidized particles are commercially useful because they will flow easily.

Hedger and Hall (27) were first to study the spheroidization of metal and metal oxide powders in an RF plasma. They injected 100–150  $\mu\text{m}$  size range powders into an argon plasma at rates up to 5 gm/min. Yields of between 50 and 70% spheroids were obtained for Cr, Mo, Ta, W, and  $\text{Al}_2\text{O}_3$  and for several uranium compounds, the remaining material being random-shaped lumps. Magnesia powder was also successfully spheroidized in a 20% oxygen-argon plasma. No obvious correlation was observed between the yield of spheroids and the melting points of the parent materials. Hedger and Hall postulated that this lack of correlation was due to ejection of particles from the plasma which they had observed photographically. The ejection could have been caused by magnetic or viscous drag effects and could result

in a percentage of particles failing to penetrate the plasma, the proportion involved varying unpredictably with the material. Plutonium dioxide, alone and mixed with other oxides (such as  $\text{UO}_2$ ,  $\text{ThO}_2$ , and  $\text{ZrO}_2$ ), has also been successfully spheroidized in an RF plasma by Jones *et al.* (31).

Waldie (56, 57), in an attempt to prepare ultrafine powders from coarser materials, obtained spheroids of oxide powders in low-power RF torches. When silica powder (50–72  $\mu\text{m}$ ) was injected into a 2.5-kW, 34-MHz argon plasma at 15 gm/hr, a 15% conversion to ultrafine particles (0.015–0.15  $\mu\text{m}$ ) and coarse spheroids were obtained. Ultrafine powders of barium oxide (50% < 0.1  $\mu\text{m}$ ) and alumina spheroids were also prepared by this technique. When alumina was injected concurrently into a 3.5-kW, 10-MHz argon plasma (57), 48% spheroidization of a 180–250  $\mu\text{m}$  powder was obtained at a feed rate of 36 gm/hr. Waldie obtained better results by use of countercurrent particle flow similar to the technique used by Hartl (26). Up to 26% spheroidization of a 300–500  $\mu\text{m}$  powder was measured for an alumina feed rate of up to 140 gm/hr. It is evident from this work that countercurrent spheroidization can achieve not only higher yields of spheroids but also spheroidization of a larger size range of solid.

Boron powder has been spheroidized by Sullenger *et al.* (48) using an induced argon plasma. When 50–100  $\mu\text{m}$  size range,  $\beta$ -rhombohedral, boron particles were injected into the plasma the main bulk of particles was spheroidized and had improved  $\beta$ -rhombohedral crystallinity. Negligible size reduction of the powder occurred, and microscopic examination of the powder revealed that no true spheres were in fact present, all the spheroids having small flattened faces. The presence of additional well-faceted crystals was also observed. These crystals were classified into four main types: (a) slightly elongated octohedra, (b) hexagonal and dodecagonal right prisms, (c) square right prisms, and (d) truncated tetrahedra. Crystal habits a, c, and d were attributed by Sullenger *et al.* to monocrystals of two known and one unknown form of boron. Type b was thought to be a polycrystalline growth of an unreported form of boron, consisting of hexagonal platelets stacked in an imprecise pattern. The unit cell lattice of 10 Å quoted by Sullenger *et al.* for this dodecagonal boron was 3 times as small as the lattice parameter of dodecagonal boron platelets formed in the hydrogen reduction of boron trichloride in an RF plasma (23).

## C. DECOMPOSITION

Warren and Shimizu (59) injected single oxides and oxide concentrates into a 2-MHz, 7-kW argon plasma. Alumina, silica, and niobium

oxide powders were nearly completely spheroidized. On a second pass through the plasma, the spheroids scarcely changed size or lost weight by vaporization. Mixed oxide concentrates, such as columbite (Fe,Mn) (Cb,Ta)<sub>2</sub>O<sub>5</sub>, pyrochlore CaNb<sub>2</sub>O<sub>8</sub>·Ca(Ti,Th)O<sub>3</sub>, scheelite CaWO<sub>4</sub>, and wolframite (Fe,Mn)WO<sub>4</sub>, were injected into the argon plasma, resulting invariably in plasma extinction even at very low feed rates. Warren and Shimizu also reported that even low concentrations of diatomic gases, such as N<sub>2</sub> and Cl<sub>2</sub>, extinguished the plasma. These findings indicate a very low coupling efficiency of the RF plasma coil and a high degree of mismatching of the impedance in the RF circuit and would, undoubtedly, explain the low tolerance of the plasma to solids.

Huska and Clump (28) investigated the decomposition of molybdenum disulfide in an RF plasma torch. Passage of 0.7 gm/hr of 74- $\mu$ m MoS<sub>2</sub> through a 5-kW argon plasma resulted in 70% conversion of molybdenite to molybdenum. The conversion decreased rapidly, however, when feed rates were increased, and only 30% conversion to molybdenum metal was obtained at 2.5 gm/hr. At feed rates greater than 3 gm/hr MoS<sub>2</sub>, the plasma became radially unstable, probably caused by asymmetric powder injection. Charles *et al.* (17) have recently reported the injection of up to 400 gm/hr of a 50- $\mu$ m powder into an argon plasma without it becoming unstable. Conversions of molybdenite to molybdenum metal of between 60 and 70% were obtained but details of particle size and feed rates were not given.

Several studies have been made of the behavior of oxide powders injected into neutral or reducing RF plasmas. Borgianni *et al.* (6) injected Al<sub>2</sub>O<sub>3</sub>, CuO, NiO, and TiO<sub>2</sub> powders along the axis of a 4-MHz argon plasma run at atmospheric pressure. They measured the extent of decomposition of the powders to lower oxide and metal as a function of the axial distance traveled by different sizes of particles and varying power inputs. For 60- $\mu$ m Al<sub>2</sub>O<sub>3</sub> particles, a maximum conversion to aluminum of 12% was obtained at 20 cm from the injection point. The plasma had a low tolerance for Al<sub>2</sub>O<sub>3</sub> powder, however, and the maximum usable mass flow was 72 gm/hr. The results for CuO, NiO, and TiO<sub>2</sub> are summarized below in Table V.

Borgianni *et al.* assumed that the rate-determining step in the decompositions was heat transfer across the particle boundary layer. They developed an equation of motion for the particle in the plasma with which they were able to explain their experimental results satisfactorily.

Capitelli *et al.* (16) investigated the decomposition of 60- $\mu$ m Al<sub>2</sub>O<sub>3</sub> in argon-N<sub>2</sub> plasmas further, using the same experimental and analytical techniques as did Borgianni *et al.* They observed a decrease in yield

TABLE V  
DECOMPOSITION OF OXIDES IN RADIO-FREQUENCY ARGON PLASMAS<sup>a</sup>

Oxide	Feed particle size ( $\mu\text{m}$ )	Power (kW)	Maximum conversion to metal (%)	Optimum distance from injection point (cm)	Maximum mass flow (gm/hr)
CuO	60	5.5	60	13	28.8
NiO	60	5.5	30	20	—
TiO <sub>2</sub>	60	5.5	20	17.5	—

(Based on O<sub>2</sub> deficiency)

<sup>a</sup> Data from Borgianni *et al.* (6).

of aluminum when nitrogen was added to the plasma. For pure argon, 12% of aluminum was formed 20 cm from the injection point. With 4 and 8% nitrogen-argon plasmas, the maximum conversion to Al metal decreased to 8%, which was attributed to shrinkage of the plasma and shortening of the plasma tail. The enthalpy available in the plasma would also be reduced due to the dissociation energy of nitrogen.

Charles and co-workers (17) obtained more encouraging results with decomposition work in an investigation of extractive metallurgical processing of various minerals in RF plasmas. Both rhodonite ( $\text{MnSiO}_3$ ) and ilmenite ( $\text{FeTiO}_3$ ) were successfully treated in a 37-mm diameter RF torch at feed rates up to 60 gm/hr. Maximum yields of 30 gm/hr of available MnO in the recovered solids were obtained from a 50- $\mu\text{m}$  rhodonite feed at 60 gm/hr feed rate and 15 kW power level.

Manganese oxide-rich solids were found to be present in the cooler regions of the apparatus, whereas SiO-rich solids collected predominantly in the torch itself. A similar quench separation into component-rich products was obtained for ilmenite, where TiO<sub>2</sub>-rich solids collected in the torch and FeO-rich solids in the quench tube. These quench separations were successfully correlated with the free energy of formation of the oxides. Charles *et al.* also processed zircon sand and measured negligible dissociation which they attributed to the high melting point of this mineral. Ferrous sulfide, however, was completely oxidized to Fe<sub>2</sub>O<sub>3</sub> at feed rates of up to 400 gm/hr.

Two methods have recently been patented for the use of RF plasma torches for processing titaniferous and other minerals. Titanium dioxide can be recovered from rutile (9) by passage of the latter at low feed rates (0.1 gm/min) through an argon-oxygen plasma. After 3 hr of operation, titania particles of 0.18–0.3  $\mu\text{m}$  size range could be recovered, the purest samples containing only 0.3% w/w iron impurity as Fe<sub>2</sub>O<sub>3</sub>. In a further development of the preceding technique (10), rutile and

other minerals were processed at higher feed rates (10 gm/min for rutile) by injecting them into the tail of oxygen or chlorine plasmas.

### VIII. Commercial Application of Radio-Frequency Plasmas

In contrast to the study of chemical syntheses in low-pressure, microwave, plasma discharges, the studies of chemical syntheses in atmospheric pressure, thermal plasmas have not given rise to any chemical compound that cannot be prepared by other techniques. The use of thermal plasma discharges does, however, offer a unique source of energized gas available at higher temperatures than normal chemical flames or other, indirect, electric heating techniques.

The philosophy behind the many investigations of chemical syntheses in thermal plasma devices must surely be that the availability of usable gas enthalpy at temperatures up to 10,000°C should permit the shortening of conventional production routes to the bulk chemicals that are prepared by endothermic reactions. This concept is pinpointed, for example, by the production of high surface-area activated silica. The present industrial process, which has been in use for the last 20 years, involves a multistage production route beginning with sand. The sand is first reduced to silicon or silicon carbide and is then chlorinated to silicon tetrachloride. The chloride is then oxidized in an oxyhydrogen flame and the oxide quenched to produce activated silica. Various workers (13-15) have shown that it is feasible to short-circuit this complicated route by evaporating or reducing sand to silicon monoxide in a plasma device and then quenching the monoxide to yield a surface-active silica. A similar chemical reaction in which the plasma could provide a shortened process is the direct formation of pigmentary titanium dioxide from rutile, bypassing the titanium tetrachloride step. This use of plasma devices in chemical synthesis is undoubtedly the most promising commercially, and it is to be expected that future development will be concentrated along these lines.

Radio-frequency plasma, in particular, offers additional advantages over DC arc plasma devices in that, because of the separation of the electrodes from the discharge chamber itself, gases normally corrosive to electrode materials (e.g., chlorine) can be readily processed. Possibly this could extend the application of RF plasma devices into the field of mineral processing, for example, by selective chlorination of rare metals. Contamination of products due to erosion of electrodes when noncorrosive gases are treated is also avoided by use of RF plasma devices and provides an additional advantage over DC devices in the field of ultrapure chemical production. The counteracting disadvantages

that RF plasma efficiencies are usually some 20% lower than DC devices must be taken into account for each individual case, especially when scale-up is considered.

The use of thermal plasma in the chemical processing industries as a production tool has been relatively slow to develop. The last decade saw a rapid development of induction plasma hardware, undoubtedly accelerated by U.S. aerospace activity. For successful economic chemical processing in RF plasma to become a reality, however, scale-up of RF induction plasma to much higher-power levels must first be achieved. Various attempts have been made to attain this goal by operation of high-power torches at lower frequencies, as the capital investment required for high-power, high-frequency plasma generators is prohibitive.

Thorpe and Scammon (52) reported the first successful operation of a high-power, low-frequency induced plasma torch. They operated a 1-MW torch on argon at 450 kHz, producing a plasma of some 10 cm in diameter. Recently, Thorpe (51) reported the successful operation of an induced plasma at the still lower frequencies of 10 and 1 kHz.

The operation of induced plasma devices at line frequency (50 Hz) is the ultimate objective of development work on torch scale-up, and Dundas (19) recently published data predicting operating powers and torch diameters for low-frequency plasma. The expected power requirement for a line frequency-induced plasma torch is circa 15 MW, and the achievement of this will clearly require considerable time and expenditure.

## IX. Conclusions

Although no economic plasma process has yet been developed in which a plasma reactor has either replaced a conventional high-temperature reactor or provided an alternative route to the production of a chemical by a well-established chemical process, this is probably only a matter of time. The commercial success of a plasma chemical process will depend partly on technological but mainly on economic factors. Taking electricity at 1¢ per kWh, the electricity cost of acetylene and boron production on the yields given earlier in this review comes, respectively, to approximately \$250 and \$1200 per ton. Such costs are unacceptable for any but high-cost products. They could be brought down by higher plasma efficiencies and could also drop if cheap electricity becomes available. Although nuclear power stations are unlikely to offer electricity at peak hours at a cost substantially lower than conventional stations, the technology of their operation might make off-peak

electricity available very cheaply and thus make electrochemical processes in general that much more practicable.

On the technological side, a notable gap is the lack of any real understanding of chemical processes in plasmas. The studies reported in this review have been largely exploratory and qualitative and have not been concerned, in detail, with this topic. To a first approximation, the high temperature of a plasma must give rise to a "molecular soup" in which reactant molecules have been partly or wholly dissociated and from which products emerge as a result of sequential reactions in the plasma and the tail gases. What is less clear is whether the products result from a series of chemical equilibria set up as the gases cool, and then frozen at temperatures decreed by thermodynamic considerations, or whether kinetic factors are also involved. In either case, is the important region of the plasma that section of the tail flame where the temperature has dropped to 2000°–2500°K? If it is, then there is the possibility that products and yields can be profoundly influenced by reactants added to the tail flame. Hamblyn (23) has shown that if boron trichloride and hydrogen are added to the tail of an argon plasma, boron is obtained in yields not much lower than those when all the gases pass through the plasma. Furthermore, as the distance between the RF coil and the  $\text{BCl}_3\text{-H}_2$  inlet is increased, the yield also increases, going through a maximum at a distance of 6 cm.

These experiments suggest that the factors affecting the yields from plasma reactors are not always the most obvious ones, and much remains to be learned about the molecular processes that occur. The difficulties involved in the study of kinetics and thermodynamics of chemical reactions in high-temperature plasma tails are formidable, but even a crude understanding might permit a degree of control over plasma reactors that does not at present exist.

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