SOME ASPECTS OF THE FORMATION OF BORON

IN A RADIO - FREQUENCY PLASMA

by

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Stephen M.L. Hamblyn
August 1972
The reduction of boron trichloride to boron by hydrogen in a radio-frequency plasma has been investigated. Published work on chemical synthesis and processing in radio-frequency plasmas has been reviewed and conventional methods of boron preparation from boron halides discussed.

A radio-frequency plasma reactor and ancillary apparatus were developed which could be operated continuously on a $\text{BCl}_3$ feed at power levels up to 30 kW. Boron formed in the plasma reactor was found to be similar to other amorphous borons. It was brown in colour, particle size ($\sim 4 \ \mu$), surface area (12.4 m$^2$/g), and was non-pyrophoric. Purity was approximately 99% with traces of oxygen and nitrogen probably arising from contact with air.

X-ray and electron diffraction photographs of the boron revealed that the particles were microcrystalline and similar to $\beta$-rhombohedral boron. Individual particles were random in shape and consisted mainly of platelets between 200 Å and 7500 Å in diameter. The presence of regular dodecagonal platelets was also observed. These had a unit cell lattice constant of 30 Å, and are believed to be a further modification of known boron structures.

The growth time for a 7000 Å platelet was calculated to be of the order of 2 msec, which is comparable to the residence times of reactants in the plasma reactor.

The ultraviolet emission spectra of various plasmas were examined and an excitation temperature of 20000°K was calculated for a 10 kW argon plasma.
Species detected in the emission spectra of Ar/BCl$_3$/H$_2$ plasmas included B, BCl, BCl$_2$, Cl$_2$, Cl$_2^+$, B$^+$, Ar$^+$, H and BH.

The variation of BCl$_3$ conversion with reactant concentration, residence time and reactant feed configuration was investigated. The reaction was approximately first order with respect to BCl$_3$ and very low order with respect to hydrogen suggesting that the latter acts merely as a scavenger for chlorine produced by plasma-induced dissociation of BCl$_3$. These and other data were discussed in terms of three different types of mechanism. The results could be interpreted partly in terms of a theory in which thermodynamic equilibrium of all species at a certain temperature was approached in the tail of the plasma, and partly in terms of a mechanism involving gaseous ions.
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CHAPTER ONE

INTRODUCTION
The word 'plasma' was first used to describe the phenomenon of electrical discharge in gas by Langmuir in the 1930's. The concept of plasma as a fourth state of matter, however, was put forward as early as 1879 by Sir William Crookes at the time that De la Rue first characterised the properties of electrical discharges (1). By the early 1900's Wilson (2) and Townsend (3) had established that electrical conductivity in gases was caused by ionisation of gas molecules by collisional processes.

Today many physicists consider that 99.9% of the Universe exists in the plasma state with small concentrations of the solid, liquid and gaseous states existing as 'cold' planets. Recently Kulik (4) has postulated that there exists a fifth state of matter which he has called "non-ideal dense plasma". Dense plasma is thought to exist outside the boundaries of particle density and temperature within which the known four states exist (Fig. 1).

The plasma state occurs naturally as the luminous channel of a flash of lightning and in the ionosphere. Since the early pioneer work on the study of electrical discharges, immense efforts have been made by physicists to harness the energy of the solar-type plasma in a terrestrial environment, e.g. the ZETA thermonuclear apparatus at Harwell achieved measured temperatures of $10^6 \, \text{K}$. Chemists and engineers have also endeavoured to use the plasma state either as a technique for producing new chemical compounds or as a more economic route to conventional chemicals. At the present time
only two full-scale chemical processes (5) are reported to be operating continuously (a) Chemische Werke Hüels 8.5 MW process for acetylene and (b) Fabwerke Hoescht 10 MW process for ethylene. However, there are probably many processes at the pilot plant development stage which could be put into full-scale production if commercial factors were favourable. Many excellent reviews have been published (6-18) in the last few years covering the application of discharge devices to chemical synthesis, metallurgical extraction and mineral processing. A considerable number of patents (19-34) have also been granted to various commercial organisations for use of plasma reactors and processes. This indicates a high degree of activity among chemical and mining companies.

A negligible amount of work has been reported on the behaviour of boron compounds in a thermal plasma environment, but much has been done on the preparation of boron compounds such as borides and borohydrides in low pressure discharges and in conventional furnaces up to temperatures of 3000°K. The uses of borides and boride composites as high temperature materials has increased rapidly during the last decade (35). In 1965, the United States Borax Research Corporation initiated a research programme to investigate the behaviour of boron compounds in a plasma discharge. This thesis describes results of research and development on one aspect of the work carried out so far; the production of elemental boron by hydrogen reduction of boron trichloride in a r.f. induced plasma discharge.
CHAPTER TWO

PLASMA AND ITS APPLICATION TO CHEMISTRY
The principal types of plasma devices can be subdivided by the method used to transfer electrical energy to the gas. In the original devices direct current flowed between two electrodes in contact with the discharge gas. This type of device has developed into the arc plasma jet. A second method of generation of plasma in a gas is by induction of energy by oscillating electric or magnetic fields via external electrodes. Examples include radio frequency (1-10 MHz) and microwave (2000 MHz) induced plasma torches, the former being used mainly at high and the latter at low pressure.

2.11 Direct-current discharges

These are best described by their current-voltage characteristic. Fig. 2 shows the variation of arc current in a low pressure gas discharge with increasing voltage between two plate electrodes. At low voltages the Townsend or dark discharge occurs if an external source of electrons is supplied. Current of the order of $10^{-5}$ amps flows and no visible glow is observed. As the applied voltage is increased, a visible, self-sustaining, glow appears between the electrodes and discharge currents rise to the 0.1 amp level. The current is maintained by emission of electrons from the cathode under the bombardment of fast ions. The visible glow between the electrodes for this discharge tube, however, is not continuous. There is a negative glow region near the cathode and then a region of discontinuity called the 'Faraday Dark Space'. After this comes the main region of continuous emission stretching to the anode, which is
called the positive column. This would typically extend 75% of the distance between electrodes. In operation under alternating current supply the glow discharge appears continuous and such discharge tubes containing a few millimeters pressure of inert gas or metal halide are the well known neon-tubes etc. in common use in advertising and lighting. Von Engel & Steenbeck (36) characterised the electrical properties of such glow discharges for various electrode pairs and have derived theories (37) which provide a qualitative basis for design of glow discharge tubes under known conditions of electric field strength, electron temperature and input energy.

As the applied voltage between electrodes is increased (Fig. 2) a third type of discharge is reached, characterised by high currents and decreasing voltages. This is known as the arc discharge or arc plasma. At low gas pressures the arc discharge contains high energy electrons and low energy molecules. As the gas pressure is raised, electron energy is transferred to the gas molecules by elastic and in-elastic collisions which produce increases in kinetic energy and ionisation of the gas molecules, until at atmospheric pressure a condition of approximately equal electron and gas temperatures exists. This condition of the arc is known as the thermal plasma. Fig. 3 shows the distribution of electron and molecular energy or temperature in a plasma arc with increasing total pressure (38). It is possible when the condition of equal electron and gas temperature is satisfied to estimate the degree of ionisation of the arc from Saha's Equation for known values of gas temperature and density (39), (212).
As the arc current between the anode and cathode is further increased, the voltage drop characteristic of the discharge changes. At the levels of current in the type of arc already described, the main voltage drop is in the arc itself, with cathode and anode voltage drops amounting to ~ 20%. At high current loads the voltage drop at the anode increases up to about 60% and in this condition of operation there is considerable energy transfer to the anode surface. This dissipation of energy causes rapid erosion of the anode and the eroded material appears as a partially ionised luminous tail flame. This is the so-called high intensity or Beck arc, first discovered in 1910 (40). The use of the high intensity arc as a technique for chemical and mineral processing was thoroughly investigated in the 1950's and early 60's by Sheer and Korman and co-workers of the Vitro Corporation in the United States and their work (43-60) will be described in more detail in Section 2.35(d). The rapid erosion of the anode material presents a novel way of introducing materials into the arc. The theory of this type of arc discharge has been described by Beck (41) and developed by Finkelnburg (42).

2.12 Induced plasma devices

The second method of plasma generation in general use in chemical and mineral processing studies is the high frequency plasma generator. A plasma discharge can be maintained in a gas stream, flowing through a tube of electrically non-conducting material, by eddy currents induced from an external coil carrying an oscillating current. This mode of energy transfer to the plasma is called inductive
coupling, and electron excitation is due to the effect of an oscillating axial magnetic field. A high frequency plasma can also be maintained by an oscillating electric field between two external ring conductors, by an energy transfer process called capacitive coupling. This type of plasma is often called the electrodeless discharge as the electrodes are remote from the plasma forming gas (see Fig. 4).

Although 0.5-50 MHz energy sources of many kilowatts have been available since the 1930's, the r.f. plasma torch has only recently been developed. With the development of radar techniques during the 2nd World War, energy sources in the range $10^3$-$10^5$ MHz became available, and the investigation of chemical reactions in low pressure microwave discharges commenced (61). This work was further spurred on by the rapid advances made in mass spectrometry, electron spin resonance and other analytical techniques, and the field of microwave discharge chemistry is now well established. McTaggart (8) has reviewed the progress in this field up to 1966.

At the same time that the investigation of microwave discharge processes began, Babat reported (62) that a thermal plasma could be maintained in argon at atmosphere pressure using a radio frequency energy source. Babat discovered that when the pressure of argon in an r.f. discharge was increased from a few torr to 1 atmosphere the discharge changed from a corona-type to a thermal type. Babat's discharge, however, although at some 100 kW power input was in a static environment. It was not until the early 1960's
that Reed (63) developed the radio-frequency plasma discharge in a moving gas stream at atmospheric pressure and theoretical studies of induced plasma were made (64).

The last decade has seen the rapid development of the induction coupled plasma torch, undoubtedly accelerated by U.S. Aerospace activity. Reed's original work on argon plasma at atmospheric pressure triggered a resurgence of interest in plasma chemistry. If successful chemical or mineral processing by r.f. plasma was to become a reality, however, a cheap induced energy source was needed. Various attempts have been made to achieve this by operation at lower frequencies.

Thorpe and Scammon reported the successful operation of a high power, low frequency induced plasma torch (65), and a 1 MWatt torch is now available operating at 450 kHz producing a plasma of some 10 cms in diameter. Recently Thorpe (66) has reported the successful operation of induced plasmas at still lower frequencies of 10 kHz and 1 kHz. The plasma diameters and power inputs for Thorpe's experiments were 14 cm at 130 kW for the 10 kHz torch and 26 cm at 800 kW for the 1 kHz torch respectively. (Reed's original torch was 2.6 cm diameter and operated at 1.5 kW and 4 MHz). Nevertheless these devices are still unacceptably expensive to operate.

The operation of induced plasmas at line frequency is the ultimate objective of development work in this field and Fig. 5 shows data recently presented (67) for the operating powers and torch diameters required for low frequency plasma.
The expected power requirements for line frequency induced plasma operation (68) is circa 15 MW and the achievement of this will clearly require considerable effort and expenditure. Although induced plasma devices are available at process power levels, it still remains for a full scale chemical process to be put on-stream using the induction technique of plasma generation.
2.2 Background to Plasma Chemistry

2.2.1 Introduction

Possibly the earliest investigations of chemical reactions in electric discharges were made by Thenard (69) and de Wilde (70) in the 1870's. They reported that acetylene decomposed readily in an electric discharge leaving a brittle, amorphous and unidentified substance and no gaseous residue. Thirty years elapsed before Losanitsch (71) subjected carbon disulphide vapour to a low pressure discharge and obtained a black substance on the walls of the discharge tube. In 1905 Warburg developed the first ozoniser (72) consisting of a series of point to plate discharge zones contained in a sealed glass tube. Oxygen could be passed through the tube while a potential was applied between the point electrodes and the plate. The ozoniser offered the first means of studying plasma reactions at pressures approaching atmospheric and in 1910 Dewar and Jones (73) also reported the formation of an unstable black deposit when they passed carbon disulphide through the ozoniser. This was later identified as the CS radical (8).

Most of the early work, however, was carried out at low pressures. The results were mostly reported qualitatively as the main interest was in the synthesis of new chemical compounds which could not be made by conventional methods. For example, Stock et al. (74) reported the first preparation of a diboron tetrahalide in a discharge device in 1925.
By 1920 Wood (75) had shown that hydrogen atoms could be produced when hydrogen was introduced to a discharge zone at 0.1-1.0 mm Hg pressure and Bonhoeffer (76) then adopted this technique to study the reactions of hydrogen atoms. In 1933 Rodebusch and Klingelhoeffer (77) reported the use of a high frequency electrodeless discharge as a method of producing atomic chlorine. They obtained up to 20% chlorine atom in a flow system while Schwab and Freiss (78) reported higher yields of atomic chlorine in a discharge tube similar to Wood's original design (75).

The use of both electrode and high frequency discharge devices for chemical synthesis grew rapidly from the 1930's and the field has been subsequently reviewed by Glockler and Lind (79) in 1939 and by both Jolly (80) and McTaggart (8) in the 1960's. The use of arc plasma in chemical synthesis has been reviewed by Landt (15), and Sayce (18) has recently discussed the application of plasma devices to extractive metallurgy. R.F. plasma work on chemical and metallurgical studies has been mentioned in some review articles, the most recent being in 1969 by Ibbeson (11), but no comprehensive or up-to-date review has appeared. This section of this thesis is intended to fill this gap. The review is restricted to high pressure operation of r.f. plasma, low pressure work having been well covered by McTaggart (8).

A survey of preparative work will first be presented, subdivided by the type of chemical reaction attempted. Consideration will then be given to the application of r.f. plasmas to physical heat treatment of powders and extractive processes, and finally theoretical studies on r.f. torch operation, temperature measurement etc. will be summarised.
2.22(a) Thermal decomposition reactions

Kanaan and Margrave (81) investigated the decomposition of carbon tetrachloride in a radio-frequency plasma and reported the formation of low yields of the benzene derivative C$_6$Cl$_6$. Using spectroscopic techniques (82) they also identified free radicals such as CCl, CF and CF$_2$ present in chlorofluorocarbon plasma. They postulated that the C$_6$Cl$_6$ present in the CCl$_4$ decomposition products was formed by polymerisation of reactive species such as CCl$_3$, CCl$_2$ and CCl.

Bequin et al (83) extended this work and investigated the decomposition of CCl$_4$, CCl$_3$F, CCl$_2$F$_2$, CClF$_3$ and CF$_4$ in a 10 kW argon plasma. They also obtained benzene derivatives such as C$_6$Cl$_6$, C$_6$Cl$_5$F, C$_6$Cl$_4$F$_2$ and C$_6$Cl$_2$F$_4$ in low yields, together with a variety of chlorofluoro-ethane and ethylene derivatives. They reported, however, that the majority of the decomposition products of reactants used were chlorine, fluorine and carbon.

Bequin et al also identified the molecule CCl$_3$-CClF$_2$ as one of the decomposition products of CClF$_3$, and postulated that as there was no CCl$_3$ present in the reactant, the CCl$_3$-CClF$_2$ must have been formed by recombination of CCl$_3$ already formed by recombination of simpler radicals. They suggested the following mechanism for CCl$_3$ formation:

\[ \text{C} + \text{Cl} \rightarrow \text{CCl} \]
\[ \text{CCl} + \text{Cl} \rightarrow \text{CCl}_2 \]
\[ \text{CCl}_2 + \text{Cl} \rightarrow \text{CCl}_3 \]

The radical CClF$_2$ could have formed by thermal decomposition of CClF$_3$ and further reaction could occur to the ethane derivative:
$\text{CCl}_3 + \text{CClF}_2 \longrightarrow \text{CCl}_3 - \text{CClF}_2$

Bequin et al stated that all identified products could be accounted for by such radical recombination reactions. They postulated that as no acetylene derivatives were identified as products it was most probable that the benzene derivatives were formed by trimerisation of acetylenic compounds such as $\text{C}_2\text{Cl}_2$, $\text{C}_2\text{F}_2$ and $\text{C}_2\text{FCl}$.

Grosse et al (99) investigated the decomposition of methane in a radiofrequency induced helium plasma operating at power levels up to 0.5 kW. They obtained high yields of carbon and hydrogen at high methane concentration, and up to 30% conversion (based on carbon content) to acetylene at low methane concentration. They extrapolated their results and predicted that a 100% conversion to acetylene would require a He/CH$_4$ ratio of 26/1. They concluded that although their radio-frequency plasma device was useful for acetylene formation, they obtained better results using a d.c. plasma jet.

Teresawa et al. (84) studied the thermal decomposition of methane to give acetylene in an r.f. induced plasma by varying argon and methane flowrates and torch dimensions. They observed that the methane decomposed completely giving 85% $\text{C}_2\text{H}_2$ in the products in a plasma torch 21 cm diameter and 13 cm long. When a 30 cm diameter torch was used not all the CH$_4$ reacted and the yield of acetylene was considerably lower, presumably due to lower reaction rates formed by a decrease in electron density in the larger torch volume.
Huska and Clump (85) investigated the decomposition of molybdenum disulphide fed as solid particles into a jet suction stabilised plasma torch. Passage of 0.7 gms/hour of 74 \mu powder through an argon plasma at 5 kW resulted in 70\% conversion of molybdenite to molybdenum. However, the conversion decreased rapidly with increasing feed rate until at 2.5 g/hour only 30\% molybdenum metal was obtained and at feed rates > 3.0 g/hour, the plasma became radially unstable, probably due to radial assymetry in the plasma gas stream caused by a high powder injection gas velocity. Recently, however, Charles et al. (86) have reported the injection of up to 400 g/hour of a 50 \mu powder into an argon plasma without it becoming unstable. Conversions of molybdenite to molybdenum metal of 60-70\% were obtained but details of the particle size and feed rates were not given.

There have been several studies of the behaviour of oxide powders injected into r.f. plasmas, in neutral or reducing atmospheres. Borgianni et al. (87) injected Al_{2}O_{3}, CuO, NiO and TiO_{2} powders along the axis of 4 MHz argon plasma at 1 atmosphere pressure. They measured the extent of decomposition of the powders, to lower oxides and metal, as a function of the distance travelled by different sizes of particles at varying power inputs. For 60 \mu Al_{2}O_{3} particles a maximum conversion of aluminium of 12\% was reached at 20 cm from the injection point in a 5.5 kW argon plasma. The plasma had a low tolerance for Al_{2}O_{3} powder, however, and the maximum mass flow which could be used was 72 g/hr. The results for CuO, NiO and TiO_{2} are summarised below in Table 1:
TABLE 1
Decomposition of oxides in r.f. argon plasmas (87)

<table>
<thead>
<tr>
<th>Oxide</th>
<th>Feed particle size, µ</th>
<th>Power, kW</th>
<th>Maximum conversion to metal %</th>
<th>Optimum distance from injection point</th>
<th>Max. mass flow g/hr.</th>
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<tr>
<td>CuO</td>
<td>60</td>
<td>5.5</td>
<td>60</td>
<td>13 cm</td>
<td>28.8</td>
</tr>
<tr>
<td>NiO</td>
<td>60</td>
<td>5.5</td>
<td>30</td>
<td>20 cm</td>
<td>-</td>
</tr>
<tr>
<td>TiO₂</td>
<td>60</td>
<td>5.5</td>
<td>20 (based on O₂ deficiency)</td>
<td>17.5 cm</td>
<td>-</td>
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</tbody>
</table>

Borgianni et al. assumed that the rate-determining step in the decompositions was heat transfer across the particle boundary layer. An equation of motion for the particle was determined and they concluded that the experimental results could be satisfactorily explained using the above assumption.

Capitelli et al. (88) further investigated the decomposition of 60 µ Al₂O₃ particles in argon-N₂ plasmas, using identical experimental and analytical techniques to Borgianni et al. (87). They observed a decrease in yield of aluminium when nitrogen was added to the argon plasma. For pure argon, a maximum of 12% aluminium was formed 20 cm from the injection point. With 4% and 8% nitrogen in argon plasmas the maximum conversion decreased to 8% because of shrinkage of the plasma and shortening of the luminous tail flame.

Rains and Kadlec (89) injected Al₂O₃ particles into a vortex-stabilised argon plasma (pure and with H₂, CH₄ and CO added) and observed that conversions to aluminium were dependent on parameters such as particle size, power input,
reducing gas and mass flow rate. For argon plasmas at 5 kW a maximum conversion of 30% was obtained at a feed rate of 6 g/min. As the feed rate was increased to 36 g/min the conversion dropped rapidly to 2%. Similar conversions and behaviour were observed when hydrogen was added to the plasma. However, when carbon monoxide or methane was added to the plasma, conversions of twice and four times that with pure argon were obtained. It was postulated that this was caused by the presence of carbon vapour in the discharge which would have a higher affinity for oxygen than hydrogen.

Jordan et al. (90) have obtained a carbon black of high specific surface (90 m²/g) by decomposition of hydrocarbon feeds in argon induced plasmas. Butene-1 was injected into the plasma at the rate of 0.007 m³/hr and after 1 hour of operation, 15 gms of carbon black was collected. High surface area carbon black has also been produced by vaporisation of a carbon feed with subsequent quenching in a halogen rich environment (91).

2.22(b) Hydrogen reductions

As discussed above Rains and Kadlec (89) have investigated the hydrogen reduction of Al₂O₃ in an r.f. plasma, but observed that there was little improvement in using Ar + H₂ as opposed to pure argon.

Miller and Ayen (92) investigated the hydrogen reduction of titanium tetrachloride in a water-cooled radio-frequency plasma torch. They obtained conversions of TiCl₄ to TiCl₃ of between 60% and 80%, at feed rates of 1.5 gm/min of TiCl₄. They observed that the conversions were independent of power
input up to 5 kW, TiCl$_4$ feed rate and also independent of
H$_2$/TiCl$_4$ ratio when greater than stoichiometry. They
injected the TiCl$_4$ vapour into an argon plasma but found
that the plasma could only tolerate up to 1 mole % TiCl$_4$
in argon at 10 kW due to low coupling efficiency.

Miller and Ayen therefore measured the coupling
efficiency of their r.f. circuit to various plasma gas
mixtures and found that with up to 2 mole % of hydrogen
in argon the efficiency was unaffected and was maintained
at 60-70%. However, when TiCl$_4$ was added to the plasma
argon the efficiency decreased rapidly from 60% to < 40%
at 0.15 mole % TiCl$_4$ in argon. They also investigated
the effect of various quench techniques on argon/TiCl$_4$
plasmas without H$_2$ in an attempt to obtain lower titanium
halides. No significant solid products were obtained,
however, under any of these conditions.

Vurzel and Polak (93) have carried out extensive
kinetic studies of the reduction of silicon tetrachloride
to silicon in plasma devices. They initially decomposed
SiCl$_4$ to SiCl$_3$ in an adiabatic compression-expansion device
and then completed the reduction in a plasma.

They claimed that the decomposition of SiCl$_4$ to silicon
proceeded by a two-stage mechanism of chlorine atom removal:

(1) SiCl$_4$ $\rightarrow$ SiCl$_3$ $\rightarrow$ SiCl$_2$  fast
(2) SiCl$_2$ $\rightarrow$ SiCl $\rightarrow$ Si  slow

They postulated that the second stage was rate controlling
and determined the rate constants for both stages in
the decomposition:
\[ k_1 = 5 \times 10^8 \exp(-88,000 \pm 5000/RT) \text{sec}^{-1} \]
\[ k_2 = 5 \times 10^7 \exp(-126,000 \pm 10,000/RT) \text{sec}^{-1} \]

From additional calculations of the thermodynamics of the decomposition of SiCl$_4$ to silicon, they predicted that the decomposition would be favoured by reducing conditions and confirmed this experimentally, obtaining high purity silicon using an r.f. plasma torch.

2.22(c) Nitrogen fixation

Timmins and Ammann (94) have recently reviewed the application of plasma discharge devices 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 d.c. devices, either arc torches or glow discharges. There have been, however, several investigations of nitrogen fixation reactions in radio-frequency plasmas and some patents have been granted protecting such processes (19, 95-102).

Nitric oxide studies

Table II summarises the published work carried out on nitric oxide preparation in radio-frequency plasmas. Two important investigations using d.c. devices have been included for comparison.

Bequin et al. (98) 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 cold traps. At power inputs to the plasma of 9-10 kW, conversions to nitric oxide of up to 2.12% were obtained. This can be seen, from Table II, to be similar to the conversions
obtained by Grosse et al. (99) when they quenched a stream of plasma nitrogen from a d.c. plasma jet with an oxygen stream.

Stokes et al. (100) reported similar conversions of oxygen in air to nitrogen oxides in a low-pressure radio-frequency plasma. After a run time of 2.5 hrs, 0.4 cc of material was collected in liquid nitrogen traps, which on analysis showed a 2% conversion of oxygen to nitrogen dioxide.

La Roche (101) demonstrated the beneficial effect of quenching, by showing that in two otherwise similar experiments, the yield of nitric oxide increased from 2% to 4%. Conversions of oxygen to nitric oxide of up to 17% by use of a capacitatively coupled r.f. torch are claimed in a British patent (19).

Timmins and Ammann (94) have reported still higher conversions of oxygen and yields of nitric oxide by the use of a d.c. 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 stabilised in this device than with the conventional plasma jet. By operation of this torch in air at gas enthalpies greater than 270 cal/g and careful control of the gas quenching, they obtained up to 7% nitric oxide in the exit gas. This amounts to 30% conversion of oxygen to nitric oxide.

It would appear from these series of investigations of nitric oxide production that, although reasonable conversions of oxygen to nitric oxide can be obtained in conditions of
excess nitrogen, the final concentrations and production rates of nitric oxide are low. The use of higher power and higher surface area plasmas combined with controlled quenching would appear to offer the most promise for a successful commercial process.

TABLE II
Summary of nitric oxide work r.f. and d.c. plasma.

<table>
<thead>
<tr>
<th>Plasma device</th>
<th>Reactants</th>
<th>Feed rates</th>
<th>Power (kW)</th>
<th>% Conv. of $O_2 \rightarrow NO$</th>
<th>% NO in product</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>5-7 MHz r.f. (atmos. press)</td>
<td>$N_2 + O_2$</td>
<td>$N_2$ 17.7 $O_2$ 14.3 (l/min)</td>
<td>10</td>
<td>2.12</td>
<td></td>
<td>(98)</td>
</tr>
<tr>
<td>d.c. plasma jet</td>
<td>$N_2 + O_2$</td>
<td>5.5 5.5 (l/min)</td>
<td>15</td>
<td>2.03</td>
<td></td>
<td>(99)</td>
</tr>
<tr>
<td>27.5 MHz r.f. plasma</td>
<td>Air</td>
<td>0.1 (l/m) 0.3</td>
<td></td>
<td>2.0</td>
<td></td>
<td>(100)</td>
</tr>
<tr>
<td>110 mm Hg pressure</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>r.f. plasma</td>
<td>Air</td>
<td>0.1 (l/m) 0.3</td>
<td></td>
<td>20.0</td>
<td>4</td>
<td>(101)</td>
</tr>
<tr>
<td>with quench</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>without quench</td>
<td></td>
<td></td>
<td></td>
<td>10.0</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>r.f. plasma</td>
<td>Air</td>
<td>0.5 (l/m) 10 (l/m)</td>
<td>90.0</td>
<td>17</td>
<td>(19)</td>
<td></td>
</tr>
<tr>
<td>(1-2 atmos.)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>d.c. constricted arc</td>
<td>Air</td>
<td>$0.43 \times 10^{-4}$ (lb/sec)</td>
<td>5.2</td>
<td>6</td>
<td>(94)</td>
<td></td>
</tr>
</tbody>
</table>

Hydrogen cyanide and hydrazine studies

There have been two recent investigations of hydrogen cyanide preparation in radio-frequency plasma torches. In one investigation, carried out at atmospheric pressure in a 1.5 kW nitrogen plasma (100), conversions of injected methane to HCN of up to 35% were obtained, with the additional formation of acetylene. The second investigation (102) was carried out mainly at pressures below 460 torr.
Passage of \( \text{N}_2 \) and \( \text{CH}_4 \) mixtures through 3.5 kW argon plasmas produced conversions of \( \text{N}_2 \) to HCN of up to 70% at \( \text{CH}_4/\text{N}_2 \) ratios greater than 2:1. These results were in good agreement with equilibrium thermodynamic calculations.

The preparation of HCN from \( \text{CH}_4 \) and \( \text{N}_2 \) in a capacitively coupled r.f. plasma was also described by Jackson & Bloom (19). Molar percents of 0.22\% HCN in the exit gases were obtained when \( \text{CH}_4 \) was added to the tail of a nitrogen plasma. The same workers claim the successful preparation of hydrazine in this r.f. plasma torch at atmospheric pressure. Ammonia and nitrogen mixed in various configurations and flow rates produced a maximum of 0.02 mole \% \( \text{N}_2\text{H}_4 \) in the product gas stream. This is slightly better in terms of the mass of hydrazine produced than other work involving low pressure glow discharges (103). A cheap route to hydrazine could be of great importance in the development of viable fuel cells.

2.22(d) Preparation of refractory materials

Oxides

Barry et al. (104) injected vapour mixtures of chromium and aluminium chlorides, and chromium and titanium chlorides into r.f. oxygen plasmas and obtained the respective mixtures of oxides.

Audsley and Bayliss (105) injected \( \text{SiCl}_4 \) vapour into the tail of an oxygen plasma and obtained 99\% oxidation to \( \text{SiO}_2 \). Injection of \( \text{SiCl}_4 \) directly into the \( \text{O}_2 \) plasma caused extinction in each of the four different torches tried. They concluded, however, that > 99\% oxidation of \( \text{SiCl}_4 \) to
SiO\textsubscript{2} could be obtained by tail feeding. The rate was limited only by kinetics and they achieved a maximum feed rate of 67 g/min SiCl\textsubscript{4}.

Kulagin et al. oxidised silicon powder to SiO by passing mixtures of SiO\textsubscript{2} and Si through an r.f. plasma (106).

**Carbides and nitrides**

A process for the formation of sub-pigmentary silicon carbide powder (0.5 \( \mu \)) has been described (25). Silica powder (44-150 \( \mu \)) was injected into an argon + methane plasma, maintained by a 10 KW induction r.f. coil. Feed rates of up to 1.5 g/min silica were quoted yielding a high conversion of micron-sized SiC powder. An interesting feature of the plasma torch used in this work was a porous plasma-containing wall through which hydrogen was passed to prevent deposition of carbon, and to increase the plasma enthalpy. Also the r.f. coil had a reverse turn at the lower end to magnetically confine the plasma tail.

The nitridations of silicon, magnesium and aluminium powders in a 2 KW, 37 MHz argon/N\textsubscript{2} plasma have been attempted by Fletcher et al. (107). Virtually no magnesium or aluminium nitrides were detected but the authors considered that a product had been formed and rapidly destroyed by atmospheric hydrolysis. 7% nitridation of silicon metal was obtained, however, with 14% nitrogen in argon plasmas. Another r.f. plasma process for the nitridation of metals or mixtures of metals has been described (33) and the results are summarised in Table III. The silicon nitride produced was described as having an opacity and brightness similar to
aluminium silicate when evaluated as a filler and extender in paper. The titanium nitride powder was reported to be in the form of 0.05-0.4\(\mu\) spherical particles. This could be possibly due to the use of a relatively low quench rate, allowing the formation of a liquid TiN phase.

**TABLE III**

**Preparation of Si\(_2\)N\(_4\) and TiN (33)**

<table>
<thead>
<tr>
<th>R.F. Plasma gas</th>
<th>Flowrate to plasma</th>
<th>(\text{NH}_3) Feed rate</th>
<th>Power KW</th>
<th>Conv. to product</th>
<th>Surface area (\text{m}^2/\text{g}) (particle size (\mu))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. SiCl(_4)</td>
<td>0.5 mole/min</td>
<td>0.65 mole/min</td>
<td>36</td>
<td>65% Si(_3)N(_4)</td>
<td>30.5 (\text{m}^2/\text{g})</td>
</tr>
<tr>
<td>2. Ar+SiCl(_4)</td>
<td>25, 0.47 l/min</td>
<td>0.69 mole/min</td>
<td>26</td>
<td>67% Si(_3)N(_4)</td>
<td>47.5 (\text{m}^2/\text{g})</td>
</tr>
<tr>
<td>3. Argon probe TiCl(_4)</td>
<td>80 l/min, 0.25 mole/min</td>
<td>0.5 l/min</td>
<td>26.5</td>
<td>70% TiN</td>
<td>0.05-0.4(\mu) (spherical particles)</td>
</tr>
</tbody>
</table>

2.23 Heat treatment and extractive processes in r.f. plasmas

By injection of refractory powders through r.f. discharges it is possible to heat treat the particles. Decomposition, vaporisation, melting or surface modification of particles can be achieved depending on the physical properties of the material, particle residence times, particle surface area and the enthalpy available in the plasma. Thermal decomposition of oxides in r.f. plasmas has already been discussed in Section 2.22. It is worthy of note, however, that theoretical equations of particle motion and heat transfer to particle surfaces have been developed (87, 88).
Reed (108) has grown crystals in a plasma torch by injecting powders at high velocity through atmospheric pressure r.f. plasmas and depositing the molten powder on a boule in the tail flame. A sapphire polycrystal, some 30mm long and 10mm diameter, was grown from sapphire powder in a pure argon plasma. Zirconium oxide and niobium crystals were also grown in a 50% oxygen in argon and 15% helium and argon plasmas respectively. Reed postulated that the correct particle size range of the powder was crucial for successful crystal growth. Powders which were too fine vaporised and those which were too coarse led to surface bubbling effects on the crystal.

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

Hedger and Hall (109) were first to study the spheroidisation of metal and metal oxide powders with the r.f. plasma. When 100-150 μ powders were injected into an argon plasma at rates of up to 5 g/min, yields of 50-70% spheroids were measured for Cr, Mo, Ta, W, Al₂O₃ and several uranium compounds, the remaining material being random-shaped lumps. Magnesia powder was also spheroidised in a 20% oxygen plasma. No obvious correlation was observed between the yield of
spheroids and the melting points of the parent materials. This was thought to be due to ejection of particles from the plasma which was observed photographically. The ejection could have been caused by magnetic or viscous drag effects, and could result in a percentage of particles failing to go through the plasma, the proportion involved varying unpredictably with the material. Plutonium dioxide, alone and mixed with other oxides (such as UO₂, ThO₂ and ZrO₂), has also been successful spheroidised in an r.f. plasma (110).

Waldie, in an attempt to make ultra-fine powders from coarser materials (111, 112), obtained spheroids of oxide powders in low power r.f. plasma torches. When silica powder (50-72 μ) was injected into a 2.5 KW, 34 MHz plasma at 15 g/hour, a 15% conversion to ultrafine particles (0.015-0.15 μ) and some coarse spheroids were obtained. He also prepared ultrafine powders of barium oxide (50% wt < 0.1 μ) and alumina spheroids.

When crushed alumina was injected concurrently into a 3.5 KW, 10 MHz argon plasma (112) 48% spheroidisation of 180-250 μ powder was obtained at a 36 g/hr feed rate. He obtained better results by counter current particle flow with the gas flowing up through the plasma and the particles dropping downwards. Up to 26% spheroidisation of a 300-500 μ powder was measured for alumina feed rates up to 140 g/hr. It is evident that counter current spheroidisation achieved not only higher yields of spheroids but also spheroidisation of a larger size range.
Boron powder has been spheroidised by use of an induced argon plasma (113). When 50-100 μ β-rhombohedral boron powder was injected into the argon plasma, the main bulk of particles were apparently spheroidised and had better defined β-rhombohedral crystallinity. Negligible size reduction occurred and on closer examination revealed that no true spheres were present, all the spheroids having small flattened faces. The presence of a small number of well-faceted crystals was also observed. These crystals fell into 4 main habits:

(i) slightly elongated octahedra
(ii) hexagonal and dodecagonal right prisms
(iii) square right prisms
(iv) truncated tetrahedra.

Crystal habits (i), (iii) and (iv) were attributed to monocrystals of two known and one unknown form of boron. The fourth habit (hexagonal and dodecagonal right prisms) was thought to be a polycrystalline growth of an unreported form of boron, apparently consisting of many hexagonal platelets stacked in imprecise pattern.

Warren and Shimizu (114) injected single oxides and oxide concentrates into a 2 MHz, 7 KW argon plasma. Alumina, silica and niobium oxide powders were nearly completely spheroidised. On a second pass through the plasma, the particles scarcely changed size or lost weight by vaporisation. Mixed oxide concentrates such as columbite (Fe,Mn)(CbTa)₂O₅, pyrochlore CaNb₂O₆·Ca(TiTh)O₃, scheelite CaWO₄ and wolframite (FeMn)WO₄ were injected into the plasma and invariably extinguished the plasma even at very low
feed rates. The same workers reported that even low concentrations of diatomic gases such as \( N_2, Cl_2 \) extinguished the plasma torch. This very low coupling efficiency in the presence of a diatomic load indicates a high degree of mismatching with the impedance of the r.f. circuit and is the probable explanation for the low tolerance of the plasma to the presence of solids.

Charles et al. (86) obtained more encouraging results in an investigation of the extractive metallurgical processing of various minerals in r.f. plasmas. Both rhodonite (\( MnSiO_3 \)) and ilmenite (\( FeTiO_3 \)) were successfully handled in a 37 mm diameter plasma torch at feed rates up to 30 g/hr without plasma extinction. Maximum yields of 60 g/hr (equivalent to lowest conversion) of available MnO in the recovered solids were obtained from a 50 g rhodonite feed at 30 g/hr.

MnO-rich solids were found to be present in the cooler regions of the apparatus; while SiO\(_2\)-rich solids predominantly collected in the torch itself. A similar quench separation into component-rich products was obtained for ilmenite, where TiO\(_2\)-rich solids collected in the torch and FeO-rich in the quench tube. These quench separations were successfully correlated with free energy of formation of the oxides. Charles et al. also processed zircon sand and measured negligible dissociation, which was attributed to the higher melting point of this mineral. Ferrous sulphide, however, was successfully oxidised to \( Fe_2O_3 \) in argon/oxygen plasmas. Two patents have been recently published for the use of r.f. plasma torches for processing titaniferous and other minerals.
Titanium dioxide can be recovered from rutile (23) by passage of the latter at low feed rates (0.1 g/min) through an argon-oxygen plasma. After 3 hours operation 0.18-0.3 \( \mu \) titania particles were recovered, the purest samples containing 0.3\% w/w iron impurity as \( \text{Fe}_2\text{O}_3 \). In a development of the above work (23) rutile and other minerals were processed at higher feed rates in the tail region of oxygen or chlorine plasmas. In most cases high degrees of vaporisation were claimed, although products were usually spheroidised.

2.24 Theoretical studies in r.f. plasmas

2.24(a) Design and operation studies

The operating characteristics of radio-frequency plasma torches were first described by Reed (63). Marynowskii and Monroe (115) carried out an extensive study of the controlling operating parameters and operating limits of an air-cooled r.f. torch. They also compared r.f. and d.c. plasma torches for suitability for various applications such as crystal growing, spheroidisation and chemical synthesis.

Gray et al. (116) investigated the performance of various r.f. torch designs as gas heaters. The efficiency of different composition plasmas as convective heaters was determined. Argon attained a mean temperature of 700°C, while air reached 2500°C under similar operating conditions. These mean temperatures were based on a calculation of the ratio of energy input to mass of gas flowing, and should not be confused with spectroscopically determined temperature profiles (see Section 2.24(b) below). From energy transfer considerations for air plasmas Gray et al. postulated that only a small fraction (\( \sim 6\% \)) of any gas actually passes
through the plasma, the remainder merely acting as a containment wall.

Armstrong and Ranz (117) developed a mathematical design model for inductively-coupled plasmas, taking into account induced energy transfer to the plasma and radiative, convective and conductive heat losses from the plasma. The model was verified experimentally by use of a 15-28 MHz plasma of 0.8-1.6 cm diameter.

Mironer and Hushfar (64) carried out a thorough mathematical analysis of the energy addition processes to high frequency plasma, making use of electrodynamic, fluid-mechanic and thermodynamic considerations. Dundas (67) has recently extended these calculations to predict the operating requirements for low frequency (<1000 Hz) plasma. (see Fig. 5).

Thorpe has studied the operation of pure hydrogen r.f. plasmas. A maximum of 70% H₂ in argon was achieved in a 4 MHz, 60 KW plasma (118). Pure H₂ heating was successfully achieved at 4 MHz by increase of the input energy to 100 KW (65).

2.24(b) Temperature measurement of r.f. plasmas

The most commonly employed methods for measuring electron and/or gas temperatures in plasmas consist of probe techniques, microwave or optical interferometry and emission spectroscopy.

Probe techniques are of little use at the high densities and temperatures to be expected in the thermal plasma environment, and apart from the difficulty in obtaining a material to withstand the extreme temperatures, the probe itself has
a disturbing influence on the local equilibrium of the system. Although microwave interferometry does not disturb the system, it is extremely difficult to propagate a microwave signal through the high electron densities which exist in thermal plasmas ($>10^{16} \text{ cm}^{-3}$) without expensive equipment. Even if a signal could be propagated, the fact that the plasma discharge is of the same magnitude as the microwave wavelength could invalidate the data obtained. Optical interferometry cannot be employed in a r.f. plasma as the interferometric pattern produced by the plasma would be overshadowed by the patterns produced by the glass and water sheaths which surround the plasma. For these reasons, emission spectroscopy is usually adopted as the most useful diagnostic tool for temperature measurement of r.f. plasmas.

Reed (63) calculated the temperature profile of a radio-frequency argon plasma from spectroscopic measurements of the relative intensity of the argon $1s^5 - 2p^6$ line at 7635 Å. He measured the relative intensity ($I_{r}$) of this line at various axial and radial positions within the discharge, and by mathematical treatment of these intensities by a method developed by Fowler & Milne (119), he calculated that a peak temperature of $16500^0\text{K}$ occurred along the axis of the plasma at 1.6KW input power. The validity of this and other techniques of plasma temperature measurement is based on the assumption, however, that local thermodynamic equilibrium LTE is attained in the plasma. Under the conditions of LTE a Maxwell distribution of energies can be assumed and the relative populations of the
chosen energy levels is related to temperature by the following Boltzmann equation:

\[
\ln \left( \frac{I_r}{\sqrt[\nu]{A_{nm} g_n}} \right) = -\frac{E_n}{k T_e} + C \quad \cdots \cdots (1)
\]

where

- \( I_r \) = relative intensity of spectral line (erg s\(^{-1}\) cm\(^{-2}\) sterad\(^{-1}\))
- \( \nu \) = frequency of spectral line (s\(^{-1}\))
- \( g_n \) = statistical weight in the upper energy level
- \( A_{nm} \) = transition probability for spontaneous emission from upper state \( n \rightarrow \) state \( m \).
- \( E_n \) = energy of upper state
- \( k \) = Boltzmann constant
- \( T_e \) = excitation temperature (K)

The temperature \( T_e \) at any position can therefore be determined from the slope of a graph of \( \ln \left( \frac{I_r}{\sqrt[\nu]{A_{nm} g_n}} \right) \) vs. \(-\frac{E_n}{k T_e}\).

By application of the above technique to the \( 3p^5 4s - 3p^5 4p \) and \( 3p^5 4s - 3p^5 5p \) groups of argon lines, Johnston (120) measured an off-axis peak temperature of \( 9500^\circ K \) for an argon plasma at 6 KW power input. A similar off-axis peak temperature of \( 9600^\circ K \) has subsequently been obtained by Russian workers (121), and Johnston has also obtained similar results by use of a line reversal technique (122). An off-axis peak temperature in an r.f. plasma could be explained by the mechanism of energy transfer to the plasma from an external electrode which could produce a toroidal energy distribution in the plasma. However, this result is clearly in disagreement with the result obtained by use of the Fowler-Milne method. Johnston has postulated that the latter method is only applicable when two different ionisation stages of the same element are present in the plasma (120).
2.3 Boron Chemistry in electrically energised systems

2.3.1 Introduction

Electrical energy has played a vital role in the efforts carried out to extract the element boron from its naturally-occurring compounds. Indeed, it was by the "electrization of boracic acid" that the English chemist, Davy, in 1807 first prepared boron as a dark-coloured combustible material. One year later, both Davy and the French chemists, Gay Lussac and Thenard (123), simultaneously announced that a similar substance could be obtained by reacting boric acid with potassium. The products they obtained probably contained at most 50% boron (124) and nearly 100 years passed before Moissan prepared samples containing over 80% boron, by reduction of boric oxide with magnesium (125).

In 1909, Weintraub passed successive alternating current arcs between a pair of water-cooled copper electrodes in a low pressure atmosphere of BCl₃ and H₂ (126). Solids deposited on the electrodes and accumulated to give fused beads of blackish material, which analysed at 99% boron. This was probably the first pure specimen of boron to be prepared. In the same year Pring and Fielding (127) experimented with the deposition of boron on heated surfaces. They passed mixtures of BCl₃ and H₂ at atmosphere pressure over an electrically-heated carbon rod. At rod temperatures between 1500-1750°C they obtained boron deposition and between 1750°C and 2150°C B₆C deposits were formed. Above 2200°C they reported that both free boron and B₆C were deposited like soot on the electrodes holding the carbon rod. Similar results were obtained at lower pressures (e.g. 0.5 atm).
In 1910, Besson and Fournier (128) treated BCl$_3$ with H$_2$ in an electric discharge and obtained pure boron, confirming Weintraub's earlier results. Weintraub then extended his work to other metals and patents were granted to him in the three years following (129-131). In 1917, Briscoe (132) reported the formation of a transparent pale-yellow substance when he subjected a BCl$_3$/H$_2$ mixture to a silent discharge at ambient temperature. This material had a B:Cl ratio of less than 1:3 and was possibly the first preparation of boron sub-chloride.

In 1918, Kroll obtained a pure boron sample by reducing BCl$_3$ with H$_2$ in a high voltage arc (133). He obtained the boron as a fine amorphous powder. Parravano and Mazzetti further investigated the deposition of boron on heated substrates, and in 1923 reported (134) the formation of a boron layer when a BCl$_3$/H$_2$ mixture was passed over an iron rod at 900°C. They also found that boron had diffused into the outer surfaces of the rod and had formed an iron/boron alloy.

In 1925 Stock et al. (74) reported the formation of diboron tetrachloride as a by-product in a low pressure arc between zinc electrodes immersed in liquid BCl$_3$. Yields of less than 1% B$_2$Cl$_4$ were obtained and it was contaminated with 12% silicon tetrachloride, but a substantial yield of elemental boron was obtained.

Since 1925 the use of electrical techniques for preparing boron compounds has become widespread. The experiments can be classified by the methods of initiation of reactions. These are:
1. Initiation at the electrodes in fused salt electrolysis.

2. Initiation at the surface of an electrically heated substrate.

3. Initiation by electrical discharges and plasmas.

2.32 Fused salt electrolysis

Method 1 was first used by Kahlenberg (135) in 1925. He claimed to have obtained 100% boron by electrolysis of a $\text{B}_2\text{O}_3$-$\text{K}_2\text{O}$-$\text{KCl}$ melt. Considerable progress has subsequently been made in electrolytic preparations of boron from various combinations of fused salts (such as $\text{B}_2\text{O}_3$, $\text{KF}$, $\text{KCl}$, $\text{KBF}_4$), the most recently reported being a $\text{B}_4\text{C}$-$\text{KCl}$-$\text{KBF}_4$-$\text{NaCl}$ melt (136). This method is used commercially to prepare isotopically enriched boron. This and related work has been excellently reviewed by Newkirk (124) and Bower (137) and discussion of it is beyond the scope of this thesis.

2.33 Reduction of boron halides at heated surfaces

The thermal decomposition of boron tribromide and triiodide and the hydrogen reduction of boron trichloride have been studied in order to determine the parameters controlling boron deposition on the surfaces of electrically-heated substrates. This last is now a well established method of manufacturing boron fibres, which are used to strengthen matrices of metals such as aluminium and magnesium. Table IV summarises the more important results of investigations carried out since the 1930's when Van Arkel (138) successfully decomposed $\text{BBr}_3$ and $\text{BI}_3$ on tungsten wires which were heated electrically to temperatures between 1300-1400°C. Mercury or granulated tin
<table>
<thead>
<tr>
<th>Reactants</th>
<th>Substrate</th>
<th>Substrate Temperature °C</th>
<th>Yield of Product</th>
<th>Comments</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1) BBr₃, BI₃</td>
<td>Tungsten wire</td>
<td>1400</td>
<td>Boron</td>
<td>Hg or Sn to absorb chlorine</td>
<td>138</td>
</tr>
<tr>
<td>2) BCl₃ + H₂</td>
<td>6 graphite rods (2&quot; dia x 4&quot; long)</td>
<td>1400</td>
<td>1 lb/hr Boron at 70% conv. or 40% conv., pure B</td>
<td>Crystalline deposit</td>
<td>139</td>
</tr>
<tr>
<td>3) BCl₃ + H₂</td>
<td>Graphite with B₄C or SiC coating</td>
<td>1000-1600</td>
<td>95-99% purity boron</td>
<td>-</td>
<td>140</td>
</tr>
<tr>
<td>4) BBr₃ + H₂</td>
<td>Tantalum filament</td>
<td>1450</td>
<td>9g/hr Boron at 90% conv</td>
<td>B purity 99.9% no deposit/filament interdiffusion</td>
<td>141</td>
</tr>
<tr>
<td>5) BCl₃ + H₂</td>
<td>Series of alloy wires precoated with graphite</td>
<td>-</td>
<td>200gB/wire</td>
<td>Geometry of deposition chamber important for high yield</td>
<td>142</td>
</tr>
<tr>
<td>6) BCl₃ + H₂</td>
<td>Titanium</td>
<td>1050-1125</td>
<td>1.0 g/hr crystalline boron at 40% conv.</td>
<td>Boron deposition dependent on H₂/BCl₃, res. time, temp &amp; mass of deposit</td>
<td>143</td>
</tr>
<tr>
<td>7) BBr₃ + H₂</td>
<td>Tantalum</td>
<td>1125-1175</td>
<td>6-8mole% BBr₃ in H₂</td>
<td>Single crystal Boron grown</td>
<td>144</td>
</tr>
<tr>
<td>8) BCl₃ + B₂H₆</td>
<td>Tantalum</td>
<td>950-1000</td>
<td>52.5% B₂H₆ decompd. + 24% BCl₃ decompd to Boron.</td>
<td>60 torr pressure</td>
<td>145</td>
</tr>
<tr>
<td>9) BCl₃ + H₂</td>
<td>RF heated Boron rod</td>
<td>1600</td>
<td>90% conv BCl₃ → B at H₂/BCl₃ = 100</td>
<td>Single crystal Boron growth</td>
<td>146</td>
</tr>
<tr>
<td>10) BCl₃ + H₂</td>
<td>RF heated Boron rod</td>
<td>1300-1600, 1600-1800</td>
<td>5% increase in yield of boron at 1600°</td>
<td>H₂/BCl₃ &gt; 100 fine powder formed.</td>
<td>147</td>
</tr>
<tr>
<td>11) Boranes</td>
<td>Tantalum</td>
<td>560-600</td>
<td>0.5 lt.hr⁻¹ cm⁻² feed rate</td>
<td>TaB eventually formed</td>
<td>148</td>
</tr>
</tbody>
</table>

(cont'd ....)
<table>
<thead>
<tr>
<th>Reactants</th>
<th>Substrate</th>
<th>Substrate Temperature°C</th>
<th>Yield of Product</th>
<th>Comments</th>
<th>Ref</th>
</tr>
</thead>
</table>
| (12)BCl₃ )  
BBBr₃( + H₂  
Bi₂ | Tantalum       | 1400                    | 15.7% conv 25.8% to 43.0% boron | At BX₃/H₂ = 0.1 | 149 |
| (13)BCl₃+H₂ | Tungsten      | 1200-1600               | Boron fibre formation | -        | 150 |
| (14)BCl₃+H₂ | graphite rod, tungsten or nickel | 1300-1500 | H₂/BCl₃ 30:1 conv to B = 85% | 0.07mm diam B per hour | 151, 152 |
| (15)BCl₃+H₂ | 25 μm W. wire | 900-1200                | 1.1 x 10⁻⁴ g/m²/cm² sec | mole%BCl₂=50% | 153, 154 |
| (16)BCl₃+H₂ | quartz tube reactor | 600-750 | 40% conv. BCl₃ to BHCl₂ | H₂/BCl₃ = 15 | 158 |
| (17)BCl₃+H₂ | W. wire (best) | 800-1400 | 140 μg Boron/sec cm² | Atmos. pressure 22 mole % BCl₃ in H₂ | 155 |
was used in the reaction chamber to adsorb the chlorine by-product. The boron deposits obtained were reported to be brittle. Powell et al. (141) extended Van Arkel's work and reduced BBr$_3$ with H$_2$ over tantalum filaments and obtained up to 90% conversion of BBr$_3$ to boron. Upto 9 g/hr of ultrapure (>99.9%) boron could be deposited in this way. Other workers (144, 149) have reported the use of BBr$_3$/H$_2$ mixtures for boron deposition but at lower efficiencies.

Most boron deposition work, however, has started from boron trichloride which has a more convenient vapour pressure at room temperature than BBr$_3$ or BI$_3$, and the reaction is thermodynamically more favourable than with BF$_3$. In the 1940's, the Norton Co. operated a small pilot plant for the manufacture of massive crystalline boron from BCl$_3$ and H$_2$ mixtures for the United States Air Force (139, 140). Six graphite rods (2" diam and 46" long) were electrically-heated in series to 1400°C by a 60 KW d.c. supply (4000 A at 100-150 V). Upto 1 lb/hr of boron could be deposited on the graphite rods, on which $\frac{1}{2}$ inch thick layers of crystalline boron built up. Mole ratios of H$_2$/BCl$_3$ of 5/1 were used and overall process efficiencies of 70% for crude product and 40% for pure 99% boron were quoted. Continuous operation of up to 60 hrs was possible. This process is most interesting historically as it was probably the first time that large quantities of elemental boron were made commercially.

The manufacture of boron fibres has been the main goal of boron deposition work. These have strengths comparable
with carbon fibres but at present cost substantially more to produce due to higher raw material costs.

Stern and Lynds (143) investigated boron deposition on various filaments including tantalum, graphite and titanium. At filament temperatures of $1100^\circ C$ and $H_2/BCl_3$ mole ratios of 12:1 they obtained 1 g/hr of boron deposited on titanium filaments at 40% conversion of $BCl_3$. They concluded that titanium was the most satisfactory material as it enabled high purity boron ($>99\%$) to be obtained by direct chlorination of the titanium impurities at $300^\circ C$. Boron does not readily react with chlorine below about $600^\circ C$. Cochran et al. (151, 152) have recently reported 85% conversion of $BCl_3$ to boron using a tungsten substrate. At temperatures of $1500^\circ C$ and $H_2/BCl_3$ mole ratios of 30/1 they obtained boron growth rates of 0.07 mm diam/hr.

Gruber (153, 154) has developed a mathematical description of experimentally-measured kinetic data for boron deposition on a 25 $\mu$ diam. tungsten wire. He considered two possible rate limiting phenomena: mass transport or diffusion limited deposition and chemical kinetic-limited deposition. Gruber fitted experimental data obtained under controlled conditions where mass transport was not limiting (i.e. high reactant velocity, normal to a horizontal substrate) to various computed rate equations. The best fit was given by the equation:

$$ V = K \frac{K_B K_H P_B^{1/2} P_H^{1/2}}{(1 + K_B P_B^{1/2} + K_H P_H^{1/2} + K_{He} P_{He})^2} \quad \cdots (2) $$
where \( V \) = reaction rate \( g/(cm^2)(sec) \)

\( K \) = rate constant

\( K_B \) = adsorption constant related to \( BCl_3 \)

\( K_H \) = " " " " \( H_2 \)

\( K_{He} \) = " " " " \( He \)

\( P_B \) = partial pressure \( BCl_3 \)

\( P_H \) = " " \( H_2 \)

\( P_{He} \) = " " \( He \)

The constants \( K, K_B, K_H \) and \( K_{He} \) were evaluated at various deposition temperatures and are shown below:

<table>
<thead>
<tr>
<th>Temp. °C</th>
<th>( K \times 10^4 )</th>
<th>( K_B )</th>
<th>( K_H )</th>
<th>( K_{He} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>800</td>
<td>1.5</td>
<td>100</td>
<td>100</td>
<td>1.6</td>
</tr>
<tr>
<td>1000</td>
<td>12</td>
<td>25</td>
<td>25</td>
<td>1.4</td>
</tr>
<tr>
<td>1200</td>
<td>55</td>
<td>7.2</td>
<td>7.2</td>
<td>1.1</td>
</tr>
</tbody>
</table>

The variation of rate with temperature enabled an activation energy of 29 Kcal/mole to be evaluated. Gruber concluded that in the absence of diffusion limitations the rate of reduction of \( BCl_3 \) with \( H_2 \) on a heated substrate corresponded to a surface reaction between adsorbed atomic hydrogen and some adsorbed B molecule which exerted an influence on the reaction rate \( \propto \sqrt{P_{BCl_3}} \)

Carlton et al. (155) also found that the deposition rate of boron on substrate was limited by the reduction of an adsorbed boron molecule believed to be either \( HBCl_2 \) or \( BCl_2 \). They measured substantial quantities of \( HBCl_2 \) in the reactor and postulated that the \( HBCl_2 \) was in equilibrium with \( BCl_3, H_2 \) and \( HCl \) at the deposition surface. They postulated the following mechanism for boron deposition:
1) \( \text{BCl}_3 (g) \rightleftharpoons \text{HBCl}_2 (g) \),
2) \( \text{BCl}_3 (\text{ads}) \rightleftharpoons \text{HBCl}_2 (g) \),
3) \( 2\text{BCl}_2 (\text{ads}) \rightleftharpoons \text{HBCl}_2 (g) \),
4) \( \text{HBCl}_2 (\text{ads}) \rightleftharpoons \text{HBCl}_2 (g) \),
5) \( \text{BCl} (\text{ads}) \rightleftharpoons \text{HBCl}_2 (g) \),
6) \( \text{H}_2\text{BCl} (\text{ads}) \rightleftharpoons \text{HBCl}_2 (g) \). BORON

They developed a Langmuir-Hinshelwood model to predict the deposition rates and found that, by assuming step 4 of the mechanism to be rate controlling, i.e. (reaction first order w.r.t. \( \text{HBCl}_2 \) and zero-order w.r.t. \( \text{H}_2 \)), an approximation to experimental results could be obtained by the following rate equation:

\[
W_B = K_0 \left[ \frac{(K'_{\text{eq}} \frac{P_{\text{BCl}_3}}{P_{\text{HCl}}})}{\frac{P_{\text{HCl}}}{K'_{\text{eq}} \frac{P_{\text{H}_2}}{P_{\text{HCl}}}}} \right] \sqrt{1 + K_{\text{HCl}P_{\text{HCl}}}} \text{gm/(cm}^2\text{)(sec)}
\]

A standard deviation of 23% was obtained for all experimental results for this rate equation and an Arrhenius plot of deposition rate against reciprocal temperature gave an activation energy of 29 Kcal/mole in excellent agreement with Gruber (153). While the agreement between the activation energies obtained by these two workers is impressive, Carlton et al.'s model is excessively complicated and fits the data poorly. It is difficult to assess the equilibria he means to include in his mechanism as molecules such as \( \text{H}_2 \) and \( \text{HCl} \) have been omitted from his equations.

The formation of \( \text{HBCl}_2 \) by the thermal reduction of \( \text{BCl}_3 \) with \( \text{H}_2 \) at temperatures between 600-750°C has also been reported by Murib et al. (158).
The pioneer work of Weintraub (126), Besson and Fournier (128), Briscoe (132) and Kroll (133) on low pressure discharges in BCl$_3$/H$_2$ mixtures has already been discussed in Section 2.31. This work laid the foundation for investigations of boron subhalide chemistry and of a commercial route to high purity boron, involving the minimum number of purification stages. In 1925, Stock et al. (74) reported the first preparation of diboron tetrachloride by striking repeated arcs in liquid BCl$_3$. Though the yield of B$_2$Cl$_4$ was <1% the idea was a fruitful one. Table V summarises the subsequent uses of electrical discharges and thermal plasmas in the investigation of the hydrogen reductions of boron halides, together with some work that has been done on boranes. A detailed discussion of these investigations will not be attempted in this thesis, rather, some of the more important developments will be indicated and any mechanistic work will be discussed.

2.34(a) B$_2$Cl$_4$ and other subhalides

The preparation of B$_2$Cl$_4$ from BCl$_3$ has been well studied both in glow discharges (156, 157, 159, 162, 163, 169, 170 and 176), and in microwave discharges (160, 161). Rates of B$_2$Cl$_4$ production of up to 200 mg/hr can be obtained by the use of copper wool electrodes where the copper acts as a chlorine-getter and improves efficiency (176). Many by-products have been identified in this reaction, such as tetraboron tetrachloride B$_4$Cl$_4$ and (BCl)$_n$ polymers (162, 190). Yields of B$_4$Cl$_4$ are low (\~1.2 mg/day) and of (BCl)$_n$ polymers even lower (162). Values of $n$ for the polymers range from 8-12 (184).
<table>
<thead>
<tr>
<th>ischarge</th>
<th>Reactants</th>
<th>Pressure</th>
<th>Electrode Material</th>
<th>Product</th>
<th>Yield</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Arc</td>
<td>BCl&lt;sub&gt;3&lt;/sub&gt;+H&lt;sub&gt;2&lt;/sub&gt;</td>
<td>Low</td>
<td>Cu</td>
<td>Boron bead</td>
<td></td>
<td>126</td>
</tr>
<tr>
<td>2. Arc</td>
<td>liq BCl&lt;sub&gt;3&lt;/sub&gt;</td>
<td>Atmos.</td>
<td>Zn</td>
<td>B+&lt;br&gt;B&lt;sub&gt;2&lt;/sub&gt;Cl&lt;sub&gt;4&lt;/sub&gt;</td>
<td>1% B&lt;sub&gt;2&lt;/sub&gt;Cl&lt;sub&gt;4&lt;/sub&gt;</td>
<td>74</td>
</tr>
<tr>
<td>3. Glow</td>
<td>BCl&lt;sub&gt;3&lt;/sub&gt;</td>
<td>1-2 torr</td>
<td>Hg</td>
<td>B&lt;sub&gt;2&lt;/sub&gt;Cl&lt;sub&gt;4&lt;/sub&gt;</td>
<td></td>
<td>156</td>
</tr>
<tr>
<td>4. Glow</td>
<td>BCl&lt;sub&gt;3&lt;/sub&gt;</td>
<td>1-2 torr</td>
<td>Hg</td>
<td>B&lt;sub&gt;2&lt;/sub&gt;Cl&lt;sub&gt;4&lt;/sub&gt;</td>
<td>1m. mole/hr</td>
<td>157</td>
</tr>
<tr>
<td>5. Glow</td>
<td>BCl&lt;sub&gt;3&lt;/sub&gt;</td>
<td>Low</td>
<td>-</td>
<td>B&lt;sub&gt;2&lt;/sub&gt;Cl&lt;sub&gt;4&lt;/sub&gt;</td>
<td></td>
<td>159</td>
</tr>
<tr>
<td>6. M/W</td>
<td>BCl&lt;sub&gt;3&lt;/sub&gt;</td>
<td>44 torr</td>
<td>-</td>
<td>B&lt;sub&gt;2&lt;/sub&gt;Cl&lt;sub&gt;4&lt;/sub&gt;</td>
<td>1m. mole/hr</td>
<td>160</td>
</tr>
<tr>
<td>7. M/W</td>
<td>BCl&lt;sub&gt;3&lt;/sub&gt;</td>
<td>-</td>
<td>-</td>
<td>B&lt;sub&gt;2&lt;/sub&gt;Cl&lt;sub&gt;4&lt;/sub&gt;</td>
<td>BCl intermediate</td>
<td>161</td>
</tr>
<tr>
<td>8. Glow</td>
<td>BCl&lt;sub&gt;3&lt;/sub&gt;</td>
<td>Low</td>
<td>Hg</td>
<td>B&lt;sub&gt;2&lt;/sub&gt;Cl&lt;sub&gt;4&lt;/sub&gt;,&lt;br&gt;B&lt;sub&gt;4&lt;/sub&gt;Cl&lt;sub&gt;4&lt;/sub&gt;+(BCl)&lt;sub&gt;n&lt;/sub&gt;</td>
<td>1-2 mg/day B&lt;sub&gt;4&lt;/sub&gt;Cl&lt;sub&gt;4&lt;/sub&gt; in 3 hrs.</td>
<td>162</td>
</tr>
<tr>
<td>9. Glow</td>
<td>BCl&lt;sub&gt;3&lt;/sub&gt;</td>
<td>Low</td>
<td>Cu</td>
<td>B&lt;sub&gt;2&lt;/sub&gt;Cl&lt;sub&gt;4&lt;/sub&gt;</td>
<td>0.18 g B&lt;sub&gt;2&lt;/sub&gt;Cl&lt;sub&gt;4&lt;/sub&gt; in 3 hrs.</td>
<td>163</td>
</tr>
<tr>
<td>10. Glow</td>
<td>BBr&lt;sub&gt;3&lt;/sub&gt;+Ar</td>
<td>Low</td>
<td>Hg/Ni</td>
<td>B&lt;sub&gt;2&lt;/sub&gt;Br&lt;sub&gt;4&lt;/sub&gt;</td>
<td></td>
<td>164</td>
</tr>
<tr>
<td>1. R.F.</td>
<td>BI&lt;sub&gt;3&lt;/sub&gt;</td>
<td>1-3 torr</td>
<td>5 MHz</td>
<td>B&lt;sub&gt;2&lt;/sub&gt;I&lt;sub&gt;4&lt;/sub&gt;</td>
<td>30% conv.</td>
<td>165</td>
</tr>
<tr>
<td>2. R.F.</td>
<td>B&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;6&lt;/sub&gt;</td>
<td>-</td>
<td>-</td>
<td>B&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;10&lt;/sub&gt;</td>
<td>40% conv.</td>
<td>166</td>
</tr>
<tr>
<td>3. R.F.</td>
<td>B&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;6&lt;/sub&gt;</td>
<td>-</td>
<td>-</td>
<td>B&lt;sub&gt;5&lt;/sub&gt;H&lt;sub&gt;11&lt;/sub&gt;</td>
<td>20% conv.</td>
<td>167</td>
</tr>
<tr>
<td>4. Arc</td>
<td>Pentaborane-9 +H&lt;sub&gt;2&lt;/sub&gt;</td>
<td>-</td>
<td>Cu</td>
<td>Decaborane -&lt;br&gt;-16</td>
<td></td>
<td>168</td>
</tr>
<tr>
<td>5. Arc</td>
<td>BCl&lt;sub&gt;3&lt;/sub&gt;</td>
<td>-</td>
<td>Cu</td>
<td>B&lt;sub&gt;2&lt;/sub&gt;Cl&lt;sub&gt;4&lt;/sub&gt;</td>
<td>200 mg/hr</td>
<td>169</td>
</tr>
<tr>
<td>6. R.F.</td>
<td>BCl&lt;sub&gt;3&lt;/sub&gt;+H&lt;sub&gt;2&lt;/sub&gt;</td>
<td>30-200 torr</td>
<td>1 kHz</td>
<td>Boron</td>
<td>1.2 g/hr 50% conv</td>
<td>171</td>
</tr>
<tr>
<td>7. Arc</td>
<td>BCl&lt;sub&gt;3&lt;/sub&gt;+H&lt;sub&gt;2&lt;/sub&gt;</td>
<td>-</td>
<td>-</td>
<td>Boron</td>
<td></td>
<td>172</td>
</tr>
<tr>
<td>8. R.F.</td>
<td>BCl&lt;sub&gt;3&lt;/sub&gt;+H&lt;sub&gt;2&lt;/sub&gt;</td>
<td>1 torr</td>
<td>3 MHz</td>
<td>Boron</td>
<td>0.18 g/hr</td>
<td>173</td>
</tr>
<tr>
<td>9. Corona</td>
<td>BCl&lt;sub&gt;3&lt;/sub&gt;+H&lt;sub&gt;2&lt;/sub&gt;</td>
<td>-</td>
<td>-</td>
<td>Boron</td>
<td></td>
<td>174</td>
</tr>
<tr>
<td>10. Arc</td>
<td>BCl&lt;sub&gt;3&lt;/sub&gt;+H&lt;sub&gt;2&lt;/sub&gt;</td>
<td>Atmos.</td>
<td>7 kW</td>
<td>Boron</td>
<td>40 g/hr</td>
<td>175</td>
</tr>
<tr>
<td>1. Glow</td>
<td>BCl&lt;sub&gt;3&lt;/sub&gt;</td>
<td>Low</td>
<td>Cu</td>
<td>B&lt;sub&gt;2&lt;/sub&gt;Cl&lt;sub&gt;4&lt;/sub&gt;</td>
<td>1m. mole/hr</td>
<td>176</td>
</tr>
<tr>
<td>2. Glow</td>
<td>BF&lt;sub&gt;3&lt;/sub&gt;</td>
<td>Low</td>
<td>Hg</td>
<td>None</td>
<td></td>
<td>177</td>
</tr>
<tr>
<td>3. Arc</td>
<td>BF&lt;sub&gt;3&lt;/sub&gt;+H&lt;sub&gt;2&lt;/sub&gt;</td>
<td>Low</td>
<td>W</td>
<td>Boron</td>
<td>Trace</td>
<td>178-</td>
</tr>
<tr>
<td>4. Glow</td>
<td>BCl&lt;sub&gt;3&lt;/sub&gt;+H&lt;sub&gt;2&lt;/sub&gt;</td>
<td>20 torr</td>
<td>Cu</td>
<td>B&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;6&lt;/sub&gt;</td>
<td>+ trace B&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;Cl</td>
<td>181</td>
</tr>
<tr>
<td>5. Glow</td>
<td>B&lt;sub&gt;10&lt;/sub&gt;H&lt;sub&gt;14&lt;/sub&gt;+H&lt;sub&gt;2&lt;/sub&gt;</td>
<td>Low</td>
<td>-</td>
<td>B&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;16&lt;/sub&gt;</td>
<td></td>
<td>182</td>
</tr>
<tr>
<td>6. Arc</td>
<td>BCl&lt;sub&gt;3&lt;/sub)&gt;+H&lt;sub&gt;2&lt;/sub&gt;</td>
<td>Atmos.</td>
<td>W</td>
<td>Boron</td>
<td>60% conv.</td>
<td>183</td>
</tr>
<tr>
<td></td>
<td>BF&lt;sub&gt;3&lt;/sub&gt;+H&lt;sub&gt;2&lt;/sub&gt;</td>
<td>Atmos.</td>
<td>W</td>
<td>Boron</td>
<td>60% conv.</td>
<td>183</td>
</tr>
</tbody>
</table>
Diboron tetrabromide has also been prepared in a glow discharge (164) together with the corresponding (BBr)$_n$ polymer and diboron tetraiodide has also been prepared, which subsequently decomposes to (BI)$_n$ (165). The mechanism of the (BX)$_n$ polymer formation is thought to be:

\[ n(B_2X_4) \rightarrow nBX_3 + (BX)_n \quad (165, 170). \]

Diener and Pflugmacher (164) have also obtained (B$_x$Br$_y$)$_n$ polymers at B:Br ratios of 5:1 and 2.5:1 by injecting argon and BBr$_3$ into a glow discharge between Hg or Ni electrodes.

The corresponding B$_2$F$_4$ has not been prepared in an electrical discharge (177), although the BF radical has been identified spectroscopically in a microwave discharge (165). BF$_3$ and H$_2$, however, when injected into a low pressure tungsten arc (178 - 180) react to give a trace of boron. At atmospheric pressure, in a thermal plasma arc, substantial yields of boron from BF$_3$/H$_2$ mixtures have been obtained (183).

2.34 (b) Boranes

The decomposition of boranes in low pressure discharges has been investigated both in radio-frequency (166, 167) and arc discharges (168, 182). Kotlinsky and Schaeffer (166) passed B$_2$H$_6$ through a low pressure r.f. discharge and obtained a 40% yield of B$_2$H$_{10}$, 20% yield of B$_5$H$_{11}$, together with trace amounts of B$_5$H$_{10}$ and B$_9$H$_{11}$. Gibbins and Shapiro (167) also identified hexaborane in the decomposition products of the diborane discharge. Grimes et al. (168) passed a mixture of pentaborane-9 and H$_2$ through an
arc discharge and obtained decaborane-16 by the following reaction:

\[ 2B_5H_9 + H_2 \xrightarrow{\text{arc}} B_{10}H_{16} + 2H_2 \]

Friedman and Dobrott (182) passed decaborane-14 through a low pressure \( H_2 \) discharge and identified \( B_{20}H_{16} \) in the products.

### 2.34(c) Boron

After Weintraub first prepared boron in an arc discharge of \( \text{BCl}_3 \) and \( H_2 \) (126), the next report of substantial boron formation in a discharge reactor was by Markovskii et al. (171) in 1958. They passed \( \text{BCl}_3/H_2 \) mixtures at 30-200 mm Hg pressure through a 1 kHz r.f. discharge and obtained up to 1.2 g/hr of 99.9% boron at 50% conversion of \( \text{BCl}_3 \) when operating at \( H_2/\text{BCl}_3 \) ratios of 5/1. Wales (174) obtained pure boron from a corona discharge in \( \text{BCl}_3/H_2 \) mixtures and postulated a mechanism for the energy transfer process (see next section).

Hultguist and Sibert (173) deposited boron on filaments moving through discharge in a \( \text{BCl}_3/H_2 \) mixture. This is essentially a deposition reaction, but as the energy comes from the discharge it has been included in this section for comparison. At a \( H_2/\text{BCl}_3 \) ratio of 1.5/1 Hultguist and Sibert obtained good uniform boron deposits on the filaments at rates up to 0.18 g/hr. As \( H_2/\text{BCl}_3 \) ratios were increased considerable sidewall deposition occurred and eventually borane formation was observed at \( H_2/\text{BCl}_3 > 10/1 \). This result is substantiated by the work of Schlesinger and Burg (181) who obtained diborane as the main product from \( \text{BCl}_3/H_2 \) in a glow discharge at a \( H_2/\text{BCl}_3 \) of 12:1.
Biggerstaff et al. (183) prepared elemental boron, as massive crystalline deposits, by passing $BF_3/H_2$ and $BCl_3/H_2$ mixtures through an atmospheric pressure argon plasma arc. $6.8 \text{ g/hr}$ boron at 60% conversion of $BCl_3$ and $1 \text{ g/hr}$ boron at 30% conversion of $BF_3$ were obtained. They claim that $BCl_3$ can also be thermally decomposed to boron by the plasma arc in the absence of hydrogen. This is in contrast to the present work where at no time has boron been obtained as a solid by the thermal decomposition of $BCl_3$. Atomic boron has been identified in the plasma by spectroscopic techniques, but no solid boron has been observed to form in the absence of hydrogen. A possible explanation of the formation of boron by passage of $BCl_3$ through an arc plasma could be reaction of $BCl_3$ with the materials of construction of the anode, usually copper. Copper is known to react with boron trichloride at relatively low temperatures to form boron and copper chloride.

$$2BCl_3 + 3Cu \rightarrow 2B + 3CuCl_2$$

Case (175) has obtained substantial yields of boron in fine powder form by feeding $BCl_3$ to the tail of a hydrogen plasma jet. $40 \text{ g/hr}$ of boron was obtained at conversions up to 90% when a $H_2/BCl_3$ ratio of 17:1 was used.

2.3.4(d) Mechanistic studies

The mechanism of $B_2Cl_4$ formation from low pressure discharges has been discussed by various workers. Moore et al. (159) suggested that the main intermediate in the formation of $B_2Cl_4$ in the mercury discharge, was $BCl_2$, as follows:
Both Holzmann and Morris (161) and Pannetier et al. (186) however, identified the BCl molecule in the emission spectrum of a BCl$_3$ microwave discharge and the following mechanism was postulated (161, 189) for the formation of B$_2$Cl$_4$ by:

$$\text{BCl}_3 \rightarrow \text{BCl} + \text{Cl}_2$$
$$\text{BCl} + \text{BCl}_3 \rightarrow \text{B}_2\text{Cl}_4$$

Recent evidence by Pannetier et al. (187) and Dessaux et al. (188) shows that both BCl and BCl$_2$ molecules are present in low pressure BCl$_3$ discharges, so the actual mechanism of B$_2$Cl$_4$ formation is in some doubt.

Wales (174) postulated the following energy transfer mechanism for boron formation at the cathode of a low pressure corona discharge:

1. Emission of electrons from the cathode.
2. Ionisation of H$_2$, Ar or He and production of secondary electrons which in turn ionise more H$_2$, Ar or He.
3. Collisions of ionised H$_2$, He or Ar with BCl$_3$ and exchange of energy.
4. Formation of positive boron radicals and HCl or Cl.
5. Transfer of positive boron radical to the cathodes.
6. Electrochemical reaction of radical to form an amorphous boron deposit.

This mechanism, although not strictly relevant to the high pressure electrodeless discharge, does suggest certain energy exchange processes which could occur in the r.f. plasma and will be discussed in a later section of the thesis.
2.35 Reactions of Boron compounds in thermal plasma

2.35(a) Preparation of metal borides

Bosch and de Vynck (191-194) have investigated the production of various metal borides including TiB$_2$, ZrB$_2$, CrB, Mo$_5$B$_3$, MoB, WB and B$_4$Si. They compressed mixtures of powdered reactants into cylindrical shapes and used these cylinders as anode extensions in a transferred d.c. arc torch. They experimented with three different electrical circuits for the transferred arc and found that they obtained the best results when an a.c. supply was superimposed on the d.c. arc. The arc was struck between the cathode and anode and passed through a nozzle which made up one terminal of the a.c. circuit. The anode sample acted as the other terminal. Table V shows the chemical reactions which Bosch and de Vynck attempted and the products which were obtained.

<table>
<thead>
<tr>
<th>Reaction attempted</th>
<th>Product obtained</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. 2B$_2$O$_3$+7C → B$_4$C+6CO</td>
<td>B$_4$C</td>
<td>(192)</td>
</tr>
<tr>
<td>2. TiH$_2$+2B → TiB$_2$+H$_2$</td>
<td>TiB$_2$</td>
<td>(193)</td>
</tr>
<tr>
<td>3. 2TiO$_2$+B$_4$C+3C → 2TiB$_2$+4CO</td>
<td>TiB$_2$+TiC</td>
<td>(&quot;&quot;&quot;)</td>
</tr>
<tr>
<td>4. ZrH$_2$+2B → ZrB$_2$+H$_2$</td>
<td>ZrB$_2$</td>
<td>(&quot;&quot;&quot;)</td>
</tr>
<tr>
<td>5. 2ZrO$_2$+3C+B$_4$C → 2ZrB$_2$+4CO</td>
<td>ZrB$_2$+ZrC</td>
<td>(&quot;&quot;&quot;)</td>
</tr>
<tr>
<td>6. 2Cr$_2$O$_3$+B$_4$C+5C → 4CrB+6CO</td>
<td>CrB+CrB$_2$+trCr$_x$By</td>
<td>(194)</td>
</tr>
<tr>
<td>7. Mo+B → MoB</td>
<td>MoB+trace MoB$_2$</td>
<td>(&quot;&quot;&quot;)</td>
</tr>
<tr>
<td>8. 20MoO$_3$+3B$_4$C+57C → 4Mo$_5$B$_3$+6OCO</td>
<td>Mo$_5$B$_3$</td>
<td>(&quot;&quot;&quot;)</td>
</tr>
<tr>
<td>9. W+B → WB</td>
<td>β and δ WB</td>
<td>(&quot;&quot;&quot;)</td>
</tr>
<tr>
<td>10. 4WO$_2$+B$_4$C+11C → 4WB+12CO</td>
<td>β and δ WB</td>
<td>(&quot;&quot;&quot;)</td>
</tr>
<tr>
<td>11. Si+4B → B$_4$Si</td>
<td>B$_4$Si</td>
<td>(&quot;&quot;&quot;)</td>
</tr>
<tr>
<td>12. B$_2$O$_3$+SiO$_2$+8C → B$_4$Si+8CO</td>
<td>B$_4$C and SiC</td>
<td>(&quot;&quot;&quot;)</td>
</tr>
</tbody>
</table>
The products were obtained as fused lumps and were identified by X-ray analysis. They were claimed to be of high purity when prepared from their constituent elements. No quantitative results were reported.

TiB₂ has also been prepared in a radiofrequency plasma (195) and an electric arc (196). The latter preparation started from a mixture of TiO₂, boric acid and carbon which was compressed into pellets. The pellets were subjected to an electric arc and the torch design was such that the carbon monoxide evolved during the reaction protected the electrode materials from oxidation. The former r.f. plasma method (195) also used compressed pellets of reactants which were placed in a graphite crucible and heated by a 12 KW, 6.3MHz argon plasma. TiB₂ was successfully prepared via the following reactions:

\[
\begin{align*}
\text{Ti} + 2\text{B} & \rightarrow \text{TiB}_2 \\
3\text{TiO}_2 + 10\text{B} & \rightarrow 3\text{TiB}_2 + 2\text{B}_2\text{O}_3 \\
\text{TiO}_2 + 2\text{B} + 2\text{C} & \rightarrow \text{TiB}_2 + 2\text{CO} \\
\text{TiO}_2 + \text{B}_2\text{O}_3 + 5\text{C} & \rightarrow \text{TiB}_2 + 5\text{CO}
\end{align*}
\]

Aluminium Boride Al₂B₁₁ has been prepared (197) by fusion of amorphous boron in liquid alumina in a centrifugal liquid wall plasma furnace.

2.35(b) Preparation of boron nitride

Bosch and de Vynck (191) synthesised boron nitride by injecting amorphous boron into an ammonia plasma jet. They also obtained trace quantities of BN in their attempted preparations of Titanium Nitride from TiB₂+N₂, and Zirconium Nitride from B₄C+ZrO₂+C+N₂. They were, however, unable to obtain boron nitride (194) in the a.c./d.c.
plasma torch when boron pellets were subjected to a nitrogen plasma. Boron nitride has been prepared by the use of a high intensity arc (199) where 50\% BN was obtained, which was subsequently purified to 90-100\% by heat treatment in a nitrogen atmosphere. Russo and Diana (198) injected boron trichloride into the tail of a d.c. nitrogen plasma which was magnetically stabilised. When the products were rapidly quenched on a rotating water-cooled drum, 10-20\% conversion of BCl$_2$ to a solid product was obtained. On analysis the product was identified as a mixture of 30\% elemental boron and 60\% BN(w/w). If the tail gases were not quenched, however, no product was obtained. Russo and Diana postulated that formation of boron nitride occurred as a result of a reaction between boron and nitrogen atoms during the quench stage and that boron atoms sublimed to the solid state before BCl$_2$ or N$_2$ molecules could be regenerated.

A recent patent (200) discloses a process for the preparation of 0.1 \mu boron nitride powder by vapour phase reaction of B$_2$O$_3$ or boric acid in a nitrogen/ammonia plasma jet. B$_2$O$_3$ (or boric acid) vapourisation is achieved either by injection of the powder into a nitrogen plasma or by heating a fixed bed of pellets with the plasma gases. Boron nitride formed as agglomerates of 200 \AA diameter crystallites. Further treatment gave \sim 100\% boron nitride.

2.35(c) Boron carbide preparations

Boron carbide has been prepared from boron and propane/butane mixtures (191) and from BCl$_3$/CH$_4$/H$_2$ mixtures (201) by use of plasma jets.
Kusch (202) vaporised boric oxide/carbon mixtures in a high intensity arc by feeding compressed rods to the arc through a hollow anode. The product was boron carbide, but by variation of the quench conditions Kusch claimed that elemental boron could also be obtained in high yield.

2.35(d) Boric oxide reactions

Sheer and Korman (54), under a contract to Wright Air Development Centre, investigated the simultaneous carbothermic reduction and chlorination of borax to boron trichloride in a high intensity arc via the reaction

$$\text{Na}_2\text{B}_4\text{O}_7 + 7\text{C} + 7\text{Cl}_2 \rightarrow 4\text{BCl}_3 + 2\text{NaCl} + 7\text{CO}. $$

Composite borax-carbon anodes were fed to the arc zone and vaporisation occurred at the anode tip. In a chlorine atmosphere high conversions of borax to BCl$_3$ were obtained, limited only by the efficiency of the vaporisation process. At a 14g/min anode feed rate, 85% vaporisation could be obtained at 16.5 kW. The main drawback to this technique was the preparation of the consumable anodes. Problems occurred with borax sweating from the anode surface as the rod approached the arc zone and this caused erosion of the electrode holders. The design and formulation of the consumable anodes are covered in a U.S. Patent (46). Sheer and Korman were able to prepare BCl$_3$ uncontaminated by borax, but with traces of CO, HCl and free chlorine, which, although expensive to produce by present standards (viz. $\$34/\text{lb. at 1 ton/day}$, as compared to $\$5/\text{lb}$), was highly successful as a plasma application. The economics of the production of up to 100 ton/day were fully investigated but the process was never used. Sheer and Korman
also reported the preparation of elemental boron by carbothermic reduction in a high intensity arc (203).

A method has been claimed by Berghaus (204) for the preparation of boron-hydrogen compounds in a glow discharge apparatus at pressures up to 500 mm Hg. Boric oxide dispersed either in a liquid or gas is fed to the discharge zone where it is mixed with hydrogen via a sparge ring. Diborane is formed according to the reaction:

\[ \text{B}_2\text{O}_3 + 3\text{H}_2 \rightarrow \text{B}_2\text{H}_6 + 3\text{H}_2\text{O} \]

Berghaus (205) describes a similar apparatus for the hydrogen reduction of various halides (incl. boron) to their parent element. These two discharge devices are complicated compared with conventional plasma devices, and moreover, the quantitative data that is reported would seem to indicate that only small amounts of material can be processed (e.g. 20 gms TiCl\textsubscript{4} converted to 3.6 gms titanium metal).

2.4 Summary

Most of the reported investigations of the use of thermal plasma devices in chemical synthesis have involved the plasma as an energy source for the activation of endothermic reactions which can also be carried out by more conventional high temperature techniques. This use of plasma hopefully results in the formation of a product either of higher purity or superior physical properties. In contrast to low pressure microwave discharges, plasma have given rise to no new chemical compounds which cannot be prepared by other techniques. Of the many publications on chemical synthesis in radiofrequency plasma, few have included a
credible mechanism for the product formation, the majority of authors being satisfied with a purely preparative approach. The studies of the behaviour of boron compounds, in particular in thermal plasma, have offered no mechanistic or kinetic data, although some inconclusive mechanisms for the low pressure formation of boron subhalides have been proposed.

Empirical kinetic equations have been presented for the vapour deposition of boron on heated substrates, but these are of little use for application to the high energy thermal plasma environment. Little is known about the growth of solid particles in a thermal plasma environment, although considerable effort has been expended in determining parameters controlling heat transfer to particles in the plasma.

It is hoped in the present work to establish the parameters controlling hydrogen reduction reactions in plasmas, in particular the reduction of BCl$_3$ to boron in a radio-frequency plasma, and to throw light on the mechanism of boron formation. In addition it is hoped that an investigation of the nature of the boron so formed could be useful in predicting growth rates of solid particles from plasmas.

The commercialisation of thermal plasma chemical processes has been relatively slow. No successful plasma processes have appeared since the original arc process for acetylene production. The BCl$_3$/H$_2$ reaction is at present of commercial interest as a route to boron fibres, and there is a small demand for high purity amorphous boron
It was hoped this demand could be met by the use of an r.f. plasma process. This has not been the case as yet since the high operating costs at intermediate power levels (20-30 KW) have proved to be a barrier to economic development. In this work, a pilot plant for boron production in a radio frequency plasma system has been built and successfully operated continuously for periods up to 70 hours.

Fig. 6 summarises chemical syntheses which have been attempted in radio frequency plasma devices. Maximum and minimum conversions are plotted on a log scale against the chemical reaction concerned.
CHAPTER 3

EXPERIMENTAL METHODS
3.1 General Experimental Techniques

To enable the hydrogen reduction of boron trichloride to be studied in a radio-frequency induced plasma at atmospheric pressure the following experimental capabilities were developed.

3.1.1 Plasma Reactor

A reliable plasma reactor was necessary which could be operated on a boron trichloride feed at power levels up to 30 KW. The plasma torch itself had to be capable of continuous operation for prolonged periods of time for pilot plant use, and also provide means for quick dismantling and reassembly between research runs. Provision for feeding mixtures of argon, hydrogen and boron trichloride into the plasma reactor had to be made, with a means of injecting various combinations of the three gases either into the plasma itself or into the plasma tail region.

3.1.2 Gas injection and control systems

A method of feeding boron trichloride vapour (bp: 12°C) to the plasma reactor at consistent and predictable rates up to 2 g/mole/min was necessary. Although a high tolerance for BCl₃ in the plasma was possible (in fact pure BCl₃ plasmas could be run under certain conditions), gross variation in BCl₃ feed rate was unacceptable. This was because it was necessary for kinetic investigation of the reaction to run the plasma torch near its limits of operation at constant power levels, and any sudden change in BCl₃ rate near a limiting condition might cause plasma extinction due to resistive overload.
3.13 Boron collection

The boron was formed as a fine dust and a solids collection system had to be devised which would reliably recover it from the effluent gases. The small particle size of the boron, the corrosive nature of the effluent gases and their high mean temperature and flow rate all posed problems.

3.14 BCl₃ recovery and HCl removal

A system for recovering unreacted BCl₃ was found to be necessary, both to avoid wastage and to reduce atmospheric pollution. An effluent gas washing facility was also necessary to remove HCl. Provision for neutralisation of the resulting acid liquors was also made.

3.15 Boron Trichloride production

Boron trichloride was prepared by the reaction of chlorine (I.C.I. Ltd) and boron carbide (Firth Brown Ltd) in a vertical fixed-bed reactor, according to the equation:

\[ B_4C + 6Cl_2 \rightarrow 4BCl_3 + C \quad \Delta H = -373 \text{ kcal/mole} \]

The chlorination of B₄C proceeds exothermically above 600°C and consequently high reaction bed temperatures were possible in the reactor. The boron carbide bed was therefore contained in a graphite tube, which was surrounded by a water-cooled mild-steel furnace casing, sealed to the graphite at both ends. Process efficiencies for the reaction with respect to B₄C as high as 70% were possible at chlorine flow rates of ~20 kg/hour. Efficiency with respect to chlorine approached 100% in the reactor.
The BCl₃ vapour leaving the B₄C bed was filtered to remove carbon dust and other solid impurities carried over in the BCl₃ gas stream. The BCl₃ was then subjected to a series of purification steps to remove B₂O₃ and trace chlorine, and finally condensed at between 5-10°C into mild steel storage cylinders. The BCl₃ produced by this process was colourless under ideal operating conditions. Under certain conditions of reactor temperature and chlorine flow rate, however, the BCl₃ could be coloured. This colour ranged from yellow through red to deep purple and was thought to be due to boron subhalides and (BCl)ₙ polymers which were formed. Massey and Lanthier (242) report that a yellow-orange polymer B₉Cl₉ and a deep purple polymer B₈Cl₈ can form when B₂Cl₄ is thermally decomposed. The coloured impurities in the BCl₃, however, were not isolated.

3.2 Development of Plasma Torch

3.21 Theory of induced plasma operation

As discussed in Section 2.12 there are two types of radio-frequency energy transfer which are used in r.f. plasma torches. The 'E-type' of discharge is generated by an oscillating electric field between two ring conductors, and the 'H-type' discharge is generated by an oscillating magnetic field from an external solenoid (see Fig. 4). In the present work the latter 'H-type' of plasma generation has been used exclusively. Energy transfer to the plasma in the H-type mode is by induction of eddy-currents in the plasma analogous to induction heating of solid conductors at lower frequencies. The plasma, although electrically neutral overall, contains free electrons and ions which act
as conductors. Joule heating of the plasma occurs due to the electrical resistance of the plasma and it reaches an equilibrium steady state where energy input is balanced by energy losses, due to such processes as radiation from excited atomic and molecular states and convective energy loss from the plasma to the surrounding gas sheath (117).

The depth of penetration of the eddy currents into the plasma is called the 'skin depth' \( S \), which is defined as (206):

\[
S = \frac{1}{2\pi\sqrt{10^{-9}\mu_r\sigma f}}
\]

where

- \( S \) = skin depth (cm)
- \( \mu_r \) = relative permeability of plasma
- \( \sigma \) = electrical conductivity of plasma gas (mho/cm)
- \( f \) = frequency of current oscillation (Hz)

For thermal plasmas \( \mu_r \) is usually taken as unity (64) and in terms of gas resistivity \( \rho \) instead of conductivity.

\[
S = \frac{1}{2\pi\sqrt{10^{-9}\rho f}} \quad (\rho = \text{resistivity in ohm-cm})
\]

From this equation it is possible to calculate the skin depth as a function of the frequency and gas resistivity only. Variation of frequency has two main effects on energy transfer to the plasma. Firstly, the skin depth will decrease as frequency rises, and for a fixed diameter gas channel, energy will therefore be transferred to a decreasing proportion of the gas (Fig. 7). Secondly, the efficiency of coupling between the coil and plasma has been shown (64) to be dependent on frequency:
\[ \eta_p = \frac{P_{\text{plasma}}}{P_{\text{coil}}} = 16\sqrt{2} \pi^2 n^2 \sqrt{\frac{\sigma_c}{\sigma_p}} r_c r_p \cdot \ln \left( \frac{r_c}{s} \right) \]  

where \( P \) = power
\( n \) = turns per unit length of coil
\( \sigma_c \) = elect. conductivity of coil material
\( \sigma_p \) = " " " plasma gas
\( r_c \) = radius of coil
\( r_p \) = " " plasma column
\( s \) = skin depth

It will be seen that \( \eta_p \) is dependent on the fixed dimensions of the coil and a function of \((r/s)_p\) which is frequency-dependent. The variation of energy transfer efficiency \( \eta_p \) from the coil to the plasma with frequency is shown in Fig. 8. It can be seen that the efficiency increases rapidly from \( 10^{-3} \) at \( 10^5 \) Hz to an asymptotic maximum of \( \sim 0.7 \) at \( 10^7 \) Hz. Further increase of frequency does not increase the efficiency.

By comparison of Fig. 7 with 8 it is apparent that these two frequency dependencies are opposing and an optimum condition must be reached for satisfactory plasma operation.

3.22 Coil Design

The frequency of operation of plasmas at the 30 KW power level is restricted to a range of 1-10 MHz by the commercial generators that are available. In this work a Radyne RD/360 30 KW r.f. generator was used which operated in a frequency range of 2-7 MHz. Within this range, the frequency could only be varied by the inductive circuit. The skin depth for argon plasmas in this range of frequencies can be
calculated from equation (4), where $\rho_{\text{argon}} = 0.03 \text{ ohm cm}$ (207).

\[
f = 2 \text{ MHz}: \quad S_2 = \frac{1}{2\pi \sqrt{\frac{0.03}{10^{-9} \times 2 \times 10^6}}} = 0.40 \text{ cm}
\]

\[
f = 7 \text{ MHz}: \quad S_7 = \frac{1}{2\pi \sqrt{\frac{0.03}{10^{-9} \times 7 \times 10^6}}} = 0.32 \text{ cm}
\]

For an even power density distribution within the plasma the skin depth should be at least half the radius of the plasma column (64). Therefore the corresponding plasma diameters are 1.6 cm and 1.2 cm respectively. Allowing for plasma containment by a flowing gas sheath or vortex, the torch wall should be slightly larger than the plasma, say 1.5 cm and 2.0 cm for 7 MHz and 2 MHz operation respectively. The skin depth can be increased considerably, however, by using gas with higher electrical resistivity. For hydrogen say, with a resistivity of 0.6 ohm-cm (207), the skin depth for a frequency of $2 \times 10^6$ Hz will be:

\[
S = \frac{1}{2\pi \sqrt{\frac{0.6}{2 \times 10^{-3}}}} = 1.7 \text{ cm}
\]

Hence the equivalent hydrogen plasma column diameter for maximum coupling efficiency would be 7 cms. It can be seen therefore that it is possible to operate a plasma at maximum coupling efficiency at a fixed frequency by choice of a suitable resistive load and torch diameter.

The coil inductance $L$ is related to the operating frequency by the formula for resonance in a series impedance circuit:

\[
f = \frac{1}{2\pi \sqrt{LC}} \quad \ldots \ldots (6)
\]
where \( f \) = frequency (Hz)
\[ L = \text{inductance of coil (}\mu\text{H}) \]
\[ C = \text{circuit capacitance (}\mu\text{F}) \]

The capacitor circuit installed in the RD360 Radyne generators is invariable and so fine adjustment of the output frequency can only be made by varying the work coil inductance.

The inductance of a coil is related to its physical dimensions by the formula (116):

\[
L = \frac{n^2 r_c^2}{10(23r_c+251)} \quad \ldots \ldots \ (7)
\]

where \( n \) = number of turns
\( r_c \) = coil radius (mm)
\( l \) = axial coil length (mm)
\( L \) = inductance (\( \mu \text{H} \))

The value of inductance required for operation at any frequency can be obtained from equation (6) if a value for the overall capacitance of the network of condensers can be estimated. However, each condenser has fairly large tolerance (\( \pm 10\% \)) and it is usually very difficult to obtain an accurate value of circuit capacitance.

However, the diameter of the coil itself can be chosen in the light of the preceding discussion. In this work radial torch dimensions of 2.5 cm internal diameter and 3.5 cm external diameter were used with an internal coil radius of 4.0 cm. The coil length was then determined empirically by measurement of the frequency obtained for various coils.
Operation at a frequency of $2 \times 10^6$ Hz was found to give optimum performance of the reactor under load and this frequency was obtained with a $5\frac{1}{2}$ turn work coil in series with a $4\frac{1}{2}$ turn coil, both in $\frac{3}{8}$" o.d. copper tubing. With this arrangement initiation of pure argon plasma was easily obtainable and a good coupling efficiency for pure BCl$_3$ was possible at flow rates to the torch in excess of 1.0 mole/min.

3.23 Torch designs

The design of r.f. torch used in the initial stages of this investigation was a simple air-cooled vortex-stabilised torch as shown in Fig. 9. The torch was constructed from 50 mm nom. bore transparent silica. A tangential inlet consisting of a short length of 6mm bore silica tubing was provided at one end for supply of gas to the coil region. Four silica side tubes (6mm bore) were also fixed to torch wall in quadrature at an angle to the torch axis as indicated in Fig. 9. These provided a means of injecting reactants to the tail region of the plasma as it passed out of the coil region. A means of sealing the torch to ancillary equipment had to be provided to prevent escape of boron and acid gases into the atmosphere. The torch was therefore tapered towards the opposite end to the tangential inlet and fitted with a short water-cooled silica cone, which was ground to match a silica socket, which was in turn incorporated in the inlet to the product collection apparatus. This design of plasma torch, together with ancillary apparatus is the subject of a recent patent specification (32) (Appendix 2).
Operation of this torch at low power levels 10 KW with argon gave an extremely stable plasma with a high coupling efficiency. Initiation of the plasma was possible by application of a low energy discharge from an external Tesla* coil. When power inputs of greater than 10 KW were used severe overheating of the silica occurred, however, and forced air cooling of the coil region was necessary. Operation with mixtures of argon, hydrogen and boron trichloride was also possible, and up to 40 mole% $\text{H}_2$ could be successfully run in the plasma gas at 18 KW. Operation at powers in excess of 20 KW, however, resulted in repeated electrical shorting of the r.f. coil which deposited copper on the outer surface of the silica tube. This deposition eventually led to mechanical fracture of the torch due to differential thermal expansion of the copper and silica. The electrical shorting (arc-out) of the coil is caused by breakdown of the dielectric (in this case, air) between the coil turns under operation when maximum voltages (5 kv) are approached. Arc-out has been prevented by the surrounding of the individual coil turns with a suitable dielectric materials such as a mineral insulating compound or boron nitride. In this case, however, the use of forced air cooling in the coil region prevented use of such a technique, and in fact increased the tendency to arc out because of insufficient drying of the compressed air supply which caused a relatively high water concentration in the air around the coil.

Hence, the main problems associated with this early torch were overheating at high power levels and the consequent necessity to force-air cool. Prolonged operation of the

*(trade name)*
torch under reactions was possible, however, and a maximum run period of 5 hours was achieved at 22 KW. When 1 mole/min BCl$_3$ was injected to the plasma 2 g/min of boron were formed at a H$_2$/BCl$_3$ ratio of 3:1. A problem associated with prolonged operation of the torch under reaction conditions was the growth of massive crystalline lumps of boron in the coil region of the torch. These growths could be of considerable size, sometimes approximating to the internal diameter of the torch. They drastically reduced coupling efficiency, by both destroying vortex flow and absorbing r.f. energy from the coil. Failure to remove the lumps of boron from the torch finally caused breakage of the torch wall due to diffusion of boron into the silica.

A further disadvantage of this torch design was the method used for sealing to ancillary apparatus. The ground silica cone at the end of the torch was water-cooled to prevent overheating, otherwise it might fuse to the socket at power levels approaching 20 KW. This led to a thermal gradient across the uncooled/cooled section of the torch. Differential thermal expansion occurred at this junction and caused the silica to crack. These accumulated problems were solved to a great extent by provision of a water cooling jacket along the complete length of the torch, except for the tangential gas inlet region, as illustrated in Fig. 10.

The external diameter of this water cooled torch was increased to 60 mm and a loss in coupling efficiency was observed. Energy losses to the cooling water occurred by both inductive heating of ionic species present in the cooling water, and convective heat transfer to the water
through the internal torch wall. These losses, however, amounted to less than 5% of the input energy. Initiation of argon plasmas could be obtained by application of a Tesla coil to the unjacketed portion of the torch near the argon inlet tube. Operation with mixtures of argon, hydrogen and BCl₃ at up to 30 KW was possible with increased yields of boron obtainable at lower H₂/BCl₃ ratios (viz: 3 g/min boron at H₂/BCl₃ of 2.5/1 with 25% conv. w.r.t. BCl₃). The growth of lumps of crystalline boron in the coil region was greatly reduced by these means, possibly due to a decrease in the number of active nucleation sites on the cooled inner surface of the plasma-containing wall. This torch design is also the subject of a patent application (App.No.60164/68).

The relatively complicated design of this torch with its gas injection and water-cooling side tubes increased the cost of fabrication substantially, and also increased the risk of accidental breakage. The torch was especially susceptible to mechanical breakage when the r.f. coil was wound into position, which on occasion caused excessive strain in the side-tubes as they passed between turns of the coil.

Efforts to overcome this problem led to the design of the plasma torch shown in Fig. 11 which was used for the bulk of the work reported here, and subsequently installed on the boron pilot plant. The plasma forming and reactant addition sections of the reactor were designed as separate units which could be compressively sealed together when in operation, but which could also be easily dismantled for
product collection or maintenance.

The silica plasma torch consists of a two-pass water channel with water inlet and outlet positioned at the same end of the torch as the plasma gas inlet. The torch was sealed to a brass tail injection manifold by axial compression onto a rubber gasket. This configuration enabled the silica torch to be separated easily from the coil and injection manifold. The external diameter of the torch was increased to 70 mm to accommodate the two water channels and a larger diameter coil was therefore necessary. The resultant loss in coupling efficiency was only marginal and argon plasma initiation was possible without the use of a Tesla coil, the carbon from the decomposed interior edge of the gasket supplying the initial electrons for the preplasma discharge. Pure boron trichloride plasmas were obtained when a 5½ turn coil of \( \frac{3}{8} \) in. od copper tube was used. Sufficient volume rate of \( \text{BCl}_3 \) was necessary, however, to provide fluid dynamic stabilisation of the plasma. The maximum hydrogen concentration which could be tolerated in this torch was as low as 20% mole, compared with the 40% possible in the uncooled torch.

Reactants were injected into the plasma tail via a water-cooled brass manifold, which also physically supported the plasma torch. The gas channel was connected to the interior of the reactor by eight \( \frac{1}{16} \) in. diam. ports, angled such that the injected reactants were initially directed in the reverse flow to the plasma gas. This reverse flow was intended to increase contact time between hot plasma gas
and tail reactant gas, and simultaneously provide effective mixing of reactants. The performance of this torch as a chemical reactor will be discussed in more detail in section 5.3. This torch has been in regular use in a pilot plant installation for producing boron and yields of up to 5 g/min boron have been obtained at 30 KW using a $\text{H}_2/\text{BCl}_3$ ratio of 5:1 with up to 2 moles/min of $\text{BCl}_3$ flow. Application for patent cover of this plasma reactor has been made (Appl.No.24495/70). Two further torches were tested and patented but were not used extensively in this work.

3.3 Laboratory Plasma Apparatus

3.3.1 Design of apparatus

Fig. 12 shows the apparatus used for the laboratory investigation of the hydrogen reduction of $\text{BCl}_3$ in a radio-frequency plasma discharge. The tail reactant injection ring was compressively sealed to a flange at one end of a vertical brass tube (4" diam. x 5' long) which was positioned underneath the work coil so that the top face of the injection ring was 1 cm from the lowest turn of the coil, and the axis of tube in line with the axis of the coil. Both coil and tube were supplied with cooling water, the former from the same closed circuit recirculation system that cooled the Radyne generator. The water-cooled brass tube provided a suitable quench volume for the hot reaction products, before the boron filtration stage. The lower end of the quench tube was flanged to match a standard 4" id Q.V.F.* Buttress fitting. Above this flange a 1" outlet tube (copper) was brazed to the quench tube which was in turn connected to a 4" diam. bag filter flange unit as shown in

* Trademark
Fig. 12. Two 4" diam. glass receivers with buttress ends, when sealed to the above flanges, provided the closed apparatus for the investigation of plasma reactions. The outlet from the bag filter flange was connected by 1" copper tube to a series of eight 4" cold fingers (see Fig. 13) in which unreacted BCl₃ was condensed from the outlet gas mixture at temperatures down to -60°C by acetone/cardice mixtures. The final outlet gas was fed to a water-scrubbing tower (which consisted of a 12' x 4" diam. glass column packed with 1/4 - 1/2" Raschig Rings) where the HCl gas dissolved in the water stream. The acid liquor so formed was neutralised with NaOH soln. and pumped to waste. Hydrogen and argon gases were released to atmosphere.

The boron powder was filtered from the gas mixture by a fine mesh polypropylene filter bag. In research runs various sizes of bags were used, from 1' long x 3" diam. to 3' long x 3" diam. depending on the capacity required. Argon and hydrogen gases (supplied by Air Products Ltd. and B.O.C. Ltd. respectively) were both dried before use over a molecular sieve (Union Carbide type 12A), and the hydrogen was also passed through a Deoxo unit (Englehart Ltd.) to remove O₂ impurities. Argon and hydrogen flow rates to the plasma reactor were controlled by standard gas flowmeters (G.A. Platon Ltd) with scales ranging up to 100 litre/min for argon and 240 litre/min for hydrogen. BCl₃, produced on site and stored in 65 kg lots, was transferred to 10 kg cylinders for research purposes. The BCl₃ was injected to the plasma by a gravity feed vapourisation
device consisting of a coil of \( \frac{3}{8} \)" od copper tube immersed in a thermostatically controlled water bath. Water temperatures of 70-80°C allowed up to 2 moles/min of BCl\(_3\) vapourisation. The feed rate of BCl\(_3\) to the plasma was controlled by a stainless steel needle valve separating the coil outlet and a standard A10 GAPmeter. The rate of feed of liquid BCl\(_3\) to the coil was dependent on the rate at which vapour was drawn off, reduction of the coil pressure allowing more liquid BCl\(_3\) to run from the storage cylinder to the coil. Constant BCl\(_3\) vapour rates up to 2 moles/min could be obtained with good reproducibility. Fig. 14 shows a comparison between BCl\(_3\) feed rates obtained under normal operating conditions, calculated from weight loss of feed cylinder and computed values of feed rate at N.T.P., as supplied by GAPmeter. Experimental figures are given for two flowmeters, and GAPmeter calibrations for three. These are in good agreement at low rates, but some scatter is evident at high rates.

3.3.2 Operation of laboratory apparatus

The apparatus was pressure tested to approx. 100 mm above atmospheric pressure before each run to avoid leakage of reactants into the laboratory. Accurate coaxial positioning of the plasma torch and work coil made it easier to initiate argon plasma. The apparatus was purged with argon for a few minutes before each run to clear BCl\(_3\) vapour from the feed lines. Application of a low r.f. voltage to the argon vortex in the torch then established a low energy "spiral" discharge (see Plate 1) spontaneously initiated by electron emission from the r.f.
heated carbon layer along the inner edge of the rubber gasket seal between torch and injection ring. A high energy argon plasma could then be established by increase of the r.f. voltage to 4 KV. Plate 2 shows the torch in operation on argon at 10 KW. Reactants were then introduced either into the plasma or tail according to the run conditions required. Runs were timed for the period of $\text{BCl}_3$ injection. Introduction of $\text{BCl}_3$ or $\text{H}_2$ into the plasma increased the resistance of the electrical load, and necessitated an increase in applied voltage to maintain the required current level. The power input for the plasma operation was taken as the product of coil voltage and current ($P = VcIc$) and was kept constant during a given run. Plate 3 shows an argon/$\text{BCl}_3$ plasma operating at 25 KW.

Mean $\text{BCl}_3$ feed rates were checked after each run by measurement of weight lost by the feed cylinder. A consistent feed rate was obtained by visual control of the float level in the flowmeter. A standard deviation of feed rate (g/min) of 1.98% was calculated for a series of eleven typical runs at the 30 g/min level. At the end of the required time period for the run the hydrogen and boron trichloride flow were stopped and the argon flow was reduced to a low purge level (~10 l/min). The boron product which had collected on the quench tube was dislodged into the powder receiver by a simple brushing technique. The total boron yield was collected and weighed.

Various safety precautions were taken during operation of the plasma apparatus. The torch itself was surrounded
by dark green perspex screens which absorbed intense and visible emission from the plasma. The enclosure also prevented accidental contact with the live r.f. coil in start up periods before plasma initiation. Ventilation ducts were also used which could be moved to various parts of the apparatus in the event of BCl$_3$ leakages.

3.4 Plasma Pilot Plant

Fig. 15 shows a schematic flow diagram of the boron pilot plant which was developed during this investigation. The plasma torch used was essentially the same as the research torch, except that a removable, water-cooled brass cap replaced the silica tangential arm (see Fig. 16). This cap had four tangential inlets to the plasma torch supplied by a gas manifold. The four tangential inlets provided a strong vortex flow pattern in the coil region which was beneficial at high power inputs to pure BCl$_3$ plasmas.

As the plant was normally operated for periods of up to 4-5 hours/shift, provision had to be made so that build-up of boron in the bag filter did not cause an unacceptable increase in pressure in the apparatus. Two bag filter units were therefore installed each containing a 6' long x 4" diam. polypropylene bag which was sufficiently large not to get blocked. Fig. 17 shows a pressure/time curve for boron buildup on a single 6' x 3" diam. bag. The maximum allowable operating pressure in the plant was dependent only on the torch/tail ring seal, and was usually limited to 10 cm Hg. The boron was collected on the outside surface of the filter bags and could be removed
in situ by the operator shaking the bag. The filter was prevented from collapse during operation by an internal spiral of stainless steel tube. When these support tubes were shaken the boron was dislodged from the filter surface and collected in narrow necked, thick walled glass receivers. After removal from the bag filter units these were rapidly sealed from the atmosphere. To obtain boron of maximum purity it was necessary to remove adsorbed gas from the surface of the boron before it was exposed to air. The collection flasks containing the boron were placed under a bell jar and pumped at ~0.1 mm Hg for 1-2 hours. The system was let up to atmospheric pressure with argon and the flasks resealed. Boron purities of ~99% boron were obtained (see Section 3.51).

Condensation of boron trichloride from the effluent gas mixture (which contained argon, hydrogen and hydrogen-chloride) was achieved in the early stages of development by a series of eight 4" diam. pyrex cold finger condensers arranged in two parallel flows and containing cardice/ acetone. Fig. 13 shows the arrangement of the cold fingers and the path of gases through them. The positions where temperature measurements were made to check the efficiency of gas cooling are also indicated. Fig. 18 shows the temperature profile against time that was obtained by continuous monitoring of the condenser temperatures with ten thermocouples connected to a multipoint recorder. It can be seen that a minimum temperature of -60°C was obtained in the final stage. A mathematical model was constructed of the condensation of BCl_3 from the non-condensable gases in order to predict condensation efficiencies for temperatures down to -100°C.
This model is presented in Appendix 3. Fig 19 shows computed overall process efficiencies against decreasing condensation temperature for a standard operating condition. Up to 70% efficiency of BCl$_3$ conversion to boron was obtained on the pilot plant at a condensation temperature of -60°C with recycle of unreacted BCl$_3$. This can be seen to be in good agreement with the model.

3.5 Analytical Methods

3.5.1 Boron Analysis

Total boron contents of samples prepared in the plasma were analysed by the sodium carbonate fusion method (217, 218). This consists of the fusion of 0.1g sample with 0.2g anhydrous sodium carbonate at 1000°C in a platinum crucible to give sodium borate. The fused melts were leached with 20% hydrochloric acid and barium carbonate added to precipitate any interfering species. Excess acid was then brought to pH 5 with sodium hydroxide solution with methyl red as indicator. Under these conditions the borate exists as boric acid which behaves as a weak monobasic acid ($K_a = 5.8 \times 10^{-10}$) and cannot therefore be titrated with standard alkali. Instead it is complexed with Mannitol reagent which transforms it to a relatively strong monobasic acid:

\[
\begin{align*}
\text{HO} - \text{B} - \text{OH} + \text{HO} & \rightarrow \text{HO} - \text{B} - \text{OH} + \text{H}_2\text{O} \\
\text{HO} - \text{B} - \text{OH} + \text{HO} & \rightarrow \text{HO} - \text{B} - \text{OH} + \text{H}_2\text{O}
\end{align*}
\]

This can be titrated against sodium hydroxide with phenolphthalein indicator.

The above method is considered best for analysis of total boron content in such things as borides, but is less
satisfactory for determinations of purities of boron in the 98-100% range. For example, boron samples (Run 176) were analysed after degassing and the following results were obtained by two different operators:

A. 99.1, 99.0, 98.4, 98.6% B; \( \sigma_A = 0.7% \)
B. 98.4, 98.5, 99.8, 99.0% B; \( \sigma_B = 1.6% \)

Analyses were repeated by one operator using an E.I.I. Electrometer for titration and yielded the following results:

99.7, 98.5, 98.3, 98.6, 99.3% B; \( \sigma_B = 1.4% \)

All reasonable precautions with respect to sample homogeneity, dryness and analytical procedure were taken to ensure the greatest accuracy. In view of the above discrepancies the only realistic conclusion to be drawn from this method of analysis of total boron is that the samples contained greater than 98% boron.

Analysis of total impurity content of the samples gave reliable figures for chlorine (< 0.1%), carbon (< 0.1%) and silica (< 0.05%), but not oxygen. Oxygen present as boric acid or boric oxide \( \text{B}_2\text{O}_3 \) can be estimated by extraction with anhydrous methanol. These materials might be formed by hydrolysis of adsorbed \( \text{BCl}_3 \) on contact with atmospheric moisture. Oxygen present as boron suboxides \( \text{B}_6\text{O} \) or \( \text{B}_7\text{O} \), however, would not be detected by these means and such substances could conceivably be formed in the plasma reduction. Two samples of boron were analysed on an AEI MS8 spark source mass spectrometer, one having been taken before and the other after the vacuum degassing process. The results are shown in Table VII. Comparison of impurities present after these two handling procedures indicates that:
### TABLE VII

**Major Impurities in Plasma Boron**

<table>
<thead>
<tr>
<th>Major impurity</th>
<th>Undegassed boron (ppm.Atom.)</th>
<th>% by wt.</th>
<th>Degassed boron (ppm.Atom.)</th>
<th>% by wt.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copper</td>
<td>15</td>
<td>0.0088</td>
<td>2</td>
<td>0.0012</td>
</tr>
<tr>
<td>Titanium</td>
<td>10</td>
<td>0.0044</td>
<td>2.8</td>
<td>0.0012</td>
</tr>
<tr>
<td>Calcium</td>
<td>10</td>
<td>0.0037</td>
<td>6</td>
<td>0.0022</td>
</tr>
<tr>
<td>Chlorine</td>
<td>3000</td>
<td>0.9800</td>
<td>24</td>
<td>0.0081</td>
</tr>
<tr>
<td>Magnesium</td>
<td>3</td>
<td>0.0007</td>
<td>60</td>
<td>0.0120</td>
</tr>
<tr>
<td>Silica</td>
<td>300</td>
<td>0.0800</td>
<td>20</td>
<td>0.0310</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>60</td>
<td>0.0078</td>
<td>2000</td>
<td>0.2590</td>
</tr>
<tr>
<td>Oxygen</td>
<td>5000</td>
<td>0.7400</td>
<td>5000</td>
<td>0.7400</td>
</tr>
<tr>
<td>Bromine</td>
<td>3</td>
<td>0.0022</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Carbon</td>
<td>600</td>
<td>0.0700</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Aluminium</td>
<td>100</td>
<td>0.0250</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Sulphur</td>
<td>60</td>
<td>0.0178</td>
<td>2</td>
<td>0.0006</td>
</tr>
<tr>
<td>Sodium</td>
<td>10</td>
<td>0.0021</td>
<td>6</td>
<td>0.0013</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td></td>
<td>1.9425</td>
<td></td>
<td>1.0566</td>
</tr>
<tr>
<td><strong>Purity by difference</strong></td>
<td></td>
<td>98.06% B</td>
<td></td>
<td>98.94% B</td>
</tr>
</tbody>
</table>
a) vacuum degassing to 0.1 mm Hg pressure reduced adsorbed chlorine from 0.98 → 0.01% w/w

b) adsorbed nitrogen content increased from 0.01% → 0.26% w/w when the boron was exposed to air after vacuum degassing. The maximum boron purity (obtained by difference) was 98.94%. Vacuum degassing did not alter the oxygen content of the boron (0.5% w/w).

3.52 Boron Trichloride Analysis

BCl$_3$ samples were examined for HCl content and other impurities on a Perkin-Elmer No. 337 infra-red absorption spectrophotometer. A calibration curve relating HCl content to 2930cm$^{-1}$ and 2850cm$^{-1}$ peak heights was prepared by hydrolysis of known weights of pure boron trichloride by known weights of water. The HCl content of the BCl$_3$ varied between 0.1 and 0.3% w/w. A number of samples were analysed on an AEI MS 12 mass spectrometer and results are shown in Fig. 20. These analyses also enabled the cracking pattern of BCl$_3$ to be established. The following molecular and ionic species derived from BCl$_3$ were present in the mass spectrum:

<table>
<thead>
<tr>
<th>IONS</th>
<th>Intensity</th>
<th>MOLECULES</th>
<th>Intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>B$_{10}^+$</td>
<td>4</td>
<td>B$_2$Cl$_6$</td>
<td>2</td>
</tr>
<tr>
<td>B$_{11}^+$</td>
<td>7</td>
<td>B$_3$Cl$_5$</td>
<td>1</td>
</tr>
<tr>
<td>Cl$_{1}^+$</td>
<td>5</td>
<td>B$_4$Cl$_4$</td>
<td>2</td>
</tr>
<tr>
<td>Cl$_{2}^+$</td>
<td>9</td>
<td>B$_4$Cl$_6$</td>
<td>5</td>
</tr>
<tr>
<td>BCl$_{1}^+$</td>
<td>9</td>
<td>B$_7$Cl$_6$</td>
<td>6</td>
</tr>
</tbody>
</table>

cont'd
<table>
<thead>
<tr>
<th>IONS</th>
<th>Intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{BCl}_2^+$</td>
<td>12</td>
</tr>
<tr>
<td>$\text{BCl}_2^{++}$</td>
<td>7</td>
</tr>
<tr>
<td>$\text{BCl}_3^+$</td>
<td>10</td>
</tr>
<tr>
<td>$\text{B}_2\text{Cl}_5^+$</td>
<td>5</td>
</tr>
<tr>
<td>$\text{B}_2\text{Cl}_5^{++}$</td>
<td>5</td>
</tr>
<tr>
<td>$\text{B}_2\text{Cl}_6^+$</td>
<td>1</td>
</tr>
</tbody>
</table>

The intensities are taken for the highest peaks for each species relative to the maximum intensity of 12 for $\text{BCl}_2^+$. The predominant ions present in the cracking pattern of $\text{BCl}_3$ at 8 KV in the mass spectrometer were found to be the following:

$\begin{align*}
\text{BCl}_2^+ & \quad \text{12 intensity} \\
\text{BCl}_3^+ & \quad \text{10} \\
\text{BCl}^+ & \quad \text{9} \\
\text{Cl}^+ & \quad \text{9} \\
\text{Cl}_2^+ & \quad \text{6}
\end{align*}$

Low concentrations of boron subchlorides, such as $\text{B}_4\text{Cl}_4$, $\text{B}_2\text{Cl}_6$, $\text{B}_4\text{Cl}_6$ which were also found in the mass spectrum could confirm their presence in the $\text{BCl}_3$ itself. However, this is by no means certain as the subchlorides could have been formed by cracking reactions in the mass spectrometer.

Total non-volatiles in the $\text{BCl}_3$ were estimated at $\sim 0.1\%$ w/w from weight remaining after evaporation.

### 3.53 Boron Powder Studies

Mean particle size of the boron powder was determined on a Fisher Sub-sieve sizer by measurement of the porosity of compressed pellets for a standard pressure and volume of pellet.
Surface area of boron was measured on a Coulter Micrometrics Surface Area Analyser, Model 2200. Samples were degassed at 150°C for 40 minutes prior to analysis, and the surface area obtained by a gas adsorption technique.

X-ray diffraction patterns of the boron were obtained by use of a Philips PW 1050 X-ray diffractometer and also a Philips X-ray 114 mm camera using Cukα tube.

Electron diffraction patterns of boron particles were obtained by use of the transmission mode of an AEI EM6G Electron Microscope. The samples were prepared by the carbon extraction replica technique(243,244). The results of these measurements are presented in Section 4.3.

3.54 BCl₃ Plasma Spectroscopy

The emission spectrum of BCl₃ plasma was examined photographically using a Hilger Medium Quartz spectrograph with Kodak B10 U.V. plates and Ilford Long Range Plates (4" x 10").

The spectrograph was first calibrated with arc discharges of pure copper, iron and graphite to enable the instrument to be correctly focussed and to give standard spectra. The optical arrangement for study of emission from the r.f. plasma torch is shown in Fig. 21.

Calibration for exposure times for various operating power levels and gas mixtures was carried out and then the spectra of gas mixtures at various positions in the plasma were photographed.

Scanning of the plasma at discrete radial or axial positions could be achieved by collimation of the emitted light by adjustment of a pinhole mounted in a rack and pinion system before it was focused on the spectrograph slit.
CHAPTER 4

EXPERIMENTAL RESULTS
4.1 Kinetic Studies

4.1.1 Effect of initial BCl$_3$ concentration

The effect of variation of the initial concentration of BCl$_3$ at constant initial hydrogen concentration was determined by injection of high levels of hydrogen into the tail of an argon, boron trichloride plasma, using the reactor shown in Fig. 11. The decrease in conversion with increasing [BCl$_3$]$_0$ is shown in Fig. 22 for two residence times. Table VIII shows the operating conditions for the runs. Residence time T was calculated as the ratio of reactor volume V to the total gas flow ($F_T$) into the reactor or $T = \frac{V}{F_T}$. Hence for a constant volume (5 cm x 20 cm long) reactor, as used in this work, the residence time is $\propto \frac{1}{F_T}$. This is not necessarily related to the time spent by the Ar/BCl$_3$ mixture in the plasma.

(Volume of reactor = 400 x 10$^{-3}$ litre

\[ T = \frac{1}{F_T} \times 400 \times 10^{-3} \times 60 = 24.0 \times 1 \text{ (secs)} (F_T \text{ in lit/min}) \]

For a fixed initial H$_2$ concentration [H$_2$]$_0$ of 0.03 gmole/litre (an excess) the conversion of BCl$_3$ to boron decreased linearly with increasing [BCl$_3$]$_0$ at 0.17 sec residence time. The decrease would appear to be non-linear, however, at the shorter residence times of 0.072 sec. At constant [H$_2$]$_0$ and residence time the conversion of BCl$_3$ to boron increased linearly with H$_2$/BCl$_3$ ratio as shown in Fig. 23 for T = 0.072 min/litre. However, at longer residence times the increase in conversion of BCl$_3$ reached a maximum of $\sim$60% at H$_2$/BCl$_3$ = 12, as shown in Fig. 25.
### Constant Hydrogen Runs

\[ [\text{H}_2]_0 = 0.03 \ \text{g.moles/litre} \]

<table>
<thead>
<tr>
<th>Plasma Argon (l/m)</th>
<th>Tail H(_2) (l/m)</th>
<th>Plasma BCl(_3) (g/m)</th>
<th>Initial BCl(_3) conc (g.mole/litre)</th>
<th>(\text{H}_2/\text{BCl}_3) mole ratio</th>
<th>BCl(_3)% conv.</th>
<th>Yield of Boron (g/m)</th>
<th>(T') (sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>48</td>
<td>240</td>
<td>43</td>
<td>1.20</td>
<td>25</td>
<td>81</td>
<td>3.2</td>
<td>0.0741</td>
</tr>
<tr>
<td>42</td>
<td>240</td>
<td>65</td>
<td>1.88</td>
<td>18</td>
<td>57.5</td>
<td>3.45</td>
<td>0.0540</td>
</tr>
<tr>
<td>42</td>
<td>240</td>
<td>86</td>
<td>2.38</td>
<td>15</td>
<td>49</td>
<td>3.5</td>
<td>0.0405</td>
</tr>
<tr>
<td>35</td>
<td>240</td>
<td>118</td>
<td>3.25</td>
<td>11</td>
<td>37.6</td>
<td>4.1</td>
<td>0.0326</td>
</tr>
<tr>
<td>27</td>
<td>240</td>
<td>153</td>
<td>4.24</td>
<td>8.5</td>
<td>28.5</td>
<td>4.0</td>
<td>0.0228</td>
</tr>
<tr>
<td>20</td>
<td>240</td>
<td>196</td>
<td>5.44(\times 10^{-3})</td>
<td>6.6</td>
<td>22.2</td>
<td>4.0</td>
<td>0.0178</td>
</tr>
</tbody>
</table>

**Power 25 kW**

\((T = 0.072 \ \text{sec})\)

<table>
<thead>
<tr>
<th>Plasma Argon (l/m)</th>
<th>Tail H(_2) (l/m)</th>
<th>Plasma BCl(_3) (g/m)</th>
<th>Initial BCl(_3) conc (g.mole/litre)</th>
<th>(\text{H}_2/\text{BCl}_3) mole ratio</th>
<th>BCl(_3)% conv.</th>
<th>Yield of Boron (g/m)</th>
<th>(T') (sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>100</td>
<td>30</td>
<td>0.0019</td>
<td>18</td>
<td>57</td>
<td>1.55</td>
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<td>100</td>
<td>45</td>
<td>0.0028</td>
<td>11.7</td>
<td>54</td>
<td>2.2</td>
<td>0.0775</td>
</tr>
<tr>
<td>30</td>
<td>100</td>
<td>70</td>
<td>0.0042</td>
<td>7.4</td>
<td>42</td>
<td>2.6</td>
<td>0.0500</td>
</tr>
<tr>
<td>30</td>
<td>100</td>
<td>90</td>
<td>0.0052</td>
<td>5.25</td>
<td>28.4</td>
<td>2.6</td>
<td>0.0388</td>
</tr>
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<td>30</td>
<td>100</td>
<td>130</td>
<td>0.0071</td>
<td>4.1</td>
<td>21.8</td>
<td>2.6</td>
<td>0.0269</td>
</tr>
<tr>
<td>30</td>
<td>100</td>
<td>145</td>
<td>0.0078</td>
<td>3.6</td>
<td>19</td>
<td>2.5</td>
<td>0.0241</td>
</tr>
</tbody>
</table>

**Power 25 kW**

\((T = 0.170 \ \text{sec})\)

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<tr>
<th>Plasma Argon (l/m)</th>
<th>Tail H(_2) (l/m)</th>
<th>Plasma BCl(_3) (g/m)</th>
<th>Initial BCl(_3) conc (g.mole/litre)</th>
<th>(\text{H}_2/\text{BCl}_3) mole ratio</th>
<th>BCl(_3)% conv.</th>
<th>Yield of Boron (g/m)</th>
<th>(T') (sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>33</td>
<td>34</td>
<td>10.8</td>
<td>0.092/69 = 0.000134</td>
<td>16.3</td>
<td>61.0</td>
<td>16.0</td>
<td>0.324</td>
</tr>
<tr>
<td>33</td>
<td>34</td>
<td>25.8</td>
<td>0.22/72 = 0.00033</td>
<td>6.8</td>
<td>37.4</td>
<td>0.184</td>
<td>0.155</td>
</tr>
<tr>
<td>33</td>
<td>34</td>
<td>30.3</td>
<td>0.26/73 = 0.00036</td>
<td>5.8</td>
<td>30.0</td>
<td>0.155</td>
<td>0.0945</td>
</tr>
<tr>
<td>33</td>
<td>34</td>
<td>37.2</td>
<td>0.32/75 = 0.000425</td>
<td>4</td>
<td>24.4</td>
<td>0.077</td>
<td>0.0420</td>
</tr>
<tr>
<td>33</td>
<td>34</td>
<td>46.0</td>
<td>0.4/76 = 0.000525</td>
<td>3.8</td>
<td>21.0</td>
<td>0.0420</td>
<td></td>
</tr>
<tr>
<td>33</td>
<td>34</td>
<td>83.0</td>
<td>0.71/83 = 0.00085</td>
<td>2.1</td>
<td>13.0</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Power 20 KW**
4.12 Effect of initial hydrogen concentration $[H_2]_0$

To determine the effect of initial $H_2$ concentration on the conversion of $BCl_3$ to boron, several series of runs were carried out at increasing $[H_2]_0$ while holding the $[BCl_3]_0$ constant for chosen 'black box' residence times (see 4.13). Table IX shows the operating conditions at which the runs were carried out. Hydrogen was injected into the tail of argon-$BCl_3$ plasmas in the mode already described and power levels were maintained as near as possible to 25 kW. Experimental results are shown in Fig. 24 and included in Table IX. From these results it is apparent that increases in initial hydrogen concentration do not have a great effect on $BCl_3$ conversions. The greatest increase in conversion was obtained for the longest residence time $T = 0.264$ sec where for a 300% increase in $[H_2]_0$ (from 0.01 to 0.04 gmoles/litre) a 20% increase in conversion occurred. At the shorter residence times, not only were the overall conversions consistently lower ($0.144$ sec: 5% lower than $T = 0.264$ sec and $0.096$ sec: 10% lower than $0.264$ sec), but large increases in $[H_2]_0$ had little effect on $BCl_3$ conversions e.g. at $T = 0.096$ sec residence time, a 100% increase in $[H_2]_0$ caused only approx. 5% increase in conversion.

Operation at constant total volume rate during these runs, to enable concentration variation to be studied without the influence of residence time variation, necessitated significant changes in the ratio of gas flowing into the tail of the plasma (in a backmixing mode) and the plasma gas flowing through the coil region of the torch.
Values of $\gamma$ in the above series of runs varied from 0.2 at $[H_2]_0 = 0.0074$ gmole/litre to 3.3 at $[H_2]_0 = 0.0334$ gmole/litre. The influence of increased $\gamma$ values on the conversions will be discussed at a later stage in the thesis.

4.13 Effect of residence time

The effect of residence time of reactants in the torch (as defined by $T = \text{ratio of torch volume/total gas flow}$) on the conversion of $\text{BCl}_3$ to boron for a series of runs where both $[H_2]_0$ and $[\text{BCl}_3]_0$ were kept constant has been investigated. Fig. 26 shows the results obtained for $\text{BCl}_3$ conversion with increasing residence times for constant composition mixtures. The operating conditions for each run are shown in Table X together with the tabulated results. For a $[\text{BCl}_3]_0$ of 0.004
### TABLE IX

**Constant BCl₃ runs**

<table>
<thead>
<tr>
<th>([H_2]_0) (\text{g moles/} \text{litre})</th>
<th>(T_1 = 0.096 \text{ sec})</th>
<th>(T_2 = 0.144 \text{ sec})</th>
<th>(T_3 = 0.264 \text{ sec})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Argon (1/\text{m})</td>
<td>(H_2 \text{ (1/\text{m})})</td>
<td>Argon (1/\text{m})</td>
<td>(H_2 \text{ (1/\text{m})})</td>
</tr>
<tr>
<td>0.0074</td>
<td>-</td>
<td>-</td>
<td>133</td>
</tr>
<tr>
<td>0.0113</td>
<td>-</td>
<td>-</td>
<td>118</td>
</tr>
<tr>
<td>0.0151</td>
<td>-</td>
<td>-</td>
<td>103</td>
</tr>
<tr>
<td>0.0185</td>
<td>132</td>
<td>114</td>
<td>88</td>
</tr>
<tr>
<td>0.0222</td>
<td>110</td>
<td>137</td>
<td>73</td>
</tr>
<tr>
<td>0.0260</td>
<td>86</td>
<td>160</td>
<td>57</td>
</tr>
<tr>
<td>0.0300</td>
<td>63</td>
<td>183</td>
<td>42</td>
</tr>
<tr>
<td>0.0334</td>
<td>40</td>
<td>205</td>
<td>27</td>
</tr>
<tr>
<td>(BCl_3) (\text{g/min})</td>
<td>120</td>
<td>80</td>
<td>40</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>([H_2]_0) (\text{g moles/} \text{litre})</th>
<th>(T=0.096)</th>
<th>(T=0.114)</th>
<th>(T=0.264)</th>
</tr>
</thead>
<tbody>
<tr>
<td>% Conv</td>
<td>% Conv</td>
<td>% Conv</td>
<td>% Conv</td>
</tr>
<tr>
<td>(BCL_3)</td>
<td>(Yield)</td>
<td>(Boron\ (\text{(g/min)})</td>
<td>(Yield)</td>
</tr>
<tr>
<td>0.0074</td>
<td>-</td>
<td>-</td>
<td>25.8</td>
</tr>
<tr>
<td>0.0113</td>
<td>-</td>
<td>-</td>
<td>33.3</td>
</tr>
<tr>
<td>0.0151</td>
<td>-</td>
<td>-</td>
<td>32.8</td>
</tr>
<tr>
<td>0.0185</td>
<td>28.7</td>
<td>3.25</td>
<td>32.3</td>
</tr>
<tr>
<td>0.0222</td>
<td>31.4</td>
<td>3.36</td>
<td>39.0</td>
</tr>
<tr>
<td>0.0260</td>
<td>32.6</td>
<td>3.5</td>
<td>42.5</td>
</tr>
<tr>
<td>0.0300</td>
<td>30.4</td>
<td>3.4</td>
<td>42.7</td>
</tr>
<tr>
<td>0.0334</td>
<td>33.0</td>
<td>3.4</td>
<td>45.5</td>
</tr>
</tbody>
</table>

Power = 25 KW  \([BCl_3]_0 = 0.004 \text{ gmole/l. throughout}\)
### TABLE X
Residence Time Effects

#### Operating Conditions

<table>
<thead>
<tr>
<th>BCl₃ rate (g/min)</th>
<th>1/min</th>
<th>H₂/BCl₃ mole ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>2</td>
</tr>
<tr>
<td>Argon l/min</td>
<td>Hydrogen l/min</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>4.0</td>
<td>33.4</td>
</tr>
<tr>
<td>30</td>
<td>5.5</td>
<td>50</td>
</tr>
<tr>
<td>40</td>
<td>7.5</td>
<td>65</td>
</tr>
<tr>
<td>50</td>
<td>9.5</td>
<td>83.5</td>
</tr>
<tr>
<td>80</td>
<td>15.0</td>
<td>13.3</td>
</tr>
<tr>
<td>120</td>
<td>23.0</td>
<td>-</td>
</tr>
</tbody>
</table>

**H₂ conc. (g.mole/litre)**

- 0.0074
- 0.015
- 0.033

**R.F. Power Input = 25 kW**

**Constant BCl₃ concentration of 0.004 gmole/litre.**

#### Experimental Results

<table>
<thead>
<tr>
<th>BCl₃ rate (g/min)</th>
<th>Total gas flow (l/min)</th>
<th>Ratio 2</th>
<th>Ratio 4</th>
<th>Ratio 9</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>% conv</td>
<td>g.B/min</td>
<td>% conv</td>
<td>g.B/min</td>
</tr>
<tr>
<td></td>
<td>T sec</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>45</td>
<td>35.6</td>
<td>0.65</td>
<td>52</td>
</tr>
<tr>
<td>30</td>
<td>67</td>
<td>33.3</td>
<td>0.94</td>
<td>50.7</td>
</tr>
<tr>
<td>40</td>
<td>88</td>
<td>32.2</td>
<td>1.17</td>
<td>40.5</td>
</tr>
<tr>
<td>50</td>
<td>111</td>
<td>25.6</td>
<td>1.19</td>
<td>35.8</td>
</tr>
<tr>
<td>80</td>
<td>180</td>
<td>25.8</td>
<td>2.0</td>
<td>32.8</td>
</tr>
<tr>
<td>120</td>
<td>270</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
gmol/litre variation of conversion to boron has been investigated for three values of $[H_2]_0 = 0.0074$, 0.0151 and 0.0334 gmoles/litre. For the low $[H_2]_0$ only a 10% increase in conversion of BCl$_3$ was observed for a four-fold increase in residence time. Greater increases in conversion were obtained, however, at the higher $[H_2]_0$ values. The results are summarised below:

<table>
<thead>
<tr>
<th>$[H_2]_0$ gmoles/litre</th>
<th>$\Delta T$ sec</th>
<th>Limits % Conversion (lower/upper)</th>
<th>Increase in Conversion %</th>
<th>$\Delta X / \Delta T$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0074</td>
<td>0.432</td>
<td>25 / 35</td>
<td>10</td>
<td>0.023</td>
</tr>
<tr>
<td>0.0151</td>
<td>0.432</td>
<td>32 / 55</td>
<td>23</td>
<td>0.053</td>
</tr>
<tr>
<td>0.0334</td>
<td>0.192</td>
<td>32 / 55</td>
<td>23</td>
<td>0.12</td>
</tr>
</tbody>
</table>

Fig. 27 shows the corresponding variation of moles of H$_2$ reacted with residence times. The conversions of H$_2$ were calculated from the stoichiometric equation BCl$_3$ + $\frac{3}{2}$ H$_2$ $\rightarrow$ B+3HCl.

Residence time of reactants in the plasma torch has up to now been defined simply as the ratio of reactor volume to total gas flow:

$$T_r = \frac{V_r}{F_T} \text{ sec}$$

The concept of residence time in a flow system where gases are being injected at two different points is not precise, especially in view of the backmixing effect ($\gamma$ ratio) which was mentioned in the last section. The above residence time $T$ can be used if the system is regarded as a stirred reactor. Other definitions of residence time are necessary to take account of the positions of injection of reactants and which of them pass through the plasma. In section 2 of this chapter results were described.
for runs at constant \( H_2 \) concentration where a fixed \( H_2 \) flow was injected in the tail and increasing BCl\(_3\) flow rates were injected into the plasma. In this circumstance if the above residence time concept is used the runs are virtually at constant residence time. However, if the residence time is taken as \( T' \propto \frac{1}{BCl_3 \text{ rate}} \), which is the residence time of a single reactant in the plasma, then other information on the behaviour of the system can be obtained.

\[
T' = \text{Volume of reactor} = 400 \times 10^{-3} \times 117 \times 22.4 = \frac{1}{M_{BCl_3}} \times 0.35 \text{ sec.}
\]

Fig. 28 shows the variations of BCl\(_3\) conversion for a \([H_2]_0 = 0.03 \text{ g moles/litre}\) run plotted as a function of \( T' \)(curve A < B). It can be seen that the conversion of BCl\(_3\) increases linearly with increasing \( T' \) up to conversion \( \sim 50\% \), whereas if the previous definition of residence time had been used there would be no significant variation of residence time over the range used, due to the high \( H_2 \) levels. The initial linear variations are summarised below as \% conversion BCl\(_3\)/sec:

\[
\left( \frac{\Delta x_{B}}{\Delta T'} \right)_{100} = 0.65/\text{sec}^{-1}; \quad \left( \frac{\Delta x_{B}}{\Delta T'} \right)_{240} = 0.95/\text{sec}^{-1}
\]

A similar residence time \( T' \) has also been used to analyse the results of a series of runs in which premixed BCl\(_3\) and hydrogen at stoichiometry were injected into the tail of an argon plasma in a non-backmixing mode. Fig. 28(D) shows the linear increase of BCl\(_3\) conversion with increasing \( T' \) (\( \propto \frac{1}{(BCl_3+H_2)_T} \)). The operating conditions and results are shown in Table XI below:
4.14 Effect of variation of feed configuration

It is possible to carry out the reduction of boron trichloride with hydrogen in the plasma reactor shown in Fig. 11 in a number of different ways. For example, BCl$_3$ and hydrogen can be premixed and injected to the tail of an argon plasma or the BCl$_3$ can be injected into the plasma with or without argon and reduced with tail hydrogen. Also up to 20% mole H$_2$ can be added to the plasma gas if required. The effects of such changes in feed configuration on the conversions of BCl$_3$ to boron were studied for a series of runs at constant power level (20KW), residence time $T = 0.36$ sec and constant $[\text{BCl}_3]_0 = 0.004$ gmoles/litre. The four modes of reactant feeding are shown below:

<table>
<thead>
<tr>
<th>Plasma Gas</th>
<th>Tail Gas</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Argon</td>
<td>BCl$_3$ + H$_2$</td>
</tr>
<tr>
<td>2. Argon + 10% v/v H$_2$</td>
<td>BCl$_3$ + H$_2$ remainder</td>
</tr>
<tr>
<td>3. Argon + BCl$_3$</td>
<td>H$_2$</td>
</tr>
<tr>
<td>4. Argon + 10% v/v H$_2$ + BCl$_3$</td>
<td>H$_2$ remainder</td>
</tr>
</tbody>
</table>

The hydrogen used in the plasma was maintained at 10% v/v of the volume rate of plasma argon to give a consistent plasma load. The operating conditions used are shown in Table XII where $[\text{BCl}_3]_0$ can be seen to have been kept constant for increasing $[\text{H}_2]_0$ by decreasing the argon level.
<table>
<thead>
<tr>
<th>Series/Run</th>
<th>Plasma Argon (l/m)</th>
<th>Plasma H₂ (l/m)</th>
<th>Plasma BCl₃ (g/m)</th>
<th>Tail BCl₃ (g/m)</th>
<th>Tail H₂ (l/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>a</td>
<td>50</td>
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<td>-</td>
<td>30</td>
<td>11.4</td>
</tr>
<tr>
<td>b</td>
<td>45</td>
<td>-</td>
<td>-</td>
<td>30</td>
<td>17</td>
</tr>
<tr>
<td>c</td>
<td>39</td>
<td>-</td>
<td>-</td>
<td>30</td>
<td>23</td>
</tr>
<tr>
<td>d</td>
<td>33</td>
<td>-</td>
<td>-</td>
<td>30</td>
<td>28.5</td>
</tr>
<tr>
<td>e</td>
<td>27</td>
<td>-</td>
<td>-</td>
<td>30</td>
<td>34</td>
</tr>
<tr>
<td>2)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>a</td>
<td>50</td>
<td>5.0</td>
<td>-</td>
<td>30</td>
<td>6.4</td>
</tr>
<tr>
<td>b</td>
<td>45</td>
<td>4.5</td>
<td>-</td>
<td>30</td>
<td>12.5</td>
</tr>
<tr>
<td>c</td>
<td>39</td>
<td>3.9</td>
<td>-</td>
<td>30</td>
<td>19</td>
</tr>
<tr>
<td>d</td>
<td>33</td>
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<td>-</td>
<td>30</td>
<td>25</td>
</tr>
<tr>
<td>e</td>
<td>27</td>
<td>2.7</td>
<td>-</td>
<td>30</td>
<td>31</td>
</tr>
<tr>
<td>3)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>a</td>
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<td>-</td>
<td>30</td>
<td>-</td>
<td>11.4</td>
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<td>b</td>
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<td>-</td>
<td>30</td>
<td>-</td>
<td>17</td>
</tr>
<tr>
<td>c</td>
<td>39</td>
<td>-</td>
<td>30</td>
<td>-</td>
<td>23</td>
</tr>
<tr>
<td>d</td>
<td>33</td>
<td>-</td>
<td>30</td>
<td>-</td>
<td>28.5</td>
</tr>
<tr>
<td>e</td>
<td>27</td>
<td>-</td>
<td>30</td>
<td>-</td>
<td>34</td>
</tr>
<tr>
<td>4)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>a</td>
<td>50</td>
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<td>30</td>
<td>-</td>
<td>6.4</td>
</tr>
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<td>45</td>
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<td>-</td>
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</tr>
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<td>c</td>
<td>39</td>
<td>3.9</td>
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<td>-</td>
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</tr>
<tr>
<td>d</td>
<td>33</td>
<td>3.3</td>
<td>30</td>
<td>-</td>
<td>25</td>
</tr>
<tr>
<td>e</td>
<td>27</td>
<td>2.7</td>
<td>30</td>
<td>-</td>
<td>31</td>
</tr>
</tbody>
</table>
The results for each series of runs were plotted as variations of BCl$_3$ conversions with increasing initial hydrogen concentration and are shown in Fig. 29. The highest conversions were obtained when BCl$_3$ was injected to the plasma. They were only greater than the other modes by 10% throughout the range of [H$_2$]$_o$ used. The addition of H$_2$ to the plasma would appear to have little effect on the conversions obtained when BCl$_3$ was in the tail, or in the plasma. With BCl$_3$ and H$_2$ in the tail, the conversions rose to a maximum of ~37% which was again only slightly increased by 10% plasma H$_2$. For the BCl$_3$ runs without H$_2$ in the plasma the conversion reached a maximum of ~50% at 0.02 gmoles/litre [H$_2$]$_o$, while with plasma H$_2$ the conversion reached a slightly lower maximum of 45% at 0.015 gmoles/litre [H$_2$]$_o$.

For the runs with BCl$_3$ in the plasma at high [H$_2$]$_o$ levels, the effect of tail H$_2$ on the plasma was very noticeable, and the considerable backmixing of hydrogen into the coil region caused an increase in resistance of the plasma load which effected the power input. In some cases the decrease in current was great enough to overload the plasma and terminate the run prematurely. Thus the drop in conversion in the BCl$_3$ plasma runs at high H$_2$ flow rates could be due to insufficient coupling of the coil to a load made more resistive by hydrogen backmixing, or quenching of the plasma by backmixing hydrogen.

In order to eliminate the possible effect of backmixing of tail gases on the conversion, a new system of tail gas injection was installed, in which the gas was injected at
right angles to the axis of the torch instead of angled back into the coil region. Fig. 30 shows this method of tail gas injection. The distance 'x' between the end of the coil and the inlet ports was kept as near as possible equal to the backmixing method.

The effect of this method of tail gas injection was tested for one run condition ([H₂]₀ = 0.018 gmoles/litre) for each of the feed configurations described above.

The variation between normal injection and backmixed injection are summarised below:

<table>
<thead>
<tr>
<th>Feed configuration</th>
<th>With normal tail injection</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Argon plasma - BCl₃+H₂ tail</td>
<td>No change in conversion</td>
</tr>
<tr>
<td>2. Argon+10% H₂ plasma - BCl₃+H₂ tail</td>
<td>7% decrease in &quot;</td>
</tr>
<tr>
<td>3. Argon+BCl₃ plasma - H₂ tail</td>
<td>5% increase in &quot;</td>
</tr>
<tr>
<td>4. Argon+10% H₂+BCl₃ plasma -H₂ tail</td>
<td>No change in conversion</td>
</tr>
</tbody>
</table>

The mode of tail gas addition had a significant effect on conversion of BCl₃ to boron when either BCl₃ or 10% H₂ were added to the plasma. The former caused a slight increase and the latter a decrease in conversion. When BCl₃ and 10% H₂ were added together to the plasma the opposing effects cancelled out and no change in conversion occurred.

Two further series of runs were carried out to study the effect of normal tail injection in more detail. The conversions with increasing [H₂]₀ were determined for feed configurations 1 and 3. Figs. 31 and 32 show
the difference in conversions obtained for normally and backmixed tail gases for argon/BCl₃ plasma and argon plasma alone. When BCl₃ and H₂ were added to the tail of an argon plasma (Fig. 31) no change in conversion occurred when [H₂]₀ was increased from 0.0074 to 0.026 gmole/l, a constant value of ~36% being maintained.

However, when BCl₃ was present in the plasma (Fig. 32) higher conversions to boron were obtained with normal tail H₂ injection than with backmixed injection. The two curves converged with increasing [H₂]₀ to equal conversions at [H₂]₀ = 0.015 and then diverged to different maxima, the maximum conversion in the normal injection mode being 15% higher than the backmixed mode. The divergence of conversion at 0.015 gmole/litre [H₂]₀ is hard to explain but could be an effect of τ ratio = tail gas rate • plasma gas rate

Fig. 33 shows the decrease in conversion of BCl₃ obtained when the [BCl₃]₀ was increased for an otherwise constant mixture of argon and hydrogen which was fed to the reactor. Argon was fed to the plasma and BCl₃ and H₂ premixed and fed to the tail in the 'normal' tail injection mode.

The conversion of BCl₃ can be seen to decrease rapidly to a minimum value when plotted against BCl₃ flow rate (∝ [BCl₃]₀). A plot of BCl₃ conversion against residence time T' is shown in Fig. 28 for comparison with other increasing [BCl₃]₀ runs. It can be seen that the conversion increased linearly with T' up to conversions of ~50% becoming non-linear above this conversion, similar to the other modes of operation.
4.15 Effect of increase of tail feed distance 'x'

All the results presented up to now were obtained by feeding reactants, either to the plasma or tail ring, using the minimum distance (∼1 cm) between the coil and the top face of feed ring (x in Fig. 30). The actual distance between the coil and tail feed ports was 4.5 cm, as the ports were 3.5 cm below the top face of the ring.

To determine the effect of increasing tail feed distances on the conversion of BCl₃ to boron, and to establish a possible half life of activated species in the plasma tail, a series of runs was carried out at increasing values of x. A 35 cm long plasma torch was used (nearly twice the normal torch length) which allowed tail distances of up to 17 cm to be reached, by lowering the apparatus while keeping the coil position fixed. Distances greater than x = 17 cm were obtained by injecting tail gases through holes bored through the wall of the quench tube. The results of a series of runs, in which premixed BCl₃ and hydrogen was injected into the tail of an argon plasma at distances of up to 40 cm from the coil, are shown in Fig. 34 and tabulated below.

As the tail ring injection distance was increased from 1 cm the conversion of BCl₃ to boron increased from 38% to a maximum of 47% at x = 6 cm. As x was increased further the conversion decreased rapidly to the initial value of 38% at x = 7.5 cm. Thereafter, the conversion decreased progressively less rapidly to 6% conversion at 40 cm. The extrapolated zero conversion is at 54 cm.
TABLE XIII
Variation of tail feed distance x

<table>
<thead>
<tr>
<th>Argon (l/m)</th>
<th>BCl(_3) (g/m)</th>
<th>H(_2)/(l/m)</th>
<th>(\text{H}_2/\text{BCl}_3) (m/m)</th>
<th>Power (kw)</th>
<th>x (cm)</th>
<th>% Conv</th>
<th>Yield Boron g/min</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>33</td>
<td>30</td>
<td>5</td>
<td>20</td>
<td>1</td>
<td>39.0</td>
<td>1.18</td>
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<tr>
<td>50</td>
<td>29</td>
<td>30</td>
<td>5</td>
<td>20</td>
<td>2</td>
<td>39.5</td>
<td>1.06</td>
</tr>
<tr>
<td>50</td>
<td>31.8</td>
<td>30</td>
<td>5</td>
<td>20</td>
<td>3</td>
<td>40.0</td>
<td>1.175</td>
</tr>
<tr>
<td>50</td>
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<td>5</td>
<td>20</td>
<td>4</td>
<td>42.5</td>
<td>1.19</td>
</tr>
<tr>
<td>50</td>
<td>28.7</td>
<td>30</td>
<td>5</td>
<td>20</td>
<td>5</td>
<td>46.5</td>
<td>1.23</td>
</tr>
<tr>
<td>50</td>
<td>31.6</td>
<td>30</td>
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<td>20</td>
<td>6.5</td>
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<td>1.31</td>
</tr>
<tr>
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<td>30</td>
<td>5</td>
<td>20</td>
<td>8.0</td>
<td>37.3</td>
<td>1.03</td>
</tr>
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<td>30.5</td>
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<td>10.0</td>
<td>33.6</td>
<td>0.94</td>
</tr>
<tr>
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<td>5</td>
<td>20</td>
<td>13.5</td>
<td>27.2</td>
<td>0.78</td>
</tr>
<tr>
<td>50</td>
<td>31.0</td>
<td>30</td>
<td>5</td>
<td>20</td>
<td>17.0</td>
<td>22.3</td>
<td>0.61</td>
</tr>
<tr>
<td>50</td>
<td>31.0</td>
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<td>5</td>
<td>20</td>
<td>30</td>
<td>11.3</td>
<td>0.33</td>
</tr>
<tr>
<td>50</td>
<td>34.6</td>
<td>30</td>
<td>5</td>
<td>20</td>
<td>40</td>
<td>6.0</td>
<td>0.20</td>
</tr>
</tbody>
</table>

Fig. 35 also shows the results of a similar series of runs in which x was increased, for the same set of operating conditions as above, but with BCl\(_3\) injected with argon to the plasma. In this case, the conversion decreased rapidly initially from 55% conversion at 1 cm, flattening out gradually to approach 30% conversion at 30 cm. At distances greater than 30 cms the conversion decreased very quickly to zero at \(x > 40\) cms. There was, however, no increase in conversion with x as in the case of a pure argon plasma.

4.16 Effect of magnetic flux on the plasma tail

To determine whether ionised species present in the tail of the plasma played any part in the reduction of BCl\(_3\) to B, a simple 1500 gauss electromagnet was constructed which could be placed around the plasma torch between the coil and
A short series of runs was carried out with the magnet in the position as shown in the figure. Firstly, a 50 l/min argon plasma was run at 20 KW to determine any possible effect of the magnetic flux on the plasma tail. No visible change occurred in the plasma tail with the magnet 6 cm from the coil as the flux was increased up to 1500 gauss. Two comparison runs with 30 g/min BCl₃ and 30 l/min H₂ injected in the tail resulted in no significant difference in conversions obtained (no magnetic flux 22.3%, with magnetic flux 18% conv.).

The magnet was then raised to a position 1 cm below the coil and the above experiment repeated. The conversion with the magnetic circuit off was 22.0% and with the magnet circuit switched on an equivalent conversion
was measured as 15.5%. A similar pair of runs, this time with the 30 g/min BCl₃ passing through the plasma, resulted in 33.5% conversion without the magnetic flux and 40.0% with the magnet on. Hence the application of a 1500 gauss magnetic flux to the tail of the argon/BCl₃ plasma increased the conversion to boron by approximately the same amount as the conversion was decreased when argon alone was present in the plasma. The results are summarised below and plotted as points in Figs. 34 and 35 for comparison.

<table>
<thead>
<tr>
<th>P = 20 KW</th>
<th>x = 16.5cm</th>
<th>% conversion BCl₃ to Boron</th>
<th>No magnet (flux B=0)</th>
<th>B=1500 gauss magnetic flux</th>
</tr>
</thead>
<tbody>
<tr>
<td>Argon Plasma (BCl₃+H₂ tail)</td>
<td>22.3</td>
<td>15.5</td>
<td>Δ conv=-6.8%</td>
<td></td>
</tr>
<tr>
<td>Argon+BCl₃ plasma H₂ tail</td>
<td>33.5</td>
<td>40.0</td>
<td>Δ conv=+6.5%</td>
<td></td>
</tr>
</tbody>
</table>

### 4.17 Boron Yields and Pilot Plant results

#### 4.17.1 Effect of reactant concentration

The data obtained from the previously described runs at constant initial reactant concentrations also provides information about their effect on boron yields. Fig. 37 shows the variation in yield of boron obtained (g/min run time) when initial \([H₂]₀\) was increased and \([BCl₃]₀\) kept constant. For the residence times 0.003 sec. a constant yield of 3.5 g/min boron was obtained even though \([H₂]₀\) was increased from 0.018 to 0.033 gmole/litre. Operation outside these limits was not possible due to resistive overload of the plasma. Yields were lower at the longer residence time of 0.0045s however, and increased to a maximum of only 2 g/min at the
4.172 Effect of residence time on yield

Fig. 39 shows more fully the decrease of boron yields obtained when the residence time in the reactor is increased with a constant $[\text{BCl}_3]_o$ of 0.004 gmoles/litre for three constant $[\text{H}_2]_o$ values. A family of curves is obtained in which the boron yield drops off rapidly with increasing residence time, reaching limiting values between 1 and 2 g/min for times $T > 0.009$ sec. Yields increased for any given residence time as the $[\text{H}_2]_o$ was increased. For example, the following table shows yield increments at $T = 0.007$ secs.

<table>
<thead>
<tr>
<th>$T$ (secs)</th>
<th>$[\text{H}_2]_o$ (gmoles/litre)</th>
<th>Yield (g/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.007</td>
<td>0.0074</td>
<td>1.5</td>
</tr>
<tr>
<td></td>
<td>0.015</td>
<td>2.0</td>
</tr>
<tr>
<td></td>
<td>0.033</td>
<td>2.5</td>
</tr>
</tbody>
</table>

It can be seen that for equal increments of yield increase (0.5 g/min) to be obtained, the $[\text{H}_2]_o$ must be doubled.

4.173 Pilot Plant Results

Table XIV shows some typical pilot plant runs and Fig. 40 is a general performance curve for yield of boron obtained plotted against $\text{BCl}_3$ feed rate. $\text{H}_2/\text{BCl}_3$ of >3:1 were used in all runs. The highest production rate
### TABLE XIV
Production Runs on Boron Plant

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Run Time (hr)</th>
<th>R.F. Power (KW)</th>
<th>Plasma Argon (l/m)</th>
<th>Hydrogen (l/m)</th>
<th>Plasma BCl₃ (g/m)</th>
<th>H₂/BCl₃ v/v</th>
<th>Conv. Per Pass (%)</th>
<th>Yield of Boron (g/m)</th>
<th>Total Boron (KG)</th>
<th>Condensation Per pass %</th>
<th>Overall % Efficiency</th>
<th>Comments (Mods, etc.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.0</td>
<td>25</td>
<td>11</td>
<td>--</td>
<td>50</td>
<td>70</td>
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<td>1.3</td>
<td>0.16</td>
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</tr>
<tr>
<td>3</td>
<td>0.65</td>
<td>24.5</td>
<td>--</td>
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<td>150</td>
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<td>0.07</td>
<td>--</td>
<td>--</td>
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<td>2.33</td>
<td>0.14</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>6</td>
<td>0.62</td>
<td>22.0</td>
<td>8</td>
<td>--</td>
<td>60</td>
<td>100</td>
<td>3.13</td>
<td>24.5</td>
<td>2.30</td>
<td>0.17</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>7</td>
<td>1.2</td>
<td>22.0</td>
<td>7</td>
<td>--</td>
<td>60</td>
<td>100</td>
<td>3.13</td>
<td>18.6</td>
<td>1.8</td>
<td>0.13</td>
<td>--</td>
<td>--</td>
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<td>8</td>
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<td>--</td>
<td>60</td>
<td>100</td>
<td>3.13</td>
<td>21.4</td>
<td>2.0</td>
<td>0.18</td>
<td>--</td>
<td>--</td>
</tr>
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<td>9</td>
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<td>8</td>
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<td>3.13</td>
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<td>2.0</td>
<td>0.13</td>
<td>--</td>
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<td>100</td>
<td>133</td>
<td>3.92</td>
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<td>1.52</td>
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<td>17</td>
<td>--</td>
<td>100</td>
<td>70</td>
<td>7.45</td>
<td>34.2</td>
<td>2.2</td>
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<td>15</td>
<td>--</td>
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<td>100</td>
<td>5.22</td>
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<td>0.17</td>
<td>--</td>
<td>--</td>
</tr>
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<td>13</td>
<td>1.51</td>
<td>21.0</td>
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<td>--</td>
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<td>90</td>
<td>5.83</td>
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<td>0.21</td>
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<td>--</td>
</tr>
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<td>1.0</td>
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<td>16</td>
<td>--</td>
<td>100</td>
<td>100</td>
<td>5.22</td>
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<td>2.23</td>
<td>0.13</td>
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<td>--</td>
</tr>
<tr>
<td>15</td>
<td>1.05</td>
<td>30</td>
<td>16</td>
<td>--</td>
<td>100</td>
<td>108</td>
<td>4.83</td>
<td>26.2</td>
<td>2.6</td>
<td>0.16</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>16</td>
<td>1.05</td>
<td>30</td>
<td>10-20</td>
<td>--</td>
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<td>175</td>
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<td>--</td>
</tr>
<tr>
<td>17</td>
<td>1.07</td>
<td>30</td>
<td>20</td>
<td>--</td>
<td>180-200</td>
<td>155</td>
<td>6.79</td>
<td>26.9</td>
<td>3.84</td>
<td>0.26</td>
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<td>--</td>
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<td>0.28</td>
<td>25</td>
<td>27</td>
<td>--</td>
<td>240</td>
<td>205</td>
<td>6.1</td>
<td>25.2</td>
<td>4.80</td>
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<td>20.25</td>
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<td>4</td>
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<td>50</td>
<td>128</td>
<td>2.06</td>
<td>15.7</td>
<td>1.85</td>
<td>2.25</td>
<td>68.4</td>
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<td>8</td>
<td>--</td>
<td>100</td>
<td>183</td>
<td>2.86</td>
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<td>3.2</td>
<td>5.68</td>
<td>57.0</td>
<td>44.0</td>
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</table>
achieved (Run BP/17) was 4.8 g/min (290 g/hr) at BCl₃ rate of 200 g/min. The highest efficiency w.r.t. BCl₃ which was achieved by BCl₃ condensation and recycle was 70% at 100 g/min BCl₃ feed which produced 2.7 g/min (160 g/hr) of boron. At 30 KW ~ 0.001 kgB/kwh were obtained at the highest production rate achieved (or 100 kwh/kg boron).

4.2 SPECTROSCOPIC RESULTS

4.21 Argon plasma

4.211 Calibration

A preliminary series of spectra of a pure argon plasma at 14 KW and 25 l/min were taken to calibrate the system for exposure time. The optical system shown in Fig. produced satisfactory photographic results for exposure of Kodak B10 plates at times up to $\frac{1}{2}$ sec in $\frac{1}{25}$th sec intervals using a standard camera shutter at f4.5. The spectrograph slit width throughout this series of runs was 0.003 mm.

Plate 4 shows the spectra obtained for an argon plasma at exposure times of 4, 6, 8, 12 and 16 x $\frac{1}{25}$th sec, and the emission present is attributable to Argon I and II atomic and ionic species.

A second series of calibration spectra were then photographed using Ilford Long Range Plates, the B10 plates being limited to the ultra-violet region of the spectrum. These results are also shown in Plate 5 and the spectrum contains emission of atomic species in the blue and red regions of the spectrum.
4.212 Measurement of Radial Intensity of an argon plasma

The radial distribution of argon atomic emission from the plasma was measured by focussing an image of the plasma on a 2" square brass plate which contained a 1 mm pinhole at its centre. The plate could be moved horizontally with a rack and pinion device. The brass plate was mounted in the light path as shown in Fig. 21 and it was possible to measure emission from nine non-overlapping radial positions at the plasma centre when using a 16 mm diameter plasma image. Table XV below shows the optical densities measured for five argon spectral lines in the blue region of the spectrum. A 10 kw, 15 l/min argon plasma was used as the source.

<table>
<thead>
<tr>
<th>Spectral line A</th>
<th>4182</th>
<th>4259</th>
<th>4266</th>
<th>4272</th>
<th>4300</th>
</tr>
</thead>
<tbody>
<tr>
<td>Posn(mm)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0 (axis)</td>
<td>0.356</td>
<td>0.870</td>
<td>0.309</td>
<td>0.625</td>
<td>0.387</td>
</tr>
<tr>
<td>1</td>
<td>0.314</td>
<td>0.778</td>
<td>0.269</td>
<td>0.558</td>
<td>0.343</td>
</tr>
<tr>
<td>2</td>
<td>0.311</td>
<td>0.786</td>
<td>0.276</td>
<td>0.558</td>
<td>0.350</td>
</tr>
<tr>
<td>3</td>
<td>0.315</td>
<td>0.780</td>
<td>0.260</td>
<td>0.550</td>
<td>0.334</td>
</tr>
<tr>
<td>4</td>
<td>0.315</td>
<td>0.798</td>
<td>0.276</td>
<td>0.562</td>
<td>0.330</td>
</tr>
<tr>
<td>5</td>
<td>0.262</td>
<td>0.683</td>
<td>0.222</td>
<td>0.468</td>
<td>0.277</td>
</tr>
<tr>
<td>6</td>
<td>0.130</td>
<td>0.385</td>
<td>0.111</td>
<td>0.254</td>
<td>0.181</td>
</tr>
<tr>
<td>7</td>
<td>0.098</td>
<td>0.266</td>
<td>0.094</td>
<td>0.202</td>
<td>0.106</td>
</tr>
<tr>
<td>8 mm from axis</td>
<td>0.049</td>
<td>0.162</td>
<td>0.044</td>
<td>0.108</td>
<td>0.054</td>
</tr>
</tbody>
</table>

The distribution of emission intensity for each of the atomic lines across the axis of the plasma is shown in Fig. 41. The intensity of each line increased gradually to a maximum value at 4 mm from the plasma centre,
decreased slightly at nearer distances at a plateau level, and then increased slightly at the axial position.

Fig. 43 shows the above results normalised at the position of maximum intensity which best fitted all lines. The 3 mm radial position was chosen for the maximum intensity as this gave the minimum number of deviations for all five lines. To enable better smoothing to be obtained for further mathematical treatment, the intensities were interpolated at 0.5 mm intervals for this normalisation curve.

4.213 Calculation of radial intensity profile

For the calculation of excitation temperatures of optically-thin radiating gases it is necessary to calculate the emission from any point within the radiation source. Assuming the plasma to be a cylindrical source, the radiation projected from the source to any measuring instrument will be comprised of radiation from various layers in the source at different temperatures. This measured intensity will therefore be an integrated value of various layers and can be represented mathematically by the Abel integral equation (Ref. 208):

\[
I(y) = 2 \int_{R}^{r} \frac{i(r)r \, dr}{r \sqrt{r^2 - y^2}} \quad \text{...... (8)}
\]

where \( I(y) \) = integrated intensity

\( R \) = radius at boundary of emission

\( r \) = radius of emitting volume from centre

\( y \) = projected axis

\( i(r) \) = emission coefficient at radius \( r \)
Analytical inversion of the Abel integral yields the emission as a function of radius of circular elements within the plasma, instead of as a function of projected chords across the circular section. Hence, after inversion:

$$I(r) = -\frac{1}{2\pi} \int_r^R \frac{dI/dy}{(y^2 - r^2)^{1/2}} \, dy \quad \ldots \ldots \ (9)$$

As $I(y)$ is usually obtained as a set of numerical data rather than as an analytical function, several numerical methods of solving the Abel inversion have been developed. In this work the method due to Barr (208) was used, which was valid for a set of numerical $I(y)$ with up to 40 radial increments. The radial emission coefficients were computed using the normalised line intensities distribution and for each separate line intensity distribution shown in Figs. 41 and 43. The results of the Abel inversion are shown graphically in Figs. 42 and 44 for the corresponding distribution.

4.21.4 Calculation of plasma temperature profile

The excitation temperature ($T_e$) of species undergoing transitions from upper to lower energy levels in optically thin plasmas can be related to the emission coefficient or intensity $I_\nu = \varepsilon_\nu$ at any frequency $\nu$ sec$^{-1}$ by the following equation; assuming thermodynamic equilibrium:

$$\varepsilon_\nu = \frac{h \nu}{4 \pi} g_n A_{nm} \frac{N(T)}{U(T)} \exp \left(-\frac{E_n}{kT_e}\right) \left[\text{ergs s}^{-1} \text{ sterad}^{-1} \text{ cm}^{-3}\right]$$

where $A_{nm} = \text{transition probability for spontaneous emission from upper state } n \text{ to lower state } m$.

$g_n = \text{statistical weight in the upper state } n$.

$N(T) = \text{number density for the ground state.}$
\[ U(T) = \text{partition function for the neutral atom} \]
\[ E_n = \text{energy of the upper state} \]
\[ h = \text{Planck's constant} \]
\[ k = \text{Boltzmann's constant} \]

Two methods are available for calculation of excitation temperature \( T_e \) from experimental relative intensity data. The first method developed by Larenz (209) and Krempl (210) is based on the fact that the intensity of emission of a given spectral line in a plasma in thermal equilibrium will increase with temperature, reach a maximum and then decrease at higher temperatures due to depopulation of the ground state when ionisation becomes extensive. Larenz (209) developed an equation expressing the emission coefficient as a function of temperature and pressure:

\[ E_o = f(T, P); \left( \frac{\partial E}{\partial T} \right)_p = 0 \rightarrow \bar{T}, \text{ norm temperature} \]

By differentiating the equation with respect to temperature and equating to zero, Larenz obtained an equation which could be solved for norm temperature.

Larenz equation:

\[
\frac{\hbar^3}{(2\pi m)^{3/2}} \times \frac{1}{2} \times \frac{g_0}{\delta n} \left( \frac{P}{V_i} \right)^{5/2} \left[ \frac{V_i}{\kappa T} \right]^{5/2} \exp(eV_i/kT) = \frac{[eN/\kappa T]^{5/2}}{[kT - 1]} - 1
\]

where \( V_i = \text{ionisation potential} \)
\( g_0 = \text{statistical weight in ground state} \)
\( T = \text{norm temperature} \)

Krempl (210) developed this mathematical expression further and obtained a solution for the norm temperature as follows:

\[
\bar{T} = \frac{950 V_i}{1 - 0.33 \times 0.37 \log(V_i/10) - 0.14 \log \left( \frac{m}{\delta n} \cdot \frac{2i+1}{2i+3} \right)} \quad (^{\circ}K)
\]

\[ \cdots \cdots \cdots \quad (12) \]
Krempl calculated the norm temperature for argon as 15,000°K and Fig. 45 shows a typical variation of emission with temperature for the 7635 Å argon line (63). By identifying the maximum in radial emission intensity obtained after Abel inversion of the normalised intensities, with the maximum emission coefficient at the norm temperature, all other temperatures can be determined by the ratio of \( I/I_{\text{max}} \).

Fig. 46 shows the temperature profile so obtained for the 10 kW argon plasma. A maximum plasma temperature of 20,000°K occurs on the axis of the plasma torch.

The second method of calculating the excitation temperature of emitting species has been described by Coates and Gaydon (256). It can be seen from equation (10) that \( T_e \) can be obtained directly if all the constants for the spectral line are known. However, in the absence of the knowledge of particle density \( \rho \) and partition coefficient \( U(T) \), it is possible to estimate \( T_e \) from the relative intensities of a number of different lines of a single emitting species, if \( A_{nm} \) and \( g_n \) are known.

viz. \( \ln \left( \frac{I_\text{obs}}{\rho g_n A_{nm}} \right) = -\frac{E_n}{kT_e} + \text{const.} \)

A plot of left-hand side against \( E_n \) should give a straight line of slope \(-1/kT_e\). Coates and Gaydon give values of \( g_n \) and \( A_{nm} \) for a range of argon atomic emission.

For this method to be used with any reliability, however, it is necessary to use as wide a range of energy levels as possible. Treatment of the 4182-4300 Å series of argon
lines was found to give poor results due to the small energy level range for the lines ($117000 < E_n < 119000 \text{ cm}^{-1}$). Use of argon atomic emission in the near infra red and argon ionic emission would provide a better basis for application of this method for plasma temperature measurement.

4.215 Discussion of plasma temperature measurement

The off-axis peaks in line intensities for the argon plasma (shown in Figs. 42 and 44) are in agreement with the results obtained by Reed (63) and Johnston (120). The on-axis peak temperature of 20,000°K calculated by Krempl's norm temperature method is some 2000°K higher than the results obtained by both Reed and Johnston using the Fowler-Milne method (119). This is most probably due to the higher power levels (10 kW) used in present work. Reed's temperature measurement was at 2 kW while Johnston used a 6 kW plasma.

The basis of the Krempl norm temperature method, i.e. an increase in ion concentration towards the centre of the plasma, is undoubtedly valid for arc plasmas which are in general small in diameter. For r.f. systems, however, larger plasma diameters are possible due to the nature of the induced energy transfer process, and it is possible that an off axis peak in emission of atomic argon could result from incomplete penetration of energy from the r.f. coil into the plasma gas. Inner regions of the plasma would then only be heated by radiation and convection process. If this phenomenon occurs, then an off axis peak temperature would be expected similar to the emission distribution. Several workers have obtained off axis peak temperatures for argon
plasmas by use of the graphical measurement technique. Application of this temperature measurement technique to argon is not very satisfactory, however, as the difference in energy levels for argon atomic emission is small, only $\Delta 14000 \text{ cm}^{-1}$ (1.8 eV). Use of excited ionic levels would increase the accuracy of this method, but transition probability data is not yet available for argon ionic states.

Several other methods of plasma temperature measurement are possible, including measurement line broadening and line shifting. These methods, however, require extremely rigorous experimental techniques and are open to more sources of errors than the relative intensity techniques.

In the present work, the presence of Ar$^+$ in the emission spectra indicates a higher degree of excitation of the plasma than in the work by Johnston, who reported only Argon I present in emission. Hence it is more probable that the off axis peak in emission is caused by depopulation of the ground state in favour of the first ionisation stage. However, in the absence of concrete evidence for the radial emission distribution of Ar$^+$ the actual temperature distribution in the plasma is open to speculation.
4.22 Argon + BCl$_3$ Plasma

4.221 Analysis

A typical ultra-violet emission spectra of an argon/BCl$_3$ plasma obtained at 25 KW is shown in Plate 6. The first five spectra are argon/BCl$_3$ plasma at 5, 8, 10, 12 and 15 x $1/25$th sec. exposure times. Table XVI presents a qualitative analysis of identifiable atomic and molecular emission for increasing wavelengths. The main emitting species present in the 25 KW argon/BCl$_3$ plasma are summarised below:

<table>
<thead>
<tr>
<th>Molecular emission</th>
<th>Atomic emission</th>
</tr>
</thead>
<tbody>
<tr>
<td>BCl v. strong(self-absorbed)</td>
<td>Argon I and II</td>
</tr>
<tr>
<td>BCl$_2$ weak</td>
<td>Boron I and Boron II</td>
</tr>
<tr>
<td>Cl$^+$ v. strong(continuum)</td>
<td>Silicon I</td>
</tr>
<tr>
<td>Cl$_2$ strong bands</td>
<td>Copper I</td>
</tr>
<tr>
<td>BO band head</td>
<td></td>
</tr>
</tbody>
</table>

The silicon, copper and oxygen are probably present as impurities in the boron trichloride used for these studies.

4.222 Axial intensity of Boron II emission

In order to establish the extent of preplasma dissociation and ionisation, a series of intensity measurements were carried out at different axial positions along the plasma torch for argon + BCl$_3$ plasma. The optical system used was as shown in Fig. 21 and the scanning positions used are indicated below:
<table>
<thead>
<tr>
<th>Measured Wavelength (Å)</th>
<th>Ref. Wavelength (Å)</th>
<th>Atomic Emission</th>
<th>Molecular Emission</th>
<th>Ref. Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>2263</td>
<td></td>
<td>Unknown Doublet Line</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2352</td>
<td></td>
<td>Argon II Line</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2387</td>
<td>2387.99</td>
<td>Boron II Line</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2428</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2433</td>
<td>2432.99</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2441</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2450</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2496</td>
<td>2496.78</td>
<td>Boron I Line</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2497</td>
<td>2497.73</td>
<td>Boron I Line</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2506</td>
<td>2506.90</td>
<td>Silicon I Line</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2513</td>
<td>2514.33</td>
<td>Silicon I Line</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2515</td>
<td>2516.12</td>
<td>Silicon I Line</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2518</td>
<td>2519.21</td>
<td>Silicon I Line</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2523</td>
<td>2524.12</td>
<td>Silicon I Line</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2528</td>
<td>2528.52</td>
<td>Silicon I Line</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2531</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2657</td>
<td>2659.8</td>
<td>r.b.h. red BCl (1,0)</td>
<td></td>
<td>(214)</td>
</tr>
<tr>
<td>2686</td>
<td></td>
<td>Doublet BCl (0,0)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2722</td>
<td>2720.0</td>
<td>b.h. (rev.) BCl (3,3)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2731</td>
<td>2727.8</td>
<td>b.h. BCl</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2783</td>
<td>2783.7</td>
<td>b.h. BCl</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2791</td>
<td>2792.4</td>
<td>b.h. BCl</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2839</td>
<td></td>
<td>BCl (4,5)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2848</td>
<td>2847.5</td>
<td>Line BCl</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2861</td>
<td></td>
<td>Line BCl</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2881</td>
<td>2881.58</td>
<td>Line BCl</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2987</td>
<td>2987.65</td>
<td>Line BCl</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3008</td>
<td></td>
<td>Line BCl</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3032</td>
<td>3032.28</td>
<td>Line BCl</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3173</td>
<td>3172.9</td>
<td>Line BCl</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3232</td>
<td></td>
<td>b.h. BCl</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3261</td>
<td>3260.74</td>
<td>BCl BCl (187)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3361</td>
<td>3360.09</td>
<td>Boron Line BCl</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3372</td>
<td></td>
<td>b.h. BCl</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3384</td>
<td></td>
<td>Line BCl</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3438</td>
<td></td>
<td>b.h. BCl</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3451</td>
<td>3451.41</td>
<td>Line BCl</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(cont'd ...)
<table>
<thead>
<tr>
<th>Measured Wavelength (Å)</th>
<th>Ref. Wavelength (Å)</th>
<th>Atomic Emission</th>
<th>Molecular Emission</th>
<th>Ref. Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>3452</td>
<td>3452.28</td>
<td>Boron II</td>
<td>b.h. BCl₂</td>
<td>(187)</td>
</tr>
<tr>
<td>3499</td>
<td>3570</td>
<td></td>
<td>Fine band structure</td>
<td></td>
</tr>
<tr>
<td>3570</td>
<td>3570</td>
<td>Line Argon I</td>
<td>R.b.h. B-H</td>
<td>(214)</td>
</tr>
<tr>
<td>3600</td>
<td></td>
<td></td>
<td>R.b.h. B-H</td>
<td></td>
</tr>
<tr>
<td>3800</td>
<td></td>
<td></td>
<td>Q.b.h. B-H</td>
<td></td>
</tr>
<tr>
<td>3820</td>
<td></td>
<td></td>
<td>R.b.h. B-O</td>
<td></td>
</tr>
<tr>
<td>3910</td>
<td>4181.88</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4180</td>
<td>4181.88</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4240</td>
<td>4245.9</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4319</td>
<td>4319.2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4330</td>
<td>4331.6</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4360</td>
<td>4363.4</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

N.B. All atomic emission from Reference 215 unless stated otherwise.
Axial positions used were \( x = 0, 2, 4, 5, 7.5 \) and 10cm. The peak heights and continua for the Boron II 2432.3 Å line were measured for six positions and a range of exposure times. Table XVII also presents the calculated optical densities obtained from the peak heights. Fig. 47 shows the increase of optical density \( E \) for the BII 2432 Å line with increasing axial distance through a 10 KW argon/BCl\(_3\) plasma. The optical density is also correlated with a time axis by multiplying the axial distance \( x \) by: \( \frac{1}{(\text{linear velocity of the gas})} \).

Fig. 48 shows the variation of optical density of the BII 2432 Å line for plasma with increasing concentrations of BCl\(_3\). As can be seen, for a 17 KW plasma at axial position \( x = 2 \), the optical density of BII approaches its maximum at \( \sim 0.5 \) atm partial pressure of BCl\(_3\).
### TABLE XVII

**OPTICAL DENSITIES OF BII 2432 Å**

a) Axial variation

<table>
<thead>
<tr>
<th>Exposure time (sec)</th>
<th>Position x (cm)</th>
<th>0</th>
<th>2</th>
<th>4</th>
<th>5</th>
<th>7.5</th>
<th>10</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
<td>0.337</td>
<td>0.036</td>
<td>0.00</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>0.414</td>
<td>0.122</td>
<td>0.020</td>
<td>0.00</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>5</td>
<td></td>
<td>0.870</td>
<td>0.461</td>
<td>0.147</td>
<td>0.00</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>10</td>
<td></td>
<td>1.284</td>
<td>0.672</td>
<td>0.318</td>
<td>0.055</td>
<td>0.00</td>
<td>-</td>
</tr>
<tr>
<td>20</td>
<td></td>
<td>1.575</td>
<td>1.252</td>
<td>0.520</td>
<td>0.180</td>
<td>0.00</td>
<td>-</td>
</tr>
<tr>
<td>50</td>
<td></td>
<td>2.256</td>
<td>1.656</td>
<td>0.860</td>
<td>0.484</td>
<td>0.00</td>
<td>-</td>
</tr>
</tbody>
</table>

b) Variation with \([\text{BCl}_3]\)

<table>
<thead>
<tr>
<th>Exposure time (sec)</th>
<th>BCl(_3) (atm)</th>
<th>2</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.047</td>
<td></td>
<td>0.146</td>
</tr>
<tr>
<td>0.19</td>
<td></td>
<td>0.238</td>
</tr>
<tr>
<td>0.375</td>
<td></td>
<td>0.327</td>
</tr>
<tr>
<td>0.90</td>
<td></td>
<td>0.351</td>
</tr>
</tbody>
</table>
Plate 5 shows a comparison between U.V. spectra of an argon plasma and an argon/hydrogen plasma. It can be seen that there are six extra atomic lines in the latter spectra which are attributable to the first series of atomic hydrogen emission:

\[
\begin{align*}
H_\alpha & = 6562.79 \text{ Å} \\
H_\beta & = 4861.33 \text{ Å} \\
H_\gamma & = 4340.47 \text{ Å} \\
H_\delta & = 4101.74 \text{ Å} \\
H & = 3970.07 \text{ Å} \\
H & = 3889.06 \text{ Å}
\end{align*}
\]

The intensities of these lines decrease with decreasing wavelength, becoming very diffuse at the lower wavelengths.

When BCl\textsubscript{3} is introduced into the system the massive continuum of the chlorine molecular emission marks these lower wavelength H atomic lines and in Plate 6 only the H\textsubscript{\beta} line persists. However, in addition to the H\textsubscript{\beta} line, there is a series of well-defined band heads at 4245.9, 4319.2 and 4331.6 Å degraded to the red. These were attributed to the BH molecules (214).
Elemental boron produced by hydrogen reduction of BCl$_3$ in an r.f. plasma had the characteristic brown colour of amorphous boron powder similar to amorphous boron prepared by other methods. The brown colour varied, however, from dark brown/black when boron was formed at low BCl$_3$ rates (< 20 g/min), to a light brown powder when formed at high BCl$_3$ feed rates. At the highest feed rates used (∼ 2 mole/min BCl$_3$) traces of yellow deposits were found on the walls of the plasma torch which could possibly be the same yellow boron monochloride reported previously by Briscoe (132) and Rosenberg (163). The boron, when removed from the collection apparatus, was in the form of a lightly compacted powder which when passed through a 60-μm sieve broke up easily to a free-flowing agglomerated powder. This powder had a bulk density of about 0.1 g/cm$^3$ compared to densities of 2.3 → 2.45 reported for bulk solid boron (221). The specific surface area of the agglomerated powder was determined as $12.4 \times 10^4$ cm$^2$/g which is a medium to low value and suggests absence of pores.

It was observed that samples of boron, on standing in normal atmospheric conditions, adsorbed some 30% by weight of water. This could be easily eliminated if the boron was heated to 105°C. When the water was not removed from a sample the presence of discrete boric acid crystals was observed. These may have been formed by hydrolysis of boric oxide present on the surface of the boron as it seems unlikely that boron reacts with water.
Boron samples prepared by various feed configurations were examined and Table XVIII shows the mean particle sizes found. The particle size apparently increases with the proportion of reactants passing through the plasma. At no time in this work was the boron found to be pyrophoric.

**Table XVIII**

<table>
<thead>
<tr>
<th>Run</th>
<th>Plasma Gas</th>
<th>Tail Gas</th>
<th>Mean particle size (μ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>144</td>
<td>Ar/H₂</td>
<td>BCl₃/H₂</td>
<td>0.5</td>
</tr>
<tr>
<td>145</td>
<td>Ar/H₂</td>
<td>BCl₃/H₂</td>
<td>0.75</td>
</tr>
<tr>
<td>146</td>
<td>Ar/BCl₃</td>
<td>H₂</td>
<td>0.9</td>
</tr>
<tr>
<td>147</td>
<td>Ar/BCl₃</td>
<td>H₂</td>
<td>0.98</td>
</tr>
<tr>
<td>148</td>
<td>Ar/BCl₃/H₂</td>
<td>H₂</td>
<td>1.7</td>
</tr>
</tbody>
</table>

A particle size distribution analysis of a typical boron sample (run 105) resulted in the detection of particles ranging from 0.6 to 14 micron in diameter, with a percent cumulative oversize distribution as shown in Fig. 49. The calculated mean particle size (μ) from this distribution disagrees markedly with the measured mean particle size. This discrepancy is probably due to differences between the methods of measurement.

When boron was formed by passage of low BCl₃ flows (< 20g/min) through an argon plasma and reduction with backmixed hydrogen, i.e. \( \text{Ar}^+ \xrightarrow{\text{BCl₃}} \text{H₂} \) clusters of shiny black crystals of boron were formed in the lower regions of the torch and on the tail ring. The crystal growths were dendritic in nature and looked like small feathers. Growth up to 0.5 cm deep covering 90°
of the torch circumference were found. Under certain operating conditions non-uniform whisker growths of boron were found in the torch, supported from the crystalline deposits. These whiskers sometimes grew to lengths of up to 10 cms. Whisker growth in two $180^\circ$ opposed directions was observed also to occur, corresponding to simultaneous growth in the same and opposite direction to the plasma gas flow.

The clusters of dendritic crystals were fairly weak and tended to break up easily, but the whiskers were strong enough to support their own weight ($\sim 1$ g. for a 10 cm length). The whiskers fractured easily however, when subjected to a slight bending stress. Typical diameters of whiskers were $0.2 - 0.6$ mm and they generally consisted of multibranched structures. The diameter of the end of one whisker branch was measured as being $10 \mu$ by optical microscopy.

Some of the whisker growths terminated in crystalline boron spheres of 1-2 mm diameter. Plates 7 - 9 show some surface detail of one such sphere, magnified by a Cambridge Scanning Electron Microscope, type "Stereoscan" Mark IIA. Plate 7 shows hexagonal crystal faces in the surface of the sphere at x96 magnification. The hexagons are approximately 0.02 cm between parallel edges. Plate 8 (x520 magn.) shows striations across the surface of the sphere and also a series of well-ordered hexagonal crystal platelets, estimated at $10 \mu$ in diameter. The striations could be caused by
thermal or chemical erosion on the sphere by the hot tail gases. Plate 9 shows stacking of the platelets in more detail and the thickness of an individual platelet is estimated to be $\sim 1\mu$.

Plates 10 to 12 show surface detail of a typical boron whisker at X1000 and X2000 magn., and Plate 11 shows individual boron polycrystals on the surface of the whisker which vary from 10 to 25 in length.

Plate 12 shows the end of a hairlike whisker which was fractured after removal from the apparatus. The fractured section shows the internal structure of the whiskers to be amorphous rather than polycrystalline.

4.32 X-ray diffraction patterns of plasma boron

Preliminary X-ray diffractometer traces and powder films obtained of plasma boron were both very diffuse and complicated. An example of a typical X-ray film of boron powder is shown in Plate 13 and is compared with the strong pattern obtained from the dendritic crystals recovered from the torch deposits. The former is very diffuse in contrast to the well crystallised $\beta$-rhombohedral structure of the latter (211). Comparison of various plasma boron diffractometer traces and powder films established that the film patterns could occasionally distinguish between certain lines which were otherwise indistinguishable on the diffractometer traces. Standardisation of the diffractometer techniques and the use of a glass-backed, instead of aluminium backed, specimen holder enabled reproducible results to be obtained for samples taken from the same bulk material. Reduction in the heights of
certain peaks was observed from a sample of boron which had been previously heated in vacuo at 800°C for 1 hour. These peaks were identified as belonging to $\text{B(OH)}_3$, presumably present due to hydrolysis of $\text{B}_2\text{O}_3$ adsorbed on the surface of the boron. The $\text{B(OH)}_3$ was removed from the bulk boron by ultrasonic agitation of the heat treated sample in alcohol and this resulted in a 5% weight loss from the boron. No further formation of $\text{B(OH)}_3$ could then be measured when the sample was exposed to atmosphere for up to 70 hours.

With removal of the $\text{B(OH)}_3$ impurities from samples the X-ray patterns then appeared very similar in all cases. The X-ray patterns were still very diffuse, however, as would be expected from the poor crystallinity of the boron. The pattern was very similar to the $\beta$-rhombohedral pattern (211) although many extra lines were present from constituents which could not be identified.

4.33 Electron Diffraction of Plasma Boron

In an attempt to elucidate the nature of the unidentified structure of the constituents of the boron, samples were examined on the transmission mode of an A.E.I. EM6G Electron Microscope at magnifications varying from X10000 to X50000.

Plates 14 and 15 show a typical boron sample prepared at 130 g/min $\text{BCl}_3$ feed rate at X10K magnification. Plate 14 shows particles with estimated sizes ranging from 1000-6000Å together with a 10,000 Å boric acid crystal. In Plate 15 a symmetrical boron platelet was observed which is an estimated 10,000 Å in diameter.
Another symmetrical boron platelet is shown in Plate 16 at X20,000 magn. which had an estimated diameter of 6700 Å and a twelve-fold symmetry. At X50,000 magn. Plate 18 shows a similar size particle (estimated diam. 7000 Å) with a very regular dodecagonal structure, while Plate 17 shows a pseudo-circular platelet of 6800 Å est. diameter. The dodecagonal particle in Plate 18 is thin enough to allow the electron beam to be transmitted through it, and is estimated at approximately 50 Å in thickness.

The main bulk of the boron powder, however, occurred as random shaped particles varying in diameter from 100 to 1000 Å.

Two Electron Diffraction patterns of typical 12-sided platelets are shown in Plates 19/20. A twelve-fold symmetry of the pattern is apparent. The size of the lattice spacing in the plane of these dodecagonal platelets was calculated from the equation
\[
\text{d.s.} = \lambda \cdot K.
\]

where
\[
d = \text{lattice spacing (mm)}
\]
\[
s = \text{distance from centre to measured point (mm)}
\]
\[
\lambda = \text{electron beam wavelength (\(=0.037\) Å at voltage 100V)}
\]
\[
K = \text{camera length = 400 mm}
\]

\((\lambda \cdot K. = \text{camera constant})\)

A lattice spacing of 29-30 Å was obtained from the pattern in Plate 20. The thickness of the 12-sided platelets was estimated as about 50 Å, equivalent to \(\sim 30\) atoms thick. Electron diffraction patterns of 2 other different shaped boron particles are shown in Pls. 21/22 but no structural identification was possible. Further interpretation of the diffraction patterns of the twelve-sided platelets was attempted using a special electron microscope cartridge which could be tilted through 30°. Diffraction patterns were obtained from a
a specimen tilted through known angles, but changes of patterns obtained did not yield useful results. The collimator of the large Philips X-ray camera was replaced by a narrower one enabling d-spacing of up to 40 Å to be measured. Using long exposure times (on a sample prepared at BCl$_3$ rate of 145 g/min), two diffuse rings of approximate 2θ values of 8° and 4° were observed on the film, corresponding to \( d = 11.6 \text{ Å} \) and \( d = 22 \text{ Å} \).

Blackening of the film and diffuseness of rings, however, prevented any accurate measurement of the rings. Two further lines were found, however, when C radiation was used. A weak line at \( d = 11.4 \text{ Å} \) and a medium line at \( d = 8.9 \text{ Å} \) were found which could not be attributed to \( \beta \)-rhombohedral boron or any other known B structure.

4.34 Variation of particle size with BCl$_3$ flow rate.

An attempt was made to relate sizes of boron particles formed with the rate of BCl$_3$ addition to an argon plasma. Table XIX shows the results obtained from electron microscopic examination of boron prepared at 30-145 g/min BCl$_3$. Fig. 50 shows the results on a minimum and maximum estimated particle size basis. No estimation of particle size distribution was possible by this technique.

Two samples of boron were examined which had been prepared with addition of preformed boron to the plasma.

The X-ray diffraction pattern showed no difference between these structures and other structures.
TABLE XIX

Variation of particle size with BCl\textsubscript{3} feed rate

<table>
<thead>
<tr>
<th>BCl\textsubscript{3} feed rate (g/min)</th>
<th>Low Magn</th>
<th>High Magn</th>
<th>Estimated particle size range Å</th>
<th>Evidence of structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>10 K</td>
<td>50 K</td>
<td>200 - 3500</td>
<td>12-sided platelets</td>
</tr>
<tr>
<td>45</td>
<td>&quot;</td>
<td>&quot;</td>
<td>200 - 3500</td>
<td>-</td>
</tr>
<tr>
<td>70</td>
<td>&quot;</td>
<td>&quot;</td>
<td>200 - 3500</td>
<td>-</td>
</tr>
<tr>
<td>90</td>
<td>&quot;</td>
<td>&quot;</td>
<td>200 - 4400</td>
<td>-</td>
</tr>
<tr>
<td>130</td>
<td>&quot;</td>
<td>&quot;</td>
<td>200 - 4800</td>
<td>12-sided platelets</td>
</tr>
<tr>
<td>145</td>
<td>&quot;</td>
<td>&quot;</td>
<td>200 - 7500</td>
<td>12-sided platelets</td>
</tr>
</tbody>
</table>
5.1 Spectroscopic Results

5.1.1 Argon Plasma

The spectrum of the rf. argon plasma at 10 KW in the visible and ultra-violet was found to contain emission from excited argon I atoms and argon ions Ar⁺. Results reported by other workers (120) indicate that singly ionised argon does not appear in the emission spectrum of a 6 KW argon plasma, suggesting that the concentration of argon ions was too low for the emission to be detected spectroscopically at these power levels. Argon ions must, by definition, be present in a plasma at a finite concentration as the plasma is maintained by an energy balance between electrons and positive ions with an overall electrical neutrality. The degree of ionisation of atoms at rf. plasma temperatures can be predicted by Saha's equation (212) which relates molar concentrations of neutral atom, ions and electrons as a function of temperature and pressure:

\[ \frac{X_M}{X_{M^+} X_e} = K(p, T) \]

where \( X_M \) = molar conc. of neutral atom
\( X_{M^+} \) = " " ion
\( X_e \) = electron concn.

In terms of degree of ionisation \( \alpha \) then:

\[ \frac{\alpha^2}{1 - \alpha^2} p = 4.9 \frac{\varepsilon_{\text{ion}}}{\varepsilon_{\text{gas}}} \cdot 10^{-4} \cdot T^{5/2} \cdot e^{-\left(\frac{eV_i}{kT}\right)} \]

where \( p \) = actual gas pressure
\( T \) = absolute temperature
\( V_i \) = ionisation potential
\( \frac{\varepsilon_{\text{ion}}}{\varepsilon_{\text{gas}}} \) = statistical wt ratio
\( k \) = Boltzmann constant
For ionisation of argon the following equilibrium will hold:

\[ \text{Ar} \rightarrow \text{Ar}^+ + e \]

The degree of ionisation of argon at atmospheric pressure has been calculated for temperatures between 1000° and 30,000°K by Bögershausen (213). Fig. 51 shows the rapid increase of ionisation for argon between 10000 and 20000°K.

Johnston (120) reports a maximum temperature of <10,000°K in a 6 kW r.f. plasma, hence a low degree of ionisation of argon would be expected, viz. 2% from Fig. 51. This low degree of ionisation of argon in an r.f. plasma at 1 atm. and 10⁴°K is consistent with the possibility that emission from Ar⁺ would not be strong enough to be detected spectrographically, since excited Ar⁺ ions (which emit radiation) will be far less abundant than argon ions themselves. Operation of argon plasmas at 10 kW and higher would probably increase the temperature of the plasma and consequently increase the degree of ionisation of argon to above the minimum detectable spectrographically.

5.12 Argon/BCl₂/H₂ plasma

The species emitting most intensely in an Argon/BCl₂ plasma was identified as the BCl molecule. The emission showed self absorption of bands, especially at high power levels (≈ 25-30 kW). The degree of line reversal increases with power input. Boron B⁺ atomic and ion B⁺ emission was also present with self absorption of the main B⁺ doublet (2496.9 and 2497.7 Å) occurring. Weak band emission in the 3570 Å region was attributed to the BCl₂ molecule, previously
These workers studied the chemiluminescence of a low pressure BCl$_3$/H$_2$ discharge and observed two distinct zones of visible emission. The first zone was a pointed yellow green flame close to the reaction zone when the discharge was operated at 2 torr pressure; the second, an orange chemiluminescence when excess H$_2$ was used up to 20 torr pressure. Most of the yellow green emission was attributed by Dessaux et al. to BCl and BH emission, with additional weak emission in the 3520 Å and 3070 Å regions. They also observed weak diffuse bands in the orange luminescent region. By use of H$_2$ and D$_2$ mixtures Dessaux et al. were able to attribute these unknown bands to the BCl$_2$ molecule. They also proposed the following mechanism for BCl$_2$ formation:

$$\text{BCl}_3 + \text{H}^+ \rightarrow \text{HCl} + \text{BCl}_2$$

In the experiments reported here involving BCl$_3$/H$_2$/Ar and BCl$_3$/Ar plasmas, an intense background continuum was observed (see Plate 6) between 2500 Å and 3420 Å which is probably due to emission from the Cl$_2$ molecule and Cl$_2^+$ ion (214). This intense continuum tended to mask any weak band or atomic emission and hence made positive identification of the BCl$_2$ molecule difficult, but a fine band structure was present between 3570 and 3580 Å which could correspond to bands for BCl$_2$ reported by Dessaux et al.

The intense Cl$_2$ and Cl$_2^+$ continuum made the positive identification of Cl atom difficult, but two weak lines at 3329 and 3353 Å could correspond to emission from this species, as given in the literature (215). The intense band emission
of the BCl molecule in the Ar/BCl$_3$ plasma suggests a high degree of dissociation of BCl$_3$ to BCl and 2Cl or Cl$_2$.

This is substantiated by results obtained in this laboratory by MacKinnon (216). He observed the visible cut-off of the plasma tail when high levels of tail gas were injected back into the plasma via the tail ring. An argon plasma was run at constant flow rate with tail argon injected via the backmixed mode tail ring at a rate high enough to quench the visible tail of the plasma. By visual observation of the level of plasma tail cut off it was possible to estimate the volume rate of tail argon required for a certain level of tail cut off to be reached. The Fig below indicates schematically the appearance of the tail cut off levels for increasing tail argon flows.

**Tail cut off phenomenon**

<table>
<thead>
<tr>
<th>Tail Argon</th>
<th>0-5 l/min</th>
<th>20 l/min</th>
<th>40 l/min</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zero or very low</td>
<td>medium argon</td>
<td>high argon</td>
<td></td>
</tr>
</tbody>
</table>
At zero or low flows of tail argon 0-5 lit/min, no plasma tail cut off occurs. As the tail argon rate is increased to 40 l/min the cut off level rises progressively to a position half-way up the coil. Above 40 l/min the plasma is extinguished due to destruction of the plasma gas vortex in the coil region.

It was observed that when plasma argon was replaced by an equivalent input volume rate of BCl₃, tail cut off was almost reduced to zero for the same tail argon rate. In order to achieve the same cut off level in the BCl₃ plasma it was necessary to inject 2-3 times as much tail argon as previously. This phenomenon could best be explained by an effective increase in volume rate through the plasma by an equal factor (x2-3). This could only be obtained if the BCl₃ dissociated almost completely:

\[ \text{BCl}_3 \xrightarrow{\text{arc}} \text{BCl} + \text{Cl}^+ + \text{Cl}^- \]

or \[ \text{BCl}_3 \rightarrow \text{B} + \text{Cl}_2 + \text{Cl}^- \]

or possibly \[ \text{BCl}_3 \rightarrow \text{BCl} + \text{Cl}_2 \]

Bequin et al (98) report identifying transient species such as CF, CCl and CF₂ when passing halocarbons through an r.f. plasma, while Baddour and Bronfin (257) report high yields (up to 70%) of C₂F₄ from passage of CF₄ through a d.c. arc. These results support the idea that halides undergo high levels of dissociation in plasmas.

A high degree of dissociation of BCl₃ in the plasma is also indicated by the presence of B⁺ ions in the plasma and preplasma regions (as discussed in Section 4.22). B⁺
ions were detected spectrographically at axial distances of up to 4 cm before the BCl$_3$ entered the r.f. coil (equivalent to 0.16 sec. before BCl$_3$ entry into the coil).

From considerations of the collision numbers of excited ions in the plasma environment, it most improbable that the preplasma ionisation of boron could be caused by argon or other excited atoms. The ionisation potential of B$^+$ is 8.26 eV and hence the energy of an excited atom must be maintained above this level while travelling 4 cm against the direction of bulk gas flow. This is clearly most improbable. It is more probable that the ionisation of B atom before the plasma is caused by electron impact. The possibility of electrons escaping along the axis of the torch within the period of voltage oscillation seems more reasonable.

The variation of intensity of B$^+$ emission at a fixed point in the plasma with increasing BCl$_3$ feed concentration (shown in Fig. 48) indicates that a maximum concentration (intensity) of B$^+$ is attained in the plasma. The initial rate of increase of [B$^+$] is very high at low [BCl$_3$], but the $\frac{d[B^+]}{d[BCl_3]}$ decreases progressively to near zero as $P_{BCl_3}$ approach 1 atmos. Two mechanisms for B$^+$ formation by electron bombardment are next considered.

Mechanism I

Step 1 - dissociation of BCl$_3$ $\rightarrow$ BCl

Step 2 - ionisation of BCl $\rightarrow$ BCl$^+$

Step 3 - equilibration of BCl$^+$ $\rightarrow$ B$^+$ + Cl

i.e. BCl$_3$ $\xrightarrow{\text{rapid}}$ BCl + 2Cl

$\xrightarrow{k_1}$ BCl $\rightarrow$ BCl$^+$ + e

$\xrightarrow{k_2}$ BCl$^+$ $\rightarrow$ B$^+$ + Cl
considering the above equilibrium reaction:

\[ k_2 [\text{BCl}^+] = k_2' [B^+][\text{Cl}^-] \]

however, \[ [B^+] = [\text{Cl}^-] \]

\[ \therefore k_2 [\text{BCl}^+] = k_2' [B^+]^2 \]

or \[ [B^+] = \sqrt{\frac{k_2 [\text{BCl}^+]}{k_2'}} \]

Assuming steady state to hold, then for \([\text{BCl}^+]\),

\[ \frac{d[\text{BCl}^+]}{dt} = 0 = k_1 [\text{BCl}_3] - k_2 [\text{BCl}^+] \]

\[ \therefore [\text{BCl}^+] = \frac{k_1}{k_2} [\text{BCl}_3] \]

and hence the equation for \([B^+]\) can be rearranged.

\[ [B^+] = \frac{k_2}{k_2'} \cdot \frac{k_1}{k_2} [\text{BCl}_3] = C \sqrt{[\text{BCl}_3]} \]

where \(C = \left(\frac{k_1}{k_2'}\right)^2\)

Thus the variation of \([B^+]\) with \([\text{BCl}_3]\) is in the form \([B^+]^2 = C [\text{BCl}_3]\) and should be linear. Fig. 52 shows the results for (optical density)\(^2\) of \(B^+ \propto [B^+]^2\) against partial pressure of \(\text{BCl}_3\). A good straight line agreement is obtained up to \(P_{\text{BCl}_3} < 0.4\) but the variation is non-linear at \(P_{\text{BCl}_3} > 0.4\) atm.
Mechanism II

Step 1 - ionisation of $\text{BCl}_3$ molecule $\text{BCl}_3 \rightarrow \text{BCl}_3^+ + e$

Step 2 - dissociation of $\text{BCl}_3^+$; $\text{BCl}_3^+ \rightarrow \text{B}^+ + \text{Cl}_2 + \text{Cl}$

A similar application of steady state theory leads to a cubic relationship between $[\text{B}^+]$ and $[\text{BCl}_3]$:

$$[\text{B}^+] = C \cdot \sqrt[3]{[\text{BCl}_3]} \quad \text{or} \quad [\text{B}^+]^3 \propto [\text{BCl}_3]$$

If the cubed intensity of $\text{B}^+$ emission is plotted against $[\text{BCl}_3]$ (see Fig. 53), another partial linearity is observed up to $P_{\text{BCl}_3} = 0.4$ atm. Hence it would appear that no simple mechanism for $\text{BCl}_3$ dissociation and boron ionisation holds above $P_{\text{BCl}_3}$ of $0.4$ atm., and that possibly both the above two mechanisms are competing at $P_{\text{BCl}_3} < 0.4$ atm.

The presence of six atomic hydrogen emission lines was observed in argon/hydrogen plasmas, but only one, the $\text{H}_\alpha$ line 4340.7 Å, was observed in the emission for an argon/hydrogen/$\text{BCl}_3$ plasma. This decrease in hydrogen atom emission when $P_{\text{BCl}_3}$ was present in the plasma could be due to two phenomena. Firstly, the formation of the BH intermediate (identified from band emission) would reduce the $[\text{H}^+]$ in the plasma by the following reaction $\text{B} + \text{H} \rightarrow \text{BH}$ ($\Delta H^0 = +3.4$ eV). The energy of formation could be supplied by the excitation energy of the hydrogen atom. BH however is not in thermodynamic equilibrium in the reaction mixture at temperatures below 2500°C, and hence almost complete dissociation should occur as the gases cool. The presence of very low concentration of $\text{B}_2\text{H}_6$ was observed, however, in samples of recovered $\text{BCl}_3$. Infrared spectra of condensed
BCl₃ contained peaks for B-H bonds at 2600 and 2610 cm⁻¹. However, the conversions to B₂H₆ were extremely low and no measurable quantity of B₂H₆ could be isolated from the effluent gases.

The second explanation for a decrease in H⁺ concentration in plasmas containing argon/hydrogen and BCl₃ could be the formation of the BCl₂ intermediate by the mechanism postulated by Dessaux et al (187); BCl₃ + H⁺ → BCl₂ + HCl. BCl₂ is in thermodynamic equilibrium at mole fraction up to 0.075 between 1600 and 2500°C (Figs. 55-57) however, and if equilibrium is attained in the plasma then corresponding concentrations of BCl₂ would be expected. BCl₂ molecules would, however, react rapidly on coding possibly by recombination with Cl⁺ to BCl₃, \( \{ \text{BCl}_2 + \text{Cl}^+ \rightarrow \text{BCl}_3 \} \) or recombination of 2 molecules of BCl₂ to give B₂Cl₄ as postulated by Moore et al (159). Identification of B₂Cl₄ in the condensed BCl₃ from effluent gases was not possible by mass spectrometer as B₂Cl₄ appears in the cracking pattern of BCl₃ (shown in Fig. 20).

5.2 Boron Powder Studies

5.21 Chemical Purity of Boron

The total boron content of boron compounds such as metal borides can be reliably estimated by the sodium carbonate fusion method (217, 218) discussed in Section 3.51. The application of this technique for the estimation of high content boron materials e.g. elemental boron approaching 99% purity, was found to be less reliable as a small variation of analytical result ±1% invalidated the purity determination. Estimation of the impurities present in plasma boron, however,
such as chlorine, carbon, silicon and nitrogen could be reliably obtained by standard analytical procedures.

The oxygen content of the boron could not be fully estimated as oxygen present as $B_6O$ and $B_7O$ could not be analysed, only the oxygen present as $B_2O_3$ being easily estimated by anhydrous methanol extraction.

By use of a spark source mass spectrometer it was possible to estimate the total impurities present in plasma boron, including oxygen bonded as boron suboxides. Table VII (Section 3.51) shows the major impurities present in two samples of boron, one taken before and one after vacuum degassing to 0.1 mm Hg at room temperature. Both of these samples were exposed to air for a short time (5-10 min) while they were pelletised before being sparked in the mass spectrometer.

**TABLE XX**

<table>
<thead>
<tr>
<th>Major Impurities in plasma boron</th>
</tr>
</thead>
<tbody>
<tr>
<td>Impurity</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>$N_2$</td>
</tr>
<tr>
<td>$O_2$</td>
</tr>
<tr>
<td>$Cl_2$</td>
</tr>
</tbody>
</table>

Table XX above shows the change in $N_2$, $O_2$ and $Cl_2$ contents of the boron for the two samples. The chlorine content of the boron was reduced from 0.98 to 0.008 % w/w by the vacuum degassing process. This was probably due to the removal of adsorbed $BCl_3$ from the surface of the boron, which left a residual chlorine content due to the vapour pressure of $BCl_3$ at 0.1 mm Hg.
The nitrogen content of the undegassed boron can be seen to be very low (∼0.008 % w/w) and on exposure to air after vacuum degassing this rose to 0.259 % w/w due to adsorption of atmospheric nitrogen on the active boron surface.

The oxygen content of the boron samples after vacuum treatment was unchanged at 0.74%. If all the chlorine present in the undegassed boron is assumed to have originated from BCl₃ then there would be an equivalent amount of B₂O₃ present on the surface of the boron formed by the reaction

\[ 2\text{BCl}_3 + \frac{3}{2} \text{O}_2 \rightarrow \text{B}_2\text{O}_3 + 3\text{Cl}_2 \]

and for 0.98% w/w Cl₂ content there would be an equivalent 0.185% w/w B₂O₃, which would be equivalent to 0.1% w/w O₂. Hence this 0.1% w/w O₂ contamination is the most that could be prevented by vacuum degassing the boron. The remaining oxygen impurities (0.74 - 0.1 = 0.64 % w/w) would most probably be present as boron oxides formed in the plasma reaction from the B₂O₃ present in the feed BCl₃. The presence of the BO intermediate was detected in the U.V. spectrum of the BCl₃ plasma while O₂⁺ and O⁺ ions were detected in the mass spectrum of BCl₃ used, though this may be due to an air background. Boron oxides, if present in the boron, would not be removed by vacuum degassing at room temperature. The oxygen content of the degassed boron sample (0.74%) would contain an equal amount (0.64% w/w) due to presence of the same boron oxide, together with ∼0.1% adsorbed oxygen. The ratio of adsorbed N₂/O₂ (3/1) is not in proportion to the atmospheric ratio (4/1) however, and could indicate a preferential adsorption of oxygen on the boron surface.
It is probable, therefore, that the boron purity after degassing and prior to atmospheric contamination could be as high as 99.3% as compared to 98.9% obtained on analysis, and that higher purities could be achieved if \( B_2O_3 \) was eliminated from the reactant \( BC\ell_3 \).

The specific surface area of boron of 12.4 m\(^2\)/g compares well with a previous measurement of surface area of 13.1 m\(^2\)/g for a standard amorphous boron by Grinberg and Zhukov (219) using a nitrogen adsorption technique and the BET equation (220) for the adsorption isotherm.

5.22 Structure of plasma boron

The three known structures of boron are the \( \alpha \)-rhombohedral, \( \alpha \)-tetragonal and \( \beta \)-rhombohedral polymorphs, each consisting of a different bonding configuration between the basic structural unit, the boron icosahedron. The boron icosahedron shown below contains 12 boron atoms with B-B bond lengths of \( \sim 1.75 \) Å.

The simplest boron crystalline structure is the \( \alpha \)-rhombohedral which consists of a threefold symmetrical bonding between the 12 unit icosahedra, as shown below:
This structure of boron is usually formed at relatively low temperatures, for example by the decomposition of carefully purified $\text{BI}_3$ (223) and boron hydrides (224) on inert substrates heated to temperatures between 800° and 1100°C.

The next most complicated structure, the $\alpha$-tetragonal polymorph, consists of four $\text{B}_{12}$ icosahedra bonded bisphe-noïdally into a tetragonal lattice. The unit cell of this structure contains 50 atoms and the lattice constants are $a = 8.75$ Å and $c = 5.00$ Å. Pure $\alpha$-tetragonal boron has been formed by the hydrogen reduction of $\text{BBr}_3$ on tantalum filaments heated to temperatures between 1200° and 1400°C (225).
$\alpha$-tetragonal boron structure (222).
The last of the known structures of boron, the \(\beta\)-rhombohedral structure, is also the most complex. The structure is shown below, and consists of eighty-four boron atoms arranged as twelve half-icosahedra about a single icosahedron. This structure was identified as recently as 1963 by Hughes et al (221, 222) and they also postulated a \(B_{156}\) unit consisting of twelve complete icosahedra arrayed around one icosahedron. The \(B_{84}\) polyhedron structure possesses the equivalent symmetry of the basic icosahedron and has a lattice constant for the unit cell of \(a = 10.145 \, \text{Å} \) with \(\alpha = 65^\circ 17'\). \(\beta\)-rhombohedral boron is stated (222) to occur generally as the main product of direct preparation of boron at temperatures ranging from the melting point 2200\(^\circ\)C down to 1500\(^\circ\)C.

The cell data for the known boron polymorphs is summarised in Table XXI below:

**TABLE XXI**

**Cell Data for Boron**

<table>
<thead>
<tr>
<th>B polymorph</th>
<th>No. of Boron atoms per unit cell</th>
<th>Lattice constants for unit cell</th>
<th>Temperature of formation ((^\circ)C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\alpha)-rhombohedral</td>
<td>(B_{12})</td>
<td>(a=5.057,\text{Å}, \alpha=55^\circ 4')</td>
<td>800-1100</td>
</tr>
<tr>
<td>(\alpha)-tetragonal</td>
<td>(B_{50})</td>
<td>(a=8.75,\text{Å}, , , c=5.06,\text{Å})</td>
<td>1200-1400</td>
</tr>
<tr>
<td>(\beta)-rhombohedral</td>
<td>(B_{84})</td>
<td>(a=10.145,\text{Å}, \alpha=65^\circ 17')</td>
<td>1500-2200</td>
</tr>
</tbody>
</table>

The x-ray diffraction patterns of plasma boron powder in this work were found to contain rings which were attributable in part to \(\beta\)-rhombohedral boron, but in general were diffuse as in amorphous boron patterns. The needle crystals and whisker growths formed on the torch wall, however, were positively identified as \(\beta\)-rhombohedral boron. This would
β-rhombohedral boron structure (222).
Electron microscope examinations of individual boron particles revealed that the majority of the boron was formed as random shaped particles of between 100 Å and 1000 Å in diameter. Transmission of the electron beam through some of the particles was observed by a darker overlapping area and darker areas beneath larger particles (see Plate 18). This shadowing effect tends to indicate that some of boron particles were in the form of platelets possibly less than 50 Å thick.

Electron diffraction patterns obtained for some of the random shaped platelets (Plates 21 - 22) were extremely complicated, however, and did not correspond to any of the known structures of boron. It was possible, however, to measure one lattice parameter for the dodecagonal platelets from the electron diffraction pattern (Plate 20). A lattice spacing in the plane of the platelet of 29-30 Å was measured which, when compared with lattice spacing in Table XXI can be seen to be very large.

The formation of twelve-sided platelets of boron could occur by various methods. A 12-sided symmetry might be obtained by twinning of a hexagonal crystal, as shown below. The resulting symmetry, however, would contain re-entrant

Twinned-hexagonal crystal - with re-entrant angles
angles at the circumference but the structure could approximate to a dodecagon as can be seen. Two other crystal structures with twelvefold symmetry are: 1) the Dihexagonal prism, and 2) the Dihexagonal bipyramid, as shown below:

1) Dihexagonal Prism (226) 2) Dihexagonal Bipyramid (226)

It can be seen that either of these structures could approximate to twelve sided platelets when short enough and especially if viewed from above. An excellent example of the above two structures is the crystal beryl, Be$_3$Al$_2$ (Si$_{16}$O$_{18}$), which contains two hexagonal prism symmetries together with a dihexagonal bipyramid symmetry (226).

Sullenger et al (113) reported the identification of several previously unknown forms of boron by passing 50-100 $\beta$-rhombohedral boron through a radiofrequency argon plasma. They found three new modifications of boron crystal habits in the product: i) a simple tetragonal boron with a lattice spacing $a=10.061\AA$ and $c=14.2\AA$ containing 190 atom/unit cell.

ii) an unreported cubic habit with a lattice spacing of $a=23.472\AA$ with an estimated 1700 atoms/unit cell.
iii) hexagonal and dodecagonal right prism compatible with hexagonal crystals with
lattice parameter $a=9.755\,\text{Å}$ and $c=10.016\,\text{Å}$.

Powder x-ray diffraction peaks of the latter crystals are given but none of the peaks corresponds to any of the major peaks found in x-ray diffraction patterns of the present boron.

The lattice parameter of $30\,\text{Å}$ obtained for the dodecagonal platelets is considerably larger than any reported lattice spacing for boron, and must be considered as a further modification to known boron structures. If the unit cell is based on a rhombohedral symmetry, it could contain say the $\beta$-rhombohedral 84-atom unit surrounded by four additional spherical arrays of boron-12 icosahedra. This would result in an extremely large number of boron atoms/unit cell, although a unit cell containing 1700 atoms was reported by Sullenger. This further modification of $\beta$-rhombohedral boron is, however, purely hypothetical as it was only possible to determine one lattice parameter. If the structure is three dimensionally symmetrical then the thickness of the dodecagonal platelets estimated at $30-50\,\text{Å}$ would approximate to the unit cell parameter.

5.23 Growth of boron particles in the plasma

The presence of boron platelets and "whiskers" in the reaction products can be considered in terms of theories developed for metals by Brenner (227) and Parker (228). The former reviewed the vapour growth of metals in general, including growth of metals from hydrogen reductions of metal halides, while the latter has reviewed the various theories
Two important concepts must be considered when dealing with growth of metals or non-metals by condensation from vapour or reaction at hot surfaces. Firstly, the vapour supersaturation $\sigma$ must be known as this determines the concentration gradient for mass transport or surface diffusion of atoms on the growing surface; secondly, the nucleation rate which determines the rate of formation of fresh growth sites on the surface. The interdependence between nucleation rate, vapour supersaturation and surface diffusion will determine whether the particle growth will be isotropic or anisotropic. If the latter case holds then the growth of whiskers or platelets is possible.

Two different relationships for determining isotropic and anisotropic growth rates have been derived under conditions of high supersaturation ($\sigma > 10^4$) and low supersaturation ($\sigma < 100$) respectively. Under conditions of low supersaturation surface diffusion to nucleation sites is usually much faster than the rate of formation of new nucleation sites, and the latter is then the rate determining step. Atoms will diffuse rapidly to initial nucleation sites, say the edge of a platelet or tip of a whisker, and anisotropic growth will occur at the edges of platelets etc. Under conditions of high vapour supersaturation, however, the rate of nucleation will be greater than the surface diffusion rate and as the formation of new nucleation sites will be isotropic, three dimensional growth of the particle will be possible and random-shaped particles will result.
Gomer (229) has developed two empirical relationships for predicting the growth of metals from vapours for both conditions of supersaturation. For low vapour supersaturation the final length \( h \) of a whisker at time \( t \) is related to its initial length by

\[
h = h_0 e^{\gamma t}
\]  \hspace{1cm} \text{(15)}

where \( \gamma = \) surface energy of solid (ergs/cm\(^2\)).

For particle growth in high supersaturated vapours, the growth was found to be dependent on the surface diffusion coefficient \( D_s \), \( \gamma \) and a linear growth parameter \( h \) in the following relationship

\[
D_s = 5.44 \gamma h^2
\]  \hspace{1cm} \text{(16)}

Piper and Polich (230) have predicted growth rates of crystals from high supersaturated vapours viz:

\[
\frac{dh}{dt} = \frac{\sigma P_0}{\rho} \left( \frac{M}{2 \pi RT} \right)^{\frac{1}{2}} \text{ cm/sec } \text{(17)}
\]

where \( h = \) linear growth parameter (cm)

\( P_0 = \) equilibrium vapour pressure of solid at temp \( T \) (gm/cm\(^2\))

\( \rho = \) solid density (gm/cm\(^3\))

\( M = \) molecular weight

\( R = \) gas constant (ergs \( ^{\circ} \text{K}^{-1} \text{ mole}^{-1} \))

\( T = \) temp. of vapour\( ^{\circ} \text{K} \)

It is possible therefore by use of the above equations to calculate the growth rates of boron particles from the plasma tail gases for conditions of low or high boron supersaturation in order to obtain information about the conditions necessary for B platelet and whisker growths.
The supersaturation of boron vapour in the plasma is given by the formula

\[ \sigma_B = \frac{P_B - P_{OB}}{P_{OB}} \]

where \( P_B \) = partial pressure of boron vapour in the plasma before condensation.

\( P_{OB} \) = equilibrium vapour pressure of solid boron at melting pt. \((2500^\circ K)\)

For a typical experiment the following gas compositions will occur before and after reaction of \( H_2 \) and \( BCl_3 \):

E.g. at \( H_2/BCl_3 = 2 \) and 25% conversion.

<table>
<thead>
<tr>
<th></th>
<th>Gas Compn. before reduction (gmole/l)</th>
<th>Gas Compn. after reduction (gmole/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar</td>
<td>0.0018</td>
<td>0.0018</td>
</tr>
<tr>
<td>BCl(_3)</td>
<td>0.004</td>
<td>0.003</td>
</tr>
<tr>
<td>( H_2 )</td>
<td>0.008</td>
<td>0.0065</td>
</tr>
<tr>
<td>HCl</td>
<td>-</td>
<td>0.003</td>
</tr>
<tr>
<td>B</td>
<td>-</td>
<td>0.001</td>
</tr>
<tr>
<td>( \sum )</td>
<td>0.0153 gmole/l</td>
<td></td>
</tr>
</tbody>
</table>

Hence the minimum boron vapour pressure in the plasma assuming all the boron vapour to condense will be:

\[ \frac{P_B}{P_{TOTAL}} = \frac{0.001}{0.0153} = 0.065 \text{ atm. (} = 50 \text{ mm Hg press)} \]

Niemyski et al (146) have plotted equilibrium boron vapour pressures up to temperature of 3300\(^\circ\)K. At 2500\(^\circ\)K they give a value for \( P_0 \) of \( 10^{-3} \) mm Hg. Hence a typical mean value of boron supersaturation in the plasma will be

\[ \sigma_B = \frac{50 - 0.001}{0.001} = 50 \times 10^3. \] This can be considered
as in the region of high supersaturation for the operating conditions chosen. However, for runs at $\text{H}_2/\text{BCl}_3 > 2$

lower values of $\sigma_B$ will occur. Hence for $\text{H}_2/\text{BCl}_3 = 10:1$ and for 25\% conversion then $P_B$ will equal 0.02 atm. and the equivalent $\sigma_B$ will be $1.5 \times 10^4$. The range of mean supersaturation can be seen, however, to still be within the $10^4$ order of magnitude. It is unlikely that, in such a turbulent system as the plasma torch, homogeneity will occur and it is most probable that there will be local regions of high and low supersaturation, especially downstream of the coil region.

Calculation of boron surface energy $\gamma_B$ at $T = 2500^\circ\text{K}$

The surface energy of a solid in contact with vapour at temperature $T^\circ\text{K}$ is given by Parker et al (231) as:

$$\gamma = \frac{P}{r} \left( \frac{2m}{\pi k T f^2} \right)^{\frac{1}{2}} \alpha'$$ .... (18)

where $P$ = partial pressure in vapour (g/cm$^2$)

$r$ = particle radius (cm)

$m$ = mass of atom (g)

$k$ = Boltzmann constant

$T$ = temperature $^\circ\text{K}$

$\rho$ = crystal density (g/cm$^3$)

$\alpha'$ = condensation coeff.

Hence for 1000 Å boron particle at its melting point in contact with a partial pressure of 5 cm Hg boron vapour:-
\[
\gamma = \frac{5 \times 13.6 \times 980}{10^{-5}} \left( \frac{2 \times 10^{-8} \times 1.66 \times 10^{-4} \times (\alpha')^2}{\pi \times 1.38 \times 10^{-16} \times 2.5 \times 10^3 \times 2.34^2} \right)
\]

\[
\therefore \quad \gamma = \frac{68 \times 980}{10^{-5}} \left( 0.675 \times 10^{-11} (\alpha')^2 \right)^{\frac{1}{2}} = 5.57 \times 980 \times 10^{2.5} \alpha'
\]

or \( \gamma = 50 \alpha' \times 10^{2.5} \)

\(\alpha'\), the condensation or sticking coefficient is a measure of the probability of an atom, which has collided with the solid surface, sticking to that surface and not re-evaporating from it. No data are readily available for \(\alpha'\) for boron vapour in contact with solid boron near its melting point, so a range of 3 probabilities 0.1, 0.5 and 1.0 will be used for calculation of \(\gamma\).

e.g. at \(\alpha' = 0.1\), \(\gamma = 5 \times 10^{2.5} = 1600 \text{ ergs/cm}^2\)

at \(\alpha' = 0.5\), \(\gamma = 25 \times 10^{2.5} = 8000 \text{ ergs/cm}^2\)

and at \(\alpha' = 1.0\), \(\gamma = 50 \times 10^{2.5} = 16000 \text{ ergs/cm}^2\)

Brenner(227) has calculated \(\gamma\) values for 27 elements (excluding boron) at temperatures up to 3250\(^\circ\)K and obtained \(95 < \gamma < 2680 \text{ erg/cm}^2\). From this it is clear that the value of \(\gamma = 1600 \text{ ergs/cm}^2\) falls within this range, and hence it will be used in further calculation of growth rates.

**Calculation of growth rates of dodecagonal boron platelets at low \(\sigma_B\).**

Using equation (15) derived by Gomer for growth at low supersaturation levels

\[ h = h_0 e^{\gamma t} \]

where \(h = \text{final platelet radius} = 3500^\circ \text{A} (= 0.35 \times 10^{-4} \text{ cm})\)

\(h_0 = \text{initial " radius say } 100^\circ \text{A} (= 10^{-6} \text{ cm})\)

\(\gamma = 1600 \text{ ergs/cm}^2\)
then \[
\frac{0.35 \times 10^{-4}}{10^{-6}} = e^{1600t}
\]

or \[
\ln (0.35 \times 10^2) = 1600t
\]

whereby \( t = \) growth time = \( \frac{\ln 35}{1600} = 3.55 = 2.2 \times 10^{-3} \) sec.

If \( \alpha' = 1.0 \) this figure decreases to \( 2.2 \times 10^{-4} \) sec.

Calculation of growth rate of isotropic boron particle \((\sigma_B=10^4)\)

Substitution of typical operating parameters for boron growth at high \( \sigma_B \) values gives:

\[
\sigma_B = 5 \times 10^4
\]

\[
P_0 = 10^{-4} \times 13.6 \times 980 \text{ g/cm}^2
\]

\[
M = 10.8 \quad (\rho = 2.34 \text{ g/cm}^3)
\]

\[
R = 8.315 \times 10^7 \text{ ergs oK}^{-1} \text{ mole}^{-1}
\]

\[
T = 2.5 \times 10^3 \text{ oK}
\]

substituted into equat. (17)

\[
\frac{dh}{dt} = \frac{\sigma P_0}{\rho} \left( \frac{M}{2 \pi R T} \right)^{\frac{1}{2}} \text{ cm/sec.}
\]

gives:

\[
\frac{dh}{dt} = \frac{5 \times 10^4 \times 10^{-4} \times 13.6 \times 980}{2.34} \times \sqrt{\frac{10.8}{2 \times 8.315 \times 10^7 \times 2.5 \times 10^3}} \text{ cm/s}
\]

\[. \]

\[
\frac{dh}{dt} = 6.5 \times 10^{-2} \text{ cm/s} \quad (= 6.5 \times 10^6 \text{ o/sec}).
\]

Hence growth times, \( t \), for a range of 500-3000 o radius boron particles which were identified in the products are:

\( (t)_{500} = 0.078 \times 10^{-3} \) sec

\( (t)_{3000} = 0.234 \times 10^{-3} \) sec.

This spread of particle growth times in the tail of the plasma can also be considered as a spread of particle residence time in the hot gases before quenching occurs.
A comparison of estimated growth times for isotropic boron particles and the dodecagonal platelets of boron is shown in the following table:

<table>
<thead>
<tr>
<th></th>
<th>Isotropic growth ((\sigma_B^{10^4}))</th>
<th>Anisotropic growth ((\sigma_B^{\text{low}}))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>10000Å final dia. 6000Å</td>
<td>7000Å dodecagon platelet</td>
</tr>
<tr>
<td>Growth time</td>
<td>0.078</td>
<td>0.234</td>
</tr>
<tr>
<td>(t m sec)</td>
<td></td>
<td>2.20</td>
</tr>
<tr>
<td>Growth distance</td>
<td>0.003cm</td>
<td>0.009cm</td>
</tr>
<tr>
<td>for 40 cm/s lin. vel.</td>
<td></td>
<td>0.09 cm</td>
</tr>
</tbody>
</table>

It can be seen therefore that particles of boron growing in the tail of the plasma, while condensation occurs in local regions of high boron concentration, will reach a final diameter dependent on the local gas velocity in the turbulent tail region, which will determine particle residence time. However, particles growing in regions of local low boron concentration and low gas velocity with associated slow quenching could grow anisotropically and form platelets or whiskers. The formation of clusters of dendritic crystals with whiskers which grew on the torch wall beneath the coil must have grown under low boron supersaturation, and indicate that a relatively static zone must be present in the vortex flow at low gas rates. Indeed the 3-dimensional whisker growth pattern could trace out regions of low boron supersaturation and local low velocity which prevail in any particular run.
5.3 Kinetic Results

The reacting system in a plasma reactor is obviously extremely complicated. Not only is a wide variety of free radicals and gaseous ions present, but in addition, the system contains free electrons, is in motion and its temperature is ill-defined. Nonetheless, the identification of intermediates and analysis of kinetic and thermodynamic data permits useful speculation on possible reaction routes.

5.3.1 Thermodynamic Equilibrium Considerations

Figs. 54-57 show the thermodynamic equilibrium compositions of boron trichloride and boron trichloride/hydrogen mixture for temperatures from 1000°K → 6000°K computed from the Janaf Thermochemical Tables (232, 233, 234). Equilibrium compositions were calculated for $\text{H}_2/\text{BCl}_3$ ratios of 1.5/1, 4/1 and 9/1 at a pressure of 1 atmosphere. Fig. 54 shows the equilibrium composition of pure $\text{BCl}_3$ at one atmosphere pressure, together with the equilibrium vapour pressure of boron. It can be seen that the partial pressure of boron on the equilibrium mixture is always lower than the equilibrium vapour pressure of boron throughout the temperature range and hence, although boron can exist as a gas in the equilibrium mixture above 3000°K, condensation of boron can never occur. This confirms experimental evidence obtained in this work in which boron was never condensed as a stable solid in the absence of hydrogen.

Figs. 55-57 show the equilibrium compositions of $\text{BCl}_3$ and hydrogen mixtures with increasing temperature and $\text{H}_2/\text{BCl}_3$ ratio. The mole fractions of boron condensed from the equilibrium mixtures are also shown and can be seen to reach
maximum at temperatures between 1500° and 2000°K for each of the H₂/BCl₃ ratios. The vertical broken line shown in each diagram represents the boron condensation temperature for the equilibrium mixture; i.e. that temperature at which the partial pressure of boron in the gas mixture is equal to the equilibrium vapour pressure of boron. This represents an upper limit for the condensation of boron above which boron will only exist as a vapour. The condensation temperature therefore represents the highest temperature at which boron can be formed directly as a solid from a reacting system, or conversely the temperature at which boron will begin to condense from an equilibrium mixture as it cools from higher temperatures. The condensation temperature for the BCl₃/H₂ system varies with the ratio of hydrogen to BCl₃ and occurs throughout the range at a temperature not far removed from the melting point of boron (2450°K). Condensation temperatures for boron at H₂/BCl₃ from 1 ½ to 100/1 are shown below:

<table>
<thead>
<tr>
<th>H₂/BCl₃ mole ratio</th>
<th>pure BCl₃</th>
<th>1.5/1</th>
<th>4/1</th>
<th>9/1</th>
<th>20</th>
<th>50</th>
<th>100</th>
</tr>
</thead>
<tbody>
<tr>
<td>Condensation Temperatures °K</td>
<td>P_B &gt; P⁰_B all temperatures</td>
<td>2400</td>
<td>2500</td>
<td>2560</td>
<td>2560</td>
<td>2520</td>
<td>2440</td>
</tr>
</tbody>
</table>

From Fig. 55 (the equilibrium composition at H₂/BCl₃ = 1.5/1,) it can be seen that the mole fraction of boron condensed from the equilibrium mixture as the temperature rises from 1000°K reaches a maximum of 0.11 at 2000°K. At higher temperatures the mole fraction of condensed boron decreases very rapidly to approach the equilibrium vapour pressure of solid boron at the condensation
temperature 2400°K. This phenomenon is due to the formation of boron subchlorides BCl and BCl\(_2\) in the equilibrium mixture. At 2400°K the distribution of boron in the chlorides at equilibrium is as follows:

<table>
<thead>
<tr>
<th>Boron present as</th>
<th>% mole</th>
</tr>
</thead>
<tbody>
<tr>
<td>BCl(_3)</td>
<td>20</td>
</tr>
<tr>
<td>BCl(_2)</td>
<td>28</td>
</tr>
<tr>
<td>BCl</td>
<td>52</td>
</tr>
<tr>
<td>B</td>
<td>negligible</td>
</tr>
</tbody>
</table>

As temperatures increase above 2400°K the proportion of boron occurring as subchlorides increases as BCl\(_3\) becomes more dissociated, and at 3000°K the mole fraction of BCl in the equilibrium mixture reaches a maximum of 0.23. At still higher temperatures BCl and BCl\(_2\) also start to dissociate and atomic boron and chlorine appear in significant concentrations in the equilibrium mixture.

Similar relationships between the equilibrium mole fractions of boron, BCl and BCl\(_2\) hold at the higher H\(_2\)/BCl\(_3\) ratios and are shown in Figs. 56 and 57. The mole fraction of condensed boron for the higher H\(_2\)/BCl\(_3\) ratios reach similar maximum values at temperatures below the boron condensation temperature. The maxima are, however, progressively lower due to the increasing concentrations of hydrogen. The table below shows the maximum equilibrium mole fractions of condensed boron for increasing H\(_2\)/BCl\(_3\) ratios, together with the corresponding conversion and temperature.
The maximum conversions of condensed boron can be seen to increase with $\text{H}_2/\text{BCl}_3$ ratio as would be expected. Fig. 58 shows the variations of conversion to boron with increasing temperature for the 1.5:1, 4:1 and 9:1 $\text{H}_2/\text{BCl}_3$ ratios. The maximum conversions for all three mixtures occur at temperatures between $1700^\circ$ and $2000^\circ$K, and decrease to low values as the temperature is decreased to $1000^\circ$K or increased to the corresponding condensation temperatures. At higher temperatures then the condensation temperature boron is again present in the equilibrium mixture due to the dissociation of BCl and BCl$_2$. Spectroscopic evidence obtained from the BCl$_3$ plasma suggests that the BCl is present in high concentrations, possibly near its maximum concentration, hence it is probable that the initial dissociation products in the plasma are the subchlorides formed above the condensation temperature of boron.

Boron atoms and ions are present in the higher temperature regions of the plasma, but unless extremely rapid quench conditions prevail which would freeze the boron from the mixture, it is probable that most of the initial boron atoms formed in the plasma will recombine to form BCl or BCl$_2$ on cooling. A zone will exist however in the tail regions of the plasma where the temperature of the cooling gas passes through the $2000^\circ$ to $1500^\circ$K range. It must be considered
more probable, therefore, if conditions of thermodynamic equilibrium are approached in the plasma reactor, that conversions to boron are dependent on an interaction between such variables as residence time in the temperature zone, and condensation rate before the gases are quenched too much.

Consideration of the mean temperature reached by the bulk gas as it passes the plasma could also give an indication as to the overall behaviour of the system.

5.32 Estimation of mean gas temperature

The mean temperature attained by a gas as it passes around and through a plasma can be estimated by a heat balance over the torch. Gray et al (116) and Biggerstaff et al (183) have calculated mean gas temperatures for plasma gases, the former for r.f. torches and the latter for an arc torch. Dundas (235) has proposed an energy balance for an r.f. plasma system and obtained an energy distribution as follows:

\[ E_I, \text{ Energy input to plasma} = \text{convection losses to gases, } E_C + \text{radiative heat losses, } E_R \]

The numerical energy balance was calculated as

\[ E_I = 0.3 \, E_C + 0.7 \, E_R \]

Hence radiation losses account for 70% of the energy transfer processes from the plasma to the surrounding environment. The remaining 30% of the input energy will be available for convective heating of the stabilising plasma gas flow. Thus, knowing the heat capacity of the gas mixture and its mass flow rate it is possible to estimate the mean temperature attained by the gas under sensible heating:
i.e. Heat input = sensible heating of gases + convective losses to torch + radiation losses.

or \[ P \text{ (kw)} = m_{\text{g}} C_{\text{P}g} \Delta T_{\text{g}} + m_{\text{w}} C_{\text{Pw}} \Delta T_{\text{w}} + Q_{R} \]

Taking the simplest case for a pure argon plasma the mean temperature attained by the argon due to convection can be calculated from equation:

\[ 0.3P = m_{\text{A}} C_{\text{PA}} (T_{2} - T_{1}) + m_{\text{w}} C_{\text{PW}} (T_{2}^{0} - T_{1}^{0}) \]

Heat losses to cooling water were measured calorimetrically and found to approx. 10% of the power input for argon plasmas. Hence \[ 0.3P (1-0.1) = m_{\text{A}} C_{\text{PA}} (T_{2} - T_{1}) \]

The heat capacity of a gas will increase with temperature and hence a mean value must be assumed or else a solution must be calculated by a reiterative technique. Biggerstaff et al give values for \( C_{\text{P}} \) argon up to 10000\(^{0}\)C and up to 7000\(^{0}\) the \( C_{\text{P}} \) value is constant at 0.13 cal \( \text{g}^{-1} \text{ °C}^{-1} \). Hence for operation at 30 KW say and 50 lit/min argon the estimated mean temperature rise would be:

\[ T = \frac{0.3 (30-3)}{C_{\text{PA}}^{0.3} C_{\text{PA}}} = \frac{8 \text{ kw}}{C_{\text{A}} 50 \times 0.15} \quad \left[ C_{\text{A}} = 1.78 \text{ g/l} \right] \]

\[ = \frac{8 \times 10^{3} \times 0.25 \times 60}{50 \times 1.78 \times 0.15} = \frac{333.0 \times 10^{3}}{134} = 2.5 \times 10^{3} \text{ deg. C} \]

Hence the calculated mean temperature of a 50 l/min argon plasma at 30 kw is 2500\(^{0}\)C.

For a pure BCl\(_{3}\) plasma at 30 kw the mean temperature can be calculated from heat capacity data given by Biggerstaff et al (183). The value of \( C_{\text{P}} \) BCl\(_{3}\) increases with temperature rise up to 0.7 cal \( \text{g}^{-1} \text{ °C}^{-1} \) at 4000\(^{0}\)C decreasing to 0.5 cal \( \text{g}^{-1} \text{ °C}^{-1} \) at higher temperatures as shown below:
Assuming a mean value of $C_p BCl_3$ of 0.5 cal g$^{-1}$ °C$^{-1}$ throughout the temperature range, the mean gas temperature rise at 1 mole/min BCl$_3$ is given by:

$$\Delta T = \frac{8 \times 0.25 \times 10^3 	imes 60}{117 \times 0.5} = 2000°C$$

The temperature rise can be seen to vary as a function of

$$\Delta T = f\left(\frac{\text{Power input}}{M_B \cdot C_{PB}}\right)$$

$M_B$ = mass rate BCl$_3$

$C_{PB}$ = heat capacity BCl$_3$

Assuming a constant mean value for $C_{PB}$ the mean temperature of a BCl$_3$ plasma gas stream will vary as a function of

$$T = f_n\left(\frac{P}{M_B}\right)$$

and a nomograph of mean temperature against power input and mass rate can be drawn up. Fig. 59 shows such a nomograph of estimated mean BCl$_3$ temperatures as function of power input and mass rate, together with experimental operating boundaries.
5.33 The concept of residence time

Two definitions of residence time of reactants in the plasma torch have been used in this work. Firstly, the definition of residence time \( T \) as the ratio of reactor volume to total gas flow rate into the reactor. In this definition the plasma torch and tail ring are considered as a stirred reactor of volume \( V \) and the reactants are fed to the reactor either premixed or separately as shown below:

\[
\text{Reactor residence time}
\]

Residence time \( T = \frac{V}{F_T} \) where \( F_T = F_A + F_B + F_H \)

This definition enables some measure of the time that a unit volume of reactant mixture spends in the reactor and has been used where the flow rates of both argon and hydrogen are varying when constant concentrations of \( \text{BCl}_3 \) were required. This concept of residence time is oversimplified, however, especially when tail \( \text{H}_2 \) is backmixed into the plasma. In this condition the effect of the reverse component of hydrogen flow is ignored by the volume residence time. The diagram below shows the actual flow pattern of plasma reactor with backmixed tail injection.
In the diagram, if the angle of $H_2$ injection is $\alpha$ to the horizontal, then the resolved axial velocity of the gas in the torch $= V_{A+B} - V_H \sin \alpha$. For the non-backmixed mode of tail injection the $V_H \sin \alpha$ term is zero and the axial velocity of the gas in the torch is $V_{A+B}$.

If axial momentum is also considered then the resultant axial gas momentum as it leaves the torch for $Ar+BCl_3$ plasma gas with $H_2$ backmixed is given by

$$M_T V_T = M_A V_A + M_B V_B - M_H V_H \sin \alpha$$

and for the non-backmixed mode $M_T V_T = M_A V_A + M_B V_B$.

The effects of momentum and velocity components of feed rates will introduce errors in the calculation of residence time $T$. This must be borne in mind when analysing results for a series of operating conditions and when comparing results with other systems. At high backmixed tail $H_2$ rates the velocity component of hydrogen flow in reverse direction to main flow could become greater than the axial velocity of the plasma.
gas. This could introduce a prolonged residence time $T$ at high tail hydrogen rates which would tend to produce greater conversions for a fixed set of operating conditions. Backmixing of high levels of hydrogen could also cause premature quenching of the reactant mixture, before thermo-dynamic equilibrium can be attained.

A second residence time $T'$ has also been used in this work when either two components of the system have been kept constant and the third varied, or when one reactant was present in excess concentration. $T'$, defined as the inverse flow rate of one reactant, must be considered to be more meaningful than $T$ as no variation of backmixing occurs through a given series of runs as all gas flows are kept constant, except the one of interest.

Neither of the above definitions of residence times is absolute, however, and both will only indicate general trends to the behaviour and to the kinetics of the system. They do not give any indication to the length of time the reactants are actually in the plasma, which is probably considerably shorter than these estimated times.

5.34 Runs at constant initial Hydrogen concentration.

To enable runs to be carried out at constant hydrogen concentration the system was operated at excess $[H_2]_0$, so that only a small proportion of hydrogen reacted, compared to the reacting $\text{BCl}_3$, allowing the reaction to be considered pseudo-unimolecular. Fig. 22 shows the conversion of $\text{BCl}_3$ to boron decreasing exponentially with increases in $[\text{BCl}_3]_0$ from 0.001 to 0.008 gmoles/litre at two levels of
tail H₂ flow (100 l/min and 240 l/min). A plot of the latter as initial BCl₃ conversion against H₂/BCl₃ ratio (Fig. 23) shows almost perfect linearity passing through the origin. H₂/BCl₃ ratios of up to 25/1 were used and conversions up to 80% obtained. At H₂/BCl₃ = 0, i.e. when no hydrogen was present, no boron was formed as a stable product. This is in disagreement with results obtained in an arc plasma torch (183) which claim that boron can be formed by thermal decomposition of BCl₃ in the arc. The presence of dissociated boron species in the BCl₃ plasma has already been discussed (Section 5.1) the neutral boron atom, and the B⁺ ion, BCl, BCl₂ and BH radicals were identified spectroscopically in the discharge. However, at no time during the work has any stable boron been formed by thermal decomposition of BCl₃.

It is apparent from Fig. 23 that the conversion of BCl₃ to boron, under conditions of excess hydrogen, is inversely proportional to the concentration of BCl₃ used. For example, a doubling of BCl₃ concentration (or halving of H₂/BCl₃ ratio) produces an approximate halving of conversion. e.g. H₂/BCl₃ reduced from 16/1 to 8/1 and conversion reduced from 50% to 25%.

This infers that a constant amount of BCl₃ is converted to boron when excess H₂ is used, independent of the argon and BCl₃ flow rates. This in turn suggests that a constant number of active species are formed at any power level (in this case 25 kw) independent of the gas flow rates.

Fig. 25 shows a comparison between two sets of runs at constant H₂ tail injection, one by backmixed mode
Conversions of BCl$_3$ to boron were plotted against H$_2$/BCl$_3$ ratio and both gave a linear dependence up to ratio 10/1, and a similar halving of the conversion by doubling [BCl$_3$]$_0$ is apparent. Deviation from linearity occurred above H$_2$/BCl$_3$ = 10/1 in both cases. These results suggest that the mode of tail hydrogen injection is not important when BCl$_3$ is present in the plasma. These results may not be strictly comparable, however, as the range of flow rates used in each was somewhat different.

### 5.35 Runs at constant initial BCl$_3$ concentration

Fig. 24 shows the dependence of BCl$_3$ conversion on increasing [H$_2$]$_0$. For these runs the initial [BCl$_3$] was kept constant by use of the plasma argon as a makeup gas to ensure a constant total inlet gas volume rate. The results were obtained for three values of total flow residence time, T = 0.096, 0.144 and 0.264 sec.

It can be seen from the graph that the dependence of reaction conversion on [H$_2$]$_0$ is very low. The maximum increase in BCl$_3$ conversion which occurs over the range of concentrations used was a 20% increase for a 300% increase in [H$_2$]$_0$ at the longest residence time T = 0.264 sec. This low dependence of conversion of BCl$_3$ on [H$_2$]$_0$ would suggest a very low order of hydrogen in the overall rate equation:

$$\frac{d[B]}{dt} = K [BCl_3]^\alpha [H_2]^\beta$$

with $\beta \ll 1$.

For all these runs the hydrogen was introduced via the backmixed mode of tail injection and this may have introduced errors into the results.
A comparison between conversions of BCl$_3$ obtained with backmixed and laminar tail injection is shown in Fig. 31. The lower curve shows the backmixed mode for which similar slight increases in conversion are obtained as $[H_2]_0$ increases. However, when the hydrogen is fed normally to the torch axis there is no increase in conversion for a range of $[H_2]_0$ increasing from 0.0074 to 0.022 gmoles/litre (i.e. 200% increase). This suggests that the reaction is zero order with respect to hydrogen in the laminar addition mode, and that operation in a turbulent addition mode increases the effective partial order, $\beta$, above zero.

This increase in partial order $\beta$ for backmixed hydrogen can also be caused by the effect of the ratio of tail gas flow to plasma gas flow ($\Upsilon$ ratio). The $\Upsilon$ ratio for this series varied from 0.2 at 0.0074 gmoles/l to 3.3 at 0.033 gmoles/l (see Section 4.12). Thus, although the concentration of BCl$_3$ was constant during the runs, the total flow residence time may not have been constant, but could have been effectively increased by the reverse velocity vector of the hydrogen feed. However, this would indicate higher conversions for the backmixed mode, but in fact the conversions were lower than for the laminar mode approaching equal conversions at higher $[H_2]_0$. Consideration of the backmixed mode results in terms of premature quenching or more effective mixing of reactants does not fully explain the lower conversions at low $[H_2]_0$. Clearly there is no simple explanation for the anomalous behaviour of the backmixed mode under these conditions, and the results must be caused by a combination of unknown variables.
5.36 Effect of residence times $T$ and $T'$

The effect of total flow residence time $T$ will be considered only for the series of runs at constant $[\text{BCl}_3]_0$. Fig. 26 shows the results of these runs for three values of initial $[\text{H}_2] = 0.0074$, 0.0151 and 0.033 gmoles/litre for a $[\text{BCl}_3]_0$ of 0.004 gmoles/litre. At the lowest hydrogen concentration, the conversion was almost constant for increasing $T$, rising by 0.023% conversion per millisec residence time. At 0.0151 gmoles/litre $[\text{H}_2]_0$, the rise in conversion was almost double i.e. 0.053%/msec, and for 0.033 gmoles/litre, the rise was 0.12%/msec. Therefore, it can be seen that the rates of increase in conversion of $\text{BCl}_3$ are approximately proportional to $[\text{H}_2]_0$. In terms of moles of $\text{BCl}_3$ and $\text{H}_2$ reacting, the table below shows the rates of reaction for the various $[\text{H}_2]_0$.

<table>
<thead>
<tr>
<th>$[\text{H}_2]_0$ gmoles/l</th>
<th>$-\frac{d[\text{BCl}_3]}{dt}$ gmoles/msec</th>
<th>$-\frac{d[\text{H}_2]}{dt}$ gmoles/msec</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0074</td>
<td>$0.92 \times 10^{-6}$</td>
<td>$1.40 \times 10^{-6}$</td>
</tr>
<tr>
<td>0.0151</td>
<td>$2.22 \times 10^{-6}$</td>
<td>$3.32 \times 10^{-6}$</td>
</tr>
<tr>
<td>0.0334</td>
<td>$4.80 \times 10^{-6}$</td>
<td>$7.2 \times 10^{-6}$</td>
</tr>
</tbody>
</table>

$[\text{BCl}_3]_0 = 0.004$ gmoles/l, Power = 25 kw

The conversions of $\text{BCl}_3$ approach the equilibrium conversion with increasing residence time. Fig. 27 shows the increase in moles of $\text{H}_2$ reacting for increasing residence time for the above runs. The moles of $\text{H}_2$ reacting rise linearly with residence time and on extrapolation to zero time apparently converge at 0.002 moles $\text{H}_2$ reacting. This
is clearly impossible and must be a result of the oversimplified assumption of residence time $T$. The linear portion of the graph, however, above $T = 0.1$ sec, could indicate a zero order dependence on hydrogen as this portion of the graph is equivalent to the zero order plot for the integrated rate equation $\frac{dx}{dt} = k$ for unimolecular reactions. However, a true zero order dependence cannot hold under conditions of backmixing, and the amount of hydrogen reacting would appear to follow the relationship:

$$-X_{H_2} = a + b \left[ H_2 \right]^8 t$$

which on differentiation gives:

$$-\frac{dX_{H_2}}{dt} = b \left[ H_2 \right] \left( = k \frac{d(X_{BCl_3})}{dt} \right)$$

(wher $a$ and $b$ are coefficients for the system).

The behaviour of the system under various operating conditions for increasing residence time $T'$ is shown in Fig. 28. Two curves (A - B) are shown for tail $H_2 240$ l/min and 100 l/min for which the conversion of $BCl_3$ increases very rapidly with residence time tending to maximum values. Both of these sets of runs are with backmixed $H_2$. Curve C shows results for a relatively low flow of $H_2$ and $BCl_3$, premixed, and fed laminarily into the tail of an argon plasma. The increase in conversion is more gradual in this case due to the lower $[H_2]_0$, but it still tends to a maximum value ($\sim 60\%$).

Curve D shows the increase in conversion for a stoichiometric mixture of $BCl_3$ and $H_2$ fed in the same way as Curve C. This rises more slowly than the latter and does not reach its maximum within the range of residence time used.
5.37 Order of reaction

Fig. 60 shows the results for curve AB D above plotted as $\ln \left( \frac{[\text{BCl}_3]_0}{[\text{BCl}_3]_0 - [\text{BCl}_3]_t} \right)$ against $T'$. This is the first order integrated rate equation plot for conditions of unimolecular reaction or excess concentration of one reactant (in this case $H_2$), or for a stoichiometric reaction mixture for unimolecular reactions. It can be seen that there is a good linearity for results A ≈ B for $T' < 0.008$ sec, above which residence time non-linearity occurs. The results for the stoichiometric mixture also show good linearity although deviation occurs at very short residence times ($< 0.005$ sec).

Under conditions of excess concentration of one reactant the following overall rate equation can be written:

$$\frac{-d[\text{BCl}_3]}{dt} = k [\text{BCl}_3]^\alpha [H_2]^\beta$$

when $[H_2]_0 \gg [\text{BCl}_3]_0$, the $[H_2]_0$ is effectively constant.

:. substitution of $k [H_2]^\beta = k'$

then $-d[\text{BCl}_3] = k' [\text{BCl}_3]^\alpha$ or pseudo-unimolecular.

For $\alpha = 1$ :

integration this gives $\ln \frac{[\text{BCl}_3]_0}{[\text{BCl}_3]_0 - [\text{BCl}_3]_t} = k' t$

\[ \text{c.f. } y = mx + c \]

Also, for stoichiometric reaction mixtures: $[H_2]_0 = \frac{3}{2} [\text{BCl}_3]_0$
therefore \[-d \left[ \text{BCl}_3 \right] = k \left[ \text{BCl}_3 \right] \left[ \text{BCl}_3 \right]^{3/2} = 3/2 k \left[ \text{BCl}_3 \right]^{3/2} \]

but \( \alpha + \beta = n \) \( \therefore -d \left[ \text{BCl}_3 \right] = 3/2 k \left[ \text{BCl}_3 \right]^{n} \)

For \( n = 1 \) a similar \( \ln \) function can be derived.

It can be seen therefore that as the plots of \( \ln ( \ln \left[ \text{BCl}_3 \right] ) \)
vs. \( T' \) are linear for excess hydrogen concentration \( T' = \frac{1}{0.008} \) sec, then the partial order of \( \text{BCl}_3 \) in the overall
rate equation is unity within this limit. Also the stoichiometric reaction mixture produced a linear plot of the
\( \ln \left[ \text{BCl}_3 \right] / T' \) and here the overall order within the limits
stated is also unity. These two results agree with the
possible zero order hydrogen dependence in the overall rate
equation, which can be stated as:

\[-d \left[ \text{BCl}_3 \right] = \frac{d \left[ \text{B} \right]}{dt} = k \left[ \text{BCl}_3 \right] \left[ \text{H}_2 \right] \]

5.38 Effect of variation of feed configuration

In all the runs carried out on the effects of reactant
feed configuration, the spread of conversion obtained for
fixed \( \text{BCl}_3 \) rate and increasing hydrogen concentration was
a maximum of 12\% for any one initial hydrogen concentration
(see Fig. 29). Hence, although some trends in the be-
behaviour of the plasma reactor were brought to light in this
series of runs, the major conclusion from the results is how
little the changes in feed configuration effected the con-
version. The effect of increasing \( \left[ \text{H}_2 \right]_0 \) can also be seen
to produce little increase in \( \text{BCl}_3 \) conversion. These
points are illustrated by the fact that for the reaction
conditions used in the series of runs a 200\% increase in
[H$_2$]$_0$ in a premixed BCl$_3$/H$_2$ tail feed produced an increase in conversion of only 9%, and the same increase was obtainable by feeding the equivalent BCl$_3$ through the plasma at the lowest [H$_2$] mixture. This series of runs therefore throws some light on the economic optimisation of the plasma reactor, as the costs of raw materials are a major expense.

It can be seen from Fig. 29 that the method of tail gas injection is also extremely important when considering optimisation of the reactor. For instance, when BCl$_3$ was passed through the plasma a higher conversion was obtained when H$_2$ was fed laminarly to the tail gases (54% as opposed to 49%). However, when hydrogen was present in the plasma there was no apparent beneficial effect of non-backmixed tail injection; in fact for the case of an Argon/H$_2$ plasma with H$_2$ + BCl$_3$ in the tail, the backmixed mode gave a 6% higher conversion. For all the different feed configurations tried on one specific reaction mixture (30 g/min BCl$_3$, at 0.004 g moles/litre concentration, 20 KW and T = 0.36 sec), the highest conversion (54%) was obtained at 0.0185 gmole/l H$_2$ by laminar hydrogen injection into an argon/BCl$_3$ plasma. The lowest conversion (33%) for the above reaction mixture was obtained by backmixed injection of BCl$_3$/H$_2$ into an argon plasma.

The difference in the effect of backmixed and laminar tail gas injection for different combinations of reactant feed is further brought out by comparison of Figs. 31 and 32. The former shows how little an effect the mode of tail gas injection has on the conversion if both BCl$_3$ and H$_2$ are premixed and fed to the tail of an argon plasma. The
latter, however, shows the completely different results that were obtained by both modes of tail injection if BCl$_3$ is fed to the plasma with argon. Fig. 31 also shows that under conditions of laminar injection of BCl$_3$/H$_2$ mixtures to the tail of an argon plasma, the conversion to boron is apparently independent of [H$_2$], or zero order w.r.t. H$_2$ for the range of operating conditions used. The initial decreased conversions obtained when the BCl$_3$ and hydrogen were backmixed could be due to a temperature effect. It has been shown that a maximum conversion exists for any equilibrium mixture between mean temperatures of 1500° - 2000°K. It is possible therefore that at low levels of backmixed hydrogen the reaction temperature is higher than that for maximum conversion, and as the hydrogen level is increased the extra hydrogen reduces the reaction temperature to that of maximum conversion. This explanation is based on the assumption, however, that thermodynamic equilibrium is established in the system.

The horizontal line obtained for the laminar mode could show that above a minimum [H$_2$]$_0$, the extent of conversion of BCl$_3$ was independent of the mass rate of activated argon atoms in the plasma tail as the argon flow was decreased throughout the series to maintain consistent [BCl$_3$]$_0$. However, the fact that higher conversions did not result from higher argon flows could also mean that there is some limitation on the energy transfer process to the BCl$_3$.

In contrast to the above, if the BCl$_3$ was injected to the plasma with argon the effect of laminar tail hydrogen injection (Fig. 32) on the conversion is very different. For the same range of [H$_2$]$_0$, the conversion of BCl$_3$ to boron is initially some 5% higher than if the BCl$_3$ was injected.
into the tail, but above 0.015 g mole/litre \([H_2]_0\), the conversion of \(BCl_3\) rises to 60% at 0.033 g mole/l. hydrogen, which is some 15% higher than in the backmixed case.

The increase in conversion obtained for the backmixed mode of hydrogen injection could also be explained by a temperature effect. As the amount of tail hydrogen increased the quenching effect produced a progressively lower temperature approaching that for maximum conversion. This explanation assumes both thermodynamic equilibrium to be attained and also that the reaction temperature at low \([H_2]_0\) is between the maximum conversion temperature for the mixture and the condensation temperature of boron.

5.39 Effect of increase of tail feed distance

Figs. 34/35 show the change in conversion of \(BCl_3\) obtained under fixed operating conditions when the distance between the coil and tail feed ring was increased. For the case of an argon plasma with \(BCl_3/H_2\) injected laminarly to the tail, the conversion increased initially as the tail distance \(x\) was increased. The conversion for \(x = 1\) cm was 39% increasing to 47% at 6 cm. This result can be most simply explained by a temperature effect if thermodynamic equilibrium is attained. Fig. 58 shows peaks in conversion of \(BCl_3\) to boron with increasing reaction temperature for different values of \(H_2/BCl_3\). As the temperature rises from 1000\(^\circ\) to 2500\(^\circ\) so the conversion rises to a maximum and then rapidly falls off to near zero conversion. For \(H_2/BCl_3 = 5\) (the value used for this series of runs), the maximum conversion reached is 70% at 1900\(^\circ\)K. The maximum conversion reached in Fig. 34 however is only 47%, indicating
that the reaction had not reached equilibrium before quenching occurred. If the above phenomenon is due to a thermal effect, the position of maximum conversion would represent the point in the gas stream where the mean gas temperature is $1900^\circ K$ and the conversion profile would represent a temperature profile of the tail gases.

The peak in conversion could also be explained on a kinetic basis by the formation of a greater proportion of excited species ($\text{BCl, BCl}_2, \text{BH, B}^+$) when the $\text{BCl}_2/\text{H}_2$ mixture is injected at $x < 6 \text{ cm}$, by collisions with excited argon atoms and ions. If no reactants are injected for 6 cm (equivalent to 0.15 sec for 50 l/min argon plasma), then a considerable number of highly excited argon atoms and ions could have lost their energy by inter-atomic collisions, thus increasing the bulk kinetic energy of the neutral argon. This redistribution of kinetic energy in the tail argon may promote more effective excitation of the reactive intermediates and hence increase the conversion of $\text{BCl}_3$ to boron.

As the tail distance was increased from 6 cm, the conversion decreased gradually to approach zero at 54 cm distance. If this portion of the curve A in Fig. 34 is plotted as ln conversion against distance, then a straight line is obtained (as shown in Fig. 61). From this straight line a half life can be calculated, as the distance axis is equivalent to time for the flowing system. A halving of conversion from 50% to 25% requires a distance of 10.4 cm. Hence for a 50 l/min argon plasma flowing through a 19.6 cm$^2$ area duct, the linear velocity of the gas will be $\frac{5 \times 10^4}{19.6 \times 60} = 42.5 \text{ cm/sec}$. 
The time equivalent to 10.4 cms for 42.5 cm/s velocity is \( \frac{10.4}{42.5} = 0.25 \) sec. If the prolonged conversion of BCl\(_3\) to boron is caused by decay of active argon, then the half life of the active species is at least \( T_{1/2} = 0.25 \) s.

Experimentally determined half lives for argon excited states are of the order of \( 10^{-6} \) - \( 10^{-9} \) sec. However, lifetimes of radicals calculated (236) from rate constant data for atoms such as Cl, Br, I, N and H give results of the order of 0.1 to 1 sec at 1 mm pressure. For excited atoms or molecules, half lives will tend to increase as the molecule becomes more complex. The more complex the structure so the efficiency of recombination by collisional processes decreases, so extending the lifetime. However, for atoms such as argon, the recombination efficiency must be considered near unity and lifetimes of atoms excited into resonant states will have lifetimes usually between \( 10^{-9} \) and \( 10^{-6} \) sec as predicted from classical radiation theory (237) and confirmed by experiment (238). Argon atoms which are excited into metastable states, i.e. states for which transition to lower energy levels are "forbidden", can however have longer lifetimes. Lifetimes of 2.2 msec for example have been measured for metastable argon atoms at 1.1 torr (239). According to other sources (237) the lifetimes of metastable atoms can be as long as several seconds.

Metastable atoms can in general be destroyed by several collisional processes, such as:

1) Collision with electrons which will gain kinetic energy.

2) Absorption of quanta which will raise the metastable to a nearby normal excited state.
3) by collision with other atoms which may transfer thermal energy to the metastable and bring it to a nearby excited state.

4) collision with another atom or molecule, which in turn will be ionised, dissociated or excited.

5) by wall collisions.

At atmospheric pressure the probability of an argon metastable atom (or an Ar⁺ ion) having a long life approaching \( T_{1/2} = 0.25 \text{ sec} \) would appear to be very low as all the collisional processes of metastable destruction would be accelerated at high pressure. Lifetimes of Ar⁺ ions of up to 10 msec have been measured experimentally (240) and in theory could be much greater. However, although the discharge from the r.f. plasma is very energetic, and recombination energy can be measured well downstream from the plasma. E.g. a recorded temperature on a Pt/Pt, Rh thermocouple placed \( \sim 150 \text{ cms} \) downstream from a nitrogen plasma gave an apparent temperature of \( 1100^\circ \text{C} \), indicating recombination of excited species, on the surface of the thermocouple, it is considered improbable that the lifetimes of excited argon atoms could be of the order of 0.5 seconds.

The decrease in conversion of BCl₃ to boron obtained at different tail feed distances for an argon/BCl₃ plasma is also shown in Fig. 35. This conversion does not show a maximum with increase in tail distance, but decreases gradually to approach zero conversion at \( > 40 \text{ cms} \). Conversions to boron at \( x = 1 \text{ cm} \) were \( \sim 15\% \) higher than with tail BCl₃ addition, indicating a more efficient energy transfer to BCl₃ when passed through the plasma. A plot of ln conversion against distance does give a straight line
but considerable deviation from the linearity occurs. The half life obtained 0.47 sec could be considered to apply to both the decay of excited argon atoms and recombination of BCl, BCl₂ with Cl atoms.

5.40 Effect of Magnetic Flux on conversion

The reduction in conversion of BCl₃ to boron obtained when a magnetic flux of 1500 gauss was applied to the tail of an argon plasma, could most probably be explained by the effective removal of Ar⁺ ions from the tail gases by an increase in wall collisions, due to bending forces from the magnetic field. The following relationship holds for an ion passing through a homogeneous magnetic flux and deflected along a circular path:

\[ rB = 143.6 \left( \frac{V}{m/e} \right)^{1/2} \]  \quad (19)

where

- \( r \) = path radius (cm)
- \( B \) = magnetic field (gauss)
- \( V \) = accelerating voltage
- \( \frac{m}{e} \) = a.m.u. \( (Ar^+ = 40) \)

The distance from the magnet to the tail ring for this experiment was \( \sim 15 \) cm. By substituting the known values in the above equation, the limiting accelerating voltage above which ions will not be deflected to the walls can be estimated:

\[ V = \frac{r^2B^2}{143.6^2 \frac{m}{e}} = \frac{225 \times 2 \times 10^6}{40 \times 2 \times 10^4} = 0.56 \text{ kV} \]

This means that any \( Ar^+ \) ion passing from the plasma into the magnetic field with energy \( > 0.56 \text{ kV} \) would not be deflected to the wall.
In a radiofrequency plasma a complete reversal of r.f. voltage and associated magnetic field occurs in a time increment equal to $\frac{1}{\text{frequency}}$. For operation at $2 \times 10^6$ Hz the period is $\frac{1}{2} \times 10^6 = 0.5$ microseconds.

If the kinetic energy ($\propto mv^2$) of an ion in vacuo is plotted against time the ion will lag the voltage variation by $\frac{\pi}{2}$ as shown below:

![Graph showing voltage and energy variation](image)

However, the variation in energy of the ion as shown neglects energy losses due to collisions. The ion will undergo an extremely high number of collisions at atmospheric pressure between each periodic energy oscillation, and the nett energy imparted to an ion flowing from the plasma zone would be relatively small. This would possibly be not much greater than the linear velocity equivalent (50 cm/s), which in terms of eV is insignificant.

Hence, by the effective removal of a proportion of argon ions from the plasma argon stream, before the BCl$_3$/H$_2$ feed ports, the role of the argon ions in the mechanism could be assessed. A decrease in conversion of BCl$_3$
was obtained when the magnetic field was used for a pure argon plasma (Fig. 34), the conversion decreasing from 23\% to 15\% for 30 g/min BCl$_3$ in 50 l/min argon. In terms of BCl$_3$ volume rate this is equivalent to a decrease in volume of reacting BCl$_3$ of 1.25 lit/min to 0.75 lit/min. Hence the presence of the magnetic field prevented 0.5 lit/min BCl$_3$ reacting to give boron. If one of the initiation stages of the mechanism to boron is considered as a charge transfer between Ar$^+$ ions and BCl$_3$ molecules to give BCl$_3^+$ by the following reaction:

$$\text{Ar}^+ + \text{BCl}_3 \rightarrow \text{BCl}_3^+ + \text{Ar}$$

then the decrease in volume of BCl$_3$ reacting/min could be explained by the absence of an equivalent volume of argon ions.

The argon rate to the plasma in this experiment was 50 l/min, so this would correspond to a minimum concentration of argon ions of $0.5/50 \times 100 = 1\%$. This is probably lower than the actual concentration of argon ions as it is unlikely that all the ions were effectively removed from the tail gases.

The degree of ionisation of argon plasmas increases rapidly in the temperature range 10000 to 20000$^\circ$K from 2 $\rightarrow$ 50\% (as shown in Fig. 51). However, for an r.f. plasma reactor only a small proportion of the bulk gas stream is actually heated to these high temperatures, so the actual degree of ionisation cannot be predicted from theoretical considerations.
From experimental results obtained for a variety of gases in r.f. plasma discharges, Gray et al (116) estimated that only $\sim 6\%$ of the gas passing through an r.f. plasma torch actually constitutes the plasma zone. The remaining gas acts as a plasma stabilising medium. Assuming this to apply to the system under consideration here, then at 50 l/min argon, only $0.06 \times 50 = 3$ l/min argon will pass through the plasma. Therefore at peak plasma temperatures of 20,000°K a high degree of ionisation of up to 50% for this 3 l/min argon is consistent with experimental results.

5.4 Possible reaction mechanism for boron formation

Several mechanisms for boron formation by hydrogen reduction of $\text{BCl}_3$ on heated substrates have been postulated and were discussed in Section 2.34. Gruber (154) concluded that the rate of boron formation was determined by a surface reaction between hydrogen, adsorbed atomically, and an adsorbed boron-containing molecule which exerted an influence on the reaction rate in proportion to $\sqrt{P_{\text{BCl}_3}}$. No postulate as to the nature of this boron compound was made.

Carlton et al (155) proposed a complex step-wise mechanism for boron formation which involved progressive substitution of chlorine atoms in $\text{BCl}_3$ by hydrogen atoms, while an equilibrium concentration of $\text{BHCl}_2$ was maintained in the gas phase. Both of the above mechanisms are molecular in nature, however, and involve no excited, metastable or ionic species. While the reduction of $\text{BCl}_3$ by hydrogen in an r.f. plasma by a molecular mechanism must be considered possible, the very nature of the plasma discharge, with its abundance of ions,
electrons and free radicals would suggest that a mechanism involving energy or charge transfer between excited, metastable or ionic species would be predominant in the gas phase reaction.

5.41 Role of argon

That argon participates in the early stages of the reaction is shown by the experiments in which BCl$_3$ and hydrogen were premixed and injected into the tail of an argon plasma. Energy must clearly be transferred to the reaction mixture from the argon gas. A complex mixture of excited species will occur when argon is passed through a plasma discharge, which will include excited and metastable argon atoms and argon ions.

Any of these species could cause excitation and even ionization of the boron trichloride. [Evidence which will be discussed later suggests that energy transfer is to boron trichloride rather than to hydrogen]. Klots (253) has shown that argon atoms in the $^3P_1$ and $^1P_1$ states (11.8 and 11.6 ev respectively above the ground state) can cause ionization of a variety of molecules, and since the ionization potential of BCl$_3$ is below 11.6 ev, they could almost certainly ionize it as well. The lifetimes of these species, however, are probably less than $10^{-7}$ sec and as the BCl$_3$/H$_2$ inlet can be 30cm away from the plasma, they are effectively ruled out as energy carriers. Metastable species are still a probability but the calculations on page 158 suggest an effective half life for the excited species of 0.25 sec. Even if this figure is two orders of magnitude in error, it is still too
long for any of the known metastable states of argon and indeed represents an astonishingly long half life for any metastable atom, especially in a system at atmospheric pressure. Electronically excited argon atoms can thus be ruled out as the main energy carriers.

The probability of $\text{Ar}^+$ ions playing a part is more difficult to rule out. The 30% reduction in conversion of $\text{BCl}_3$ which occurred when a magnetic field was applied to the tail of the argon plasma indicates the presence of argon ions and their participation in the mechanism. Certainly the recombination energy of an argon ion (15.8 ev) is sufficient both to ionize and to fragment a $\text{BCl}_3$ molecule.

$$
\text{Ar}^+ + \text{BCl}_3 \rightarrow \text{Ar} + \text{BCl}_3^+ , \Delta H = -110 \text{ kcal/mole}
\text{BCl}_3^+ \rightarrow \text{BCl}^+ + \text{Cl}_2 , \Delta H = +45 \text{ kcal/mole}
$$

The reduction in conversion was equivalent (on a one argon ion to one $\text{BCl}_3$ molecule basis) to the removal of 0.5 l/min argon ions which is ~1% of the total argon flow. This was shown in the last section to be consistent with experimental results. It is uncertain, however, whether the remaining conversion was promoted by argon ions which were not removed from the plasma tail by the magnetic field or by other active species. The data could also be explained by postulation of a chain mechanism initiated by ions so that each argon ion converted many $\text{BCl}_3$ molecules, but such mechanisms have not previously been devised.

The participation of argon ions cannot, therefore, be ruled out. The hypothesis has certain unattractive features but is supported by the simplest interpretation of the magnet experiment.
A final possibility is that the argon simply acts as a source of thermal energy. Calculations of the temperature of the plasma give values of 20,000°K for the peak and 10,000°K for the mean plasma temperature. The argon atoms would thus be highly excited translationally. At 10000°K, RT = 20 kcal, and even allowing for the tail gases to cool on their passage from plasma to gas inlet, the energy available to dissociate the BCl$_3$ could still be considerable.

5.42 Fragmentation of BCl$_3$ in the plasma

When BCl$_3$ is passed through the plasma, it undergoes fragmentation to give products which must participate in reaction in the presence of hydrogen but recombine to give BCl$_3$ in its absence. Mass spectrographic analysis of BCl$_3$ samples with 70 ev electrons has shown that the major species present in the cracking pattern (Fig. 20) are as follows:

BCl$_2^+$ (12), BCl$_3^+$ (10), BCl$^+$ (9), Cl$_2^+$ (6)  (relative intensities in parentheses)

Spectrographic examination of the emission from an argon/BCl$_3$ plasma has shown that the main decomposition products of BCl$_3$ which emit radiation are:

BCl, B, B$^+$, Cl$_2$, Cl$_2^+$ (+ BCl$_2$).

The predominant emitting species was found to be BCl, which exhibited intense self absorption (band reversal) in proportion to the energy input to the plasma.

When BCl$_3$ passes through the plasma it is possible that complete dissociation occurs according to the following reactions:

\[
\begin{align*}
\text{BCl}_3 & \rightarrow \text{B} + \text{Cl}_2 + \text{Cl} & \Delta H &= +257 \text{ kcal/mole} \\
\text{BCl}_3 & \rightarrow \text{BCl} + \text{Cl}_2 & \Delta H &= +130 \text{ kcal/mole}
\end{align*}
\]
A combination of these two reactions will give the 2-3 volume increase when BCl$_3$ is injected in the plasma gas, observed to occur in the torch by the tail turbulence technique (Ref. p. 125). A similar pair of reactions can also be written for the corresponding ionic species, viz:

\[
\begin{align*}
\text{BCl}_3^+ & \rightarrow \text{B}^+ + \text{Cl}_2 + \text{Cl}, \quad \Delta H = +103 \text{ kcal/mole} \\
\text{and } \text{BCl}_3^+ & \rightarrow \text{BCl}^+ + \text{Cl}_2, \quad \Delta H = +45 \text{ kcal/mole}
\end{align*}
\]

BCl$_2^+$ may be an important ionic intermediate as may BCl$_2$ if it is found in a non-excited state. The latter would presumably be formed by BCl$_3$ → BCl$_2$ + Cl, but concrete evidence is lacking.

In the absence of hydrogen, therefore, the BCl$_3$ could be considered to undergo decomposition in the plasma to give a combination of ionic and neutral species, possibly in accordance with the cracking pattern of BCl$_3$. These products in the absence of hydrogen will undergo recombination and charge neutralisation to give BCl$_3$ again. It is also possible, however, that small amounts of boron subchlorides are formed, for instance small quantities of B$_2$Cl$_4$ maybe formed by reactions

\[
\begin{align*}
\text{BCl} + \text{BCl}_3 & \rightarrow \text{B}_2\text{Cl}_4, \quad \Delta H = -55 \text{ kcal/mole} \\
or \text{BCl}_2 + \text{BCl}_2 & \rightarrow \text{B}_2\text{Cl}_4, \quad \Delta H = -77 \text{ kcal/mole}
\end{align*}
\]

as suggested by Moore et al (159) and Holzman and Morris (161) respectively. No evidence for the presence of lower chlorides of boron was obtained in this work.

5.43 The role of hydrogen

The effect of hydrogen on the conversion of BCl$_3$ to boron has been shown to be dependent partly on the method of
injection of reactants to the plasma reactor. If BCl$_3$ and H$_2$ are premixed and injected into the tail of the argon plasma in a non-backmixed mode, then the conversion of boron was found to be independent of hydrogen concentration, thus indicating a zero order w.r.t. hydrogen. If the hydrogen and BCl$_3$ were backmixed to the plasma, however, a tendency for the conversion to increase with hydrogen concentration was observed. Therefore, the role of hydrogen in the reaction must be considered both from a chemical point of view and a physical point of view i.e. the effects of hydrogen on quenching of the reaction.

The zero order w.r.t. hydrogen in one experiment and near zero order in others suggests that hydrogen does not participate in the early rate-determining steps in the reaction but acts to prevent recombination of dissociated BCl$_3$. The hydrogen-chlorine reaction to give hydrogen chloride is known to be a rapid chain reaction, (254).

$$\text{Cl} + \text{H}_2 \rightarrow \text{HCl} + \text{H} \quad \Delta H = 0.5 \text{ kcal/mole}, E = 5.5 \text{kcal/mole}$$

$$\text{H} + \text{Cl}_2 \rightarrow \text{HCl} + \text{Cl} \quad \Delta H = 45.1 \text{ kcal/mole}, E = 2-3.6 \text{kcal/mole}$$

These processes will compete with the recombination reactions giving BCl$_3$, and the hydrogen and chlorine atoms may also participate in other reactions such as

$$\text{Cl} + \text{BCl}_3 \rightarrow \text{BCl}_2 + \text{Cl}_2 \quad \Delta H = +87 \text{ kcal/mole}$$

and

$$\text{H} + \text{BCl}_3 \rightarrow \text{BCl}_2 + \text{HCl} \quad \Delta H = +42 \text{ kcal/mole}$$

or

$$\text{H} + \text{BCl} \rightarrow \text{B}_2 + \text{HCl} \quad \Delta H = +27 \text{ kcal/mole}$$

These remove H and Cl atoms from the system but the supply of atoms from the plasma is certainly large enough to maintain the hydrogen/chlorine chains in spite of this. The second of the above reactions was postulated by Dessaux et al.
The recombination reactions will, however, be competing with one another and with the chain reaction, and the final extent of HCl formation will also depend on physical parameters such as quenching and mixing in the tail gases. Reaction of tail H₂ with BCl to give the BH radical could also occur at high temperatures as another competitive reaction, viz:

\[ \text{BCl} + \text{H}_2 \rightarrow \text{BH} + \text{HCl} , \quad \Delta H = +49.9 \text{ kcal/mole} \]

5.44 Ionic Mechanisms

The experimental evidence from the magnet experiment in which a decrease in conversion of BCl₃ to boron was obtained when a magnetic field was placed in the path of the plasma argon before mixing with BCl₃ and H₂, indicates that argon ions play a part in the mechanism of boron formation.

Argon ions (Ar⁺) can occur in the plasma from the reaction Ar (plasma) → Ar⁺ + e, ΔH = +15.8 ev. It is unlikely that any higher excitation levels of argon (such as Ar⁺⁺) would be present in the plasma, as the 2nd ionisation potential of +43 ev is extremely high for this type of system.

In the presence of BCl₃, charge transfer from Ar⁺ could occur to give BCl₃⁺ as an intermediate ion by the reaction:

\[ \text{Ar}^+ + \text{BCl}_3 \rightarrow \text{BCl}_3^+ + \text{Ar} \quad \Delta H = -4.68 \text{ ev} \]

\[ = -110 \text{ kcal/mole}. \]

The charge transfer would involve an exotherm of 4.68 ev which would probably be present as internal excitation in the BCl₃⁺. This would promote fragmentation of the ion
giving products similar to those in a mass spectrometer. The fragmentation products of BCl$_3$ in a mass spectrometer include BCl$_2^+$, BCl$^+$ and Cl$_2^+$. Reactions to give these fragmentation products are highly endothermic as can be seen below:

\[
\begin{align*}
\text{BCl}_3^+ & \rightarrow \text{BCl}^+ + \text{Cl}_2, \quad \Delta H = +45 \text{ kcal/mole (2.0 ev)} \\
\text{BCl}_3^+ & \rightarrow \text{BCl} + \text{Cl}_2^+, \quad \Delta H = +80 \text{ kcal/mole (3.5 ev)} \\
\text{BCl}_3^+ & \rightarrow \text{BCl}_2^+ + \text{Cl}, \quad \Delta H = +76 \text{ kcal/mole (3.5 ev)}
\end{align*}
\]

The energy for the first reaction to give BCl$^+$ could be easily supplied by the charge transfer reaction (4.68 ev), and this reaction must be considered most likely. The latter two reactions to give BCl and BCl$_2^+$ boron compounds are both possible theoretically, but the lower energy margin available makes them less probable. A combination of the above three reactions would lead to the formation of a complex mixture of ionic and neutral species containing at least the following six species:

BCl$^+$, BCl, BCl$_2^+$, Cl, Cl$_2$ and Cl$_2^+$. In the absence of hydrogen, recombination and charge neutralisation would occur giving BCl$_3$ as the main product with possibly a trace of B$_2$Cl$_4$. In the presence of hydrogen however, HCl would be formed by the rapid H$_2$/Cl$_2$ chain reaction, together with a possible ionic H$_2$/Cl$_2$ reaction occurring between H$_2$ and Cl$_2^+$:

\[
\text{viz: } \text{H}_2 + \text{Cl}_2^+ \rightarrow \text{HCl}_2^+ + \text{H}^.
\]

BCl$^+$ and BCl$_2^+$ species could react with hydrogen to form the respective neutral molecules and the resultant BCl and BCl$_2$ would undergo further reaction with hydrogen, as in the
thermal mechanism (q.v.) to form boron.

The initiation reaction in this mechanism, if BCl$_3$ does not go through the plasma, is charge exchange between Argon and BCl$_3$. This process like most charge transfer processes involving polyatomic molecules, will probably have a large cross-section; it will nonetheless have to compete with charge transfer between argon and hydrogen and with the rapid reaction

\[ \text{Ar}^+ + \text{H}_2 \rightarrow \text{ArH}^+ + \text{H}^- \]

which has been extensively studied by a large number of workers cited by Reuben and Friedman (255).

In a system as complex and energetic as a thermal plasma, the number of such possible ion-molecule reactions is extremely large and unfortunately the ion-molecule reactions of boron have not yet been extensively studied. However, the important steps of such an ionic mechanism for boron formation from BCl$_3$ can be stated thus:

1) initiation step involving Ar$^+$
2) formation of BCl$^+$ or BCl$_2^+$ in fragmentation products of BCl$_3^+$
3) charge neutralisation of BCl$^+$, BCl$_2^+$ to give BCl and BCl$_2$, followed by "scavenging" of chlorine by hydrogen and reduction of BCl and BCl$_2$.
4) an ionic mechanism would have greater credibility if it were a chain mechanism i.e. if each Ar$^+$ ion caused conversion of a number of BCl$_3$ molecules.
5.45 Thermal mechanism for boron formation

It may be that consideration of the plasma as containing ions, metastables etc. is overcomplicated and it should be thought of simply as a heated zone in which thermal energy can be transferred to BCl\(_3\) either directly (by passage of the latter through the plasma), or indirectly (via argon as a carrier). Suppose the reaction occurs at mean gas temperatures between 1500°C and 2500°C and assume that something approaching thermodynamic equilibrium is attained in the heated zone. Presumably thermal decomposition of BCl\(_3\) will occur to give products predicted by the thermodynamic equilibrium diagram (Figs.54-57). BCl\(_3\) would undergo direct decomposition when passed through the plasma, or decomposition initiated by collisional processes (possibly by non-ionic collisions with electrons) by the following overall reactions:

\[
\begin{align*}
\text{BCl}_3 & \xrightarrow{\text{plasma}} B + \frac{1}{2}\text{Cl}_2 & \Delta H = +96 \text{ kcal/mole} \\
\text{BCl}_3 & \xrightarrow{\text{plasma}} \text{BCl} + \text{Cl}_2 & \Delta H = +130 \text{ kcal/mole} \\
\text{or BCl}_3 + e & \xrightarrow{\text{plasma}} \text{BCl} + \text{Cl}_2 + e & (""
\end{align*}
\]

The first reaction would be favoured by intermediate temperatures (1500 - 2000°C) in which case direct condensation of boron would be possible in the presence of hydrogen, which would react with the chlorine. The other two reactions would be favoured by higher temperatures (> 2000°C). The ratio of B to BCl formed by this mechanism would be primarily dependent on the mean temperature attained in the reactant mixture; high conversions to boron being favoured by intermediate temperatures. Similar considerations apply if the heating of the BCl\(_3\) is indirect.
The BCl formed by any of the above reactions would become unstable when the reaction products began to cool. Recombination of BCl with chlorine to BCl$_3$ would occur in the absence of hydrogen, by the reaction:

$$\text{BCl} + \text{Cl}_2 \longrightarrow \text{BCl}_3, \quad \Delta H = -130 \text{ kcal/mole}.$$  

However, if hydrogen is present, then the chlorine content of the gas mixture is reduced considerably by chain reaction of H$_2$ with Cl$_2$. Hence the BCl must react with other species to attain the stabler state of elemental boron. It is unlikely that further decomposition of BCl would occur (except at very high temperatures) as the reaction BCl $\longrightarrow$ B+Cl (\( \Delta H = +130 \text{ kcal/mole} \)) is highly endothermic.

Possible reactions of BCl to form boron are as follows:

$$\begin{align*}
\text{BCl} + \text{H}_2 & \longrightarrow \text{BH} + \text{HCl}, \quad \Delta H = +49.9 \text{ kcal/mole} \\
\text{BH} + \text{BCl} & \longrightarrow \text{B}_2 + \text{HCl}, \quad \Delta H = +34 \text{ kcal/mole} \\
\text{BCl} + \text{BCl} & \longrightarrow \text{B}_2 + \text{Cl}_2, \quad \Delta H = +127 \text{ kcal/mole} \\
\text{BH} + \text{Cl} & \longrightarrow \text{B} + \text{HCl}, \quad \Delta H = +34 \text{ kcal/mole}
\end{align*}$$

Of the above four reactions to form boron, the steps involving the BH molecule are the most likely to occur as they are of relatively low endothermicity. Another possible reaction that can be considered to occur at this stage is the reaction of BCl with BCl$_3$ to give B$_2$Cl$_4$, as postulated by Moore et al (159).

The thermal mechanism which is proposed may broadly be described as follows:

1) BCl$_3$ is decomposed either by heating in the plasma or by contact with hot argon tail gases. B, BCl, Cl$_2$ and
Cl atoms are formed in amounts approaching those which would be present at thermodynamic equilibrium. The steps leading to the attainment of equilibrium are unclear, but concentrations of free radicals in the region 1500 - 2500°C are undoubtedly high and BCl₃ itself is unstable at such temperatures.

2) Elemental boron is favoured by intermediate temperatures.

3) Free chlorine tends to be scavenged by hydrogen to give hydrogen chloride.

Proposed Thermal mechanism for boron formation:

1. BCl₃ $\xrightarrow{\text{plasma}}$ B + ½Cl₂
2. BCl₃ $\xrightarrow{\text{plasma}}$ BCl + Cl₂
3. BCl₃ + e $\xrightarrow{\text{plasma}}$ BCl + Cl₂ + e
4. Ar $\xrightarrow{\text{plasma}}$ Ar*
5. Ar* + BCl₃ $\rightarrow$ BCl + Cl₂ + Ar
6. BCl + H₂ $\rightarrow$ BH + HCl
7. BH + BCl $\rightarrow$ B₂ + HCl
8. BH + Cl $\rightarrow$ B + HCl
9. H₂ + Cl₂ $\rightarrow$ 2HCl (by the usual chain mechanism)

This mechanism explains many of the experimental results, in particular the variation of yield with residence time, T, and with distance of the BCl₃/H₂ inlet from the plasma. Fig. 58 shows the variation of boron conversion with temperature for various H₂/BCl₃ ratios as predicted by the thermodynamic equilibrium diagrams. It can be seen that the peak conversions for each ratio occur at $\sim 2100^\circ$K. These maximum conversions are as follows:
The latter conversion was taken from an interpolated curve at ratio 2/1. Comparison of these maximum conversions with experimental conversions at increasing residence times (T) shown in Fig. 26 shows that the experimental conversions tend toward the maximum equilibrium value for each ratio at residence times T > 0.5 sec. Hence these experimental results are consistent with the thermal mechanism if the assumption is valid that at a constant power level, the mean gas temperature increases with increasing residence time T. The residence time T is defined as proportional to the increase of the total gas flow to the plasma, hence it is reasonable that for increased residence time (i.e. decreased gas flows) the mean gas temperature should increase. The values of conversions obtained at the higher gas flowrates (T = 0.1 sec) as predicted from the equilibrium curve, are in the 1400°-1600°K temperature range. This is consistent with the calculated mean gas temperature.

By application of the thermal mechanism to the results from the experiments on variation of tail gas distance, it is possible to relate the variation in conversion to boron to the reaction temperature. Figs. 62(a) and 62(b) show the reaction temperature profiles obtained by identifying experimental conversions with equilibrium conversions from Figs. 34/35. The temperature profile for the cooling argon plasma was obtained by assuming the maximum conversion to boron to occur at 1900°K and constructing an interpolated conversion curve from

<table>
<thead>
<tr>
<th>H₂/BCl₃ Ratio</th>
<th>9</th>
<th>4</th>
<th>2</th>
</tr>
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<tbody>
<tr>
<td>Peak conversion</td>
<td>74%</td>
<td>56%</td>
<td>35% (interpolated)</td>
</tr>
</tbody>
</table>
the required 47% peak conversion. This curve corresponded to a $\text{H}_2/\text{BCl}_3$ ratio of 3/1, as opposed to the experimental 5/1 ratio. This discrepancy could be due to inefficient transfer of energy to the reactants from the argon, resulting in only partial attainment of thermodynamic equilibrium.

When $\text{BCl}_3$ is present in the plasma with argon, however, the conversion to boron exhibits no maximum when the tail $\text{H}_2$ distance is increased. The conversion at zero distance (60%) is, however, very close to the maximum thermodynamic conversion for an interpolated 5/1 ratio curve. The resulting temperature profile obtained by taking the zero position 60% conversion at 1900$^\circ$K is shown in Fig. 62(b). Comparison of these two temperature profiles indicates that the mean gas temperature for an argon plasma is higher than for a mixed argon-$\text{BCl}_3$ plasma up to 20 cms from the coil. This is consistent with enthalpy considerations as the mean gas temperature at a constant power level should be lower if $\text{BCl}_3$ and argon are both present in the plasma. The presence of $\text{BCl}_3$ in the plasma, however, although lowering the mean gas temperature, allows a near equilibrium dissociation of $\text{BCl}_3$ to occur before $\text{H}_2$ is added, resulting in higher conversions.

5.46 Limitations of Proposed Mechanisms

Neither of the above two mechanisms for boron formation will explain the experimental results fully. The thermal mechanism explains the maximum in conversions obtained as tail addition distances are increased. These results indicate that the critical temperature range in the plasma tail is that between the maximum conversion temperature and
the condensation temperature, as given by the thermodynamic equilibrium diagram. However, no definite conclusions can be drawn from experimental evidence, in the absence of any control over the temperature in the reaction system.

The decrease in conversion obtained when a magnetic field was applied to the tail of an argon plasma, indicates that Ar\(^+\) ions play a part in energy transfer to BCl\(_3\) for this mode of operation.

When BCl\(_3\) was present in the plasma together with argon, higher conversions were in general obtained, indicating that more efficient charge or energy transfer to the BCl\(_3\) was possible under these conditions of operation. The presence of hydrogen in the plasma did not apparently effect conversions, and thus supports the idea that the role of hydrogen is primarily as a scavenger of chlorine.

When BCl\(_3\) was put through the plasma, energy transfer to BCl\(_3\) was possible at greatly reduced argon concentrations, and even with no argon present. In this latter case, it is probable that BCl\(_3\) can dissociate according to the mass spectrometric fragmentation pattern and form such species as BCl\(^+\), BCl\(_2^+\) and Cl\(_2^+\), which would undergo excitation in the plasma and then charge neutralisation to form BCl and BCl\(_2\), which would proceed to boron via the thermal mechanism. The direct transfer of energy to BCl\(_3\) could be initiated by electron impact in the pre-plasma zone producing BCl\(^+\) and B\(^+\) species which would be excited by the alternating magnetic field.
Summary

Boron formation from $\text{H}_2/\text{BCl}_3/\text{Ar}$ mixtures in radio-frequency plasma reactor systems may take place by an ionic or a thermal mechanism. Intermediate temperatures in the mixing gases favour the formation of boron and this seems to reflect the thermodynamics of the system. Identification of individual reactions is a matter of speculation, but there is strong evidence that the early stages of the reaction involve energy transfer to $\text{BCl}_3$ followed by its dissociation into two or three fragments. In the absence of hydrogen these recombine to give $\text{BCl}_3$, but if it is present it reacts with the chlorine atoms or molecules to give hydrogen chloride.
CHAPTER SIX
CONCLUSIONS
6. Conclusions

The following conclusions can be made as a result of this study:

1) Amorphous boron, containing approximately 1% total impurities, can be prepared by the hydrogen reduction of boron trichloride in a radio-frequency induced plasma. In general, the conversion of BCl$_3$ to boron is dependent on the concentration of BCl$_3$ in the reaction mixture, the residence time of the reactants in the plasma reactor and the configuration of the reactant feed to the reactor. High conversions of BCl$_3$ to boron are obtained at low BCl$_3$ concentrations and at high residence time values, (e.g. 80% conversion at BCl$_3$ =0.002g/ml and T =0.07 sec ). Boron can be prepared at rates up to 250 g/hr which compares well with existing industrial boron processes. High rates of boron formation are favoured by high BCl$_3$ concentrations and low residence times.

2) The main impurities present in boron prepared this way are oxygen (0.74% w/w) and nitrogen (0.26% w/w). Both these impurities are attributable in part to surface adsorption on exposure of the boron to air, but oxygen contamination of the boron by boron oxides present in the BCl$_3$ also occurs. The use of ultrapure BCl$_3$ and rigorous powder handling techniques should improve the boron purity.

3) The boron forms as a fine microcrystalline powder, similar in appearance to other amorphous borons. X-ray examination of the boron reveals that it is only weakly crystalline and similar to $\beta$-rhombohedral boron in structure. The boron contains particles which range from 200-7500 $A$
in size and are generally random in shape. Platelets of boron are also formed and can be dodecagonal in shape. The majority of boron platelets are similar in structure to $\beta$-rhombohedral boron, but the structure of the dodecagonal platelets is unknown. These platelets have a 30 Å lattice spacing which does not correspond to any previously reported boron structure, and must therefore be considered to be a further modification of known boron structures. Calculated growth times of boron particles in the plasma vary from 0.078 msec to 2.2 msec for the 200 Å to 7500 Å particles respectively.

4) The degree of conversion of $\text{BCl}_3$ to boron in the plasma reactor is thought to be controlled by $\text{BCl}_3$ concentration, reaction time and mean gas temperature at any given power level. Runs carried out under conditions of constant hydrogen concentration resulted in a first order dependence of conversion on $\text{BCl}_3$ concentration. Runs at constant $\text{BCl}_3$ concentration, however, resulted in little change in conversion over a wide range of $\text{H}_2$ concentration, and under conditions of laminar reactant flow the $\text{BCl}_3$ conversion was found to be independent of $\text{H}_2$ concentration. Runs at stoichiometry resulted in a first order dependence for the overall reaction, which supports the zero-order for hydrogen in the rate equation. It is clear then that hydrogen does not play an important part in the rate-limiting chemical step in the formation of boron in a plasma.

5) High levels of dissociation are believed to occur when $\text{BCl}_3$ is passed through the r.f. plasma with argon, or is mixed with excited atomic and ionic argon from the plasma. Spectro-
graphic examination of the Argon/BCl$_3$ plasma confirms that BCl, Cl$_2^+$ and Cl$_2$ are present in considerable concentrations in the plasma, together with smaller amounts of BCl$_2$ and Cl. Both neutral and singly ionised argon and boron are also present in the emission spectra of the argon/BCl$_3$ plasma. When hydrogen is present with the argon and BCl$_3$, the BH radical is also formed. Although atomic boron is present in the argon/BCl$_3$ plasma, solid boron can not be formed in the absence of hydrogen.

6) The presence of singly ionised argon and boron in the U.V. emission spectra of argon/BCl$_3$ plasma above 10 kW leads to the belief that high degrees of excitation exist in the plasma, and tends to support a peak plasma temperature of 20000°K as calculated from the radial distribution of ArI emission.

7) Most of the quantitative kinetic results are satisfactorily explained by two possible reaction mechanisms. The first mechanism involves charge transfer to BCl$_3$ atoms from Ar$^+$ ions and supports the decrease in conversion observed when a magnetic field is applied to the tail of the argon plasma. The second mechanism involves a pure thermal decomposition of BCl$_3$ according to the thermodynamic equilibrium predictions and is supported by several experimental results. Although the role of argon ions is clearly important under certain operating conditions, the thermal mechanism is considered the more important of the two, BCl$_3$ dissociating towards an equilibrium composition at the mean gas temperature and hydrogen acting as a chlorine scavenger.
CHAPTER SEVEN

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Fig. 1: Non-ideal dense plasma (ref. 4).

Fig. 2: Electrical discharge characteristics.
Fig 3. Variation of gas & elect. temp. with pressure.

Fig 4. Modes of radio-frequency coupling.
Fig. 5. Low frequency induction plasma power requirements. (67).
Fig. 6: Summary of r.f. plasma chemical reactions.
Fig 7. Power density distribution (ref 64)

Fig 8. Coupling efficiency (ref 64)
Fig 9. Air-cooled plasma torch

Fig 10. Single pass water cooled torch
Fig 11.
Laboratory Plasma Reactor.

rgon + Cl₃ IN

c.w. out

H₂ IN

c.w. in

c.w. out

c.w. out
Fig 12: Laboratory Plasma Apparatus

argon + BCl₃ → plasma torch

induction coil

H₂ → quench tube

H₂

collector

powder

bag

filter
Fig. 13. Measurement of gas temperature through BCl₃ condenser.
Fig 14. Calibration curve for BCl₃.

Fig 17. Operating pressure / time curve.
Fig 15.
Fig 16. TORCH
FEED MANIFOLD

sect. AA
argon + BCl₃
c.w. out
c.w. in

sect. BB
Fig 18.

Gas Temperature
in BCl\textsubscript{3} Condenser.
\[ \eta = \frac{1}{1 + \frac{V^2}{2} (\frac{A}{B} + \frac{C}{2} + n + 1)} \]

Loss/pass = C \left( \frac{1}{\eta} - 1 \right)

Data calculated for:
- \( n = 2 \pm 1 \)
- \( C = 25\% \)
- \( A = 10 \text{ L/m} \)
- \( B = 19 \text{ L/m} \)

Fig 19.
Fig. 20. Mass spectrum of $\text{BCl}_3$ (ex Borax)

mass number

[Diagram showing mass spectrum with labeled peaks for $\text{BCl}_2^+$, $\text{B}_2\text{Cl}_3^{++}$, $\text{BCl}_3^+$, $\text{B}_4\text{Cl}_4^+$, $\text{B}_2\text{Cl}_5^+$, $\text{B}_3\text{Cl}_5^+$, $\text{B}_2\text{Cl}_6^+$, $\text{B}_4\text{Cl}_6^+$, $\text{B}_6\text{Cl}_6^+$, $\text{B}_4\text{Cl}_7^+$, with corresponding mass numbers 6, 12, 18, 24, 30, 36, 42, 48, 54, 60, 66, 72, 84, 90, 96, 102, 108, 114, 120, 135, 150, 165, 180, 195, 210, 225, 240, 255, 270, 285, 300]
Fig 22. BCl₃ conversion v. concentration

Fig 23. BCl₃ conversion v. H₂/BCl₃ mole ratio
**Fig 24. BCl$_3$ conversion v. H$_2$ conc.**

- \[ [\text{BCl}_3]_0 = 0.004 \text{ gmole/l} \]

- \[ [\text{H}_2]_0 \text{ (gmoles/litre)} \]

**Fig 25. BCl$_3$ conversion v. H$_2$/BCl$_3$ mole ratio**

- + 100 l/min H$_2$
- o 34 l/min H$_2$
Fig 26. BCl₃ conversion v. residence time T

Fig 27. H₂ conversion v. residence time T

\[
[H_2]_0 \text{ g mole/l} = 0.036, 0.016, 0.008, 0.004
\]

\[
[BCl₃]_0 = 0.004
\]

equilm. conv. 74%
Fig. 28. BCl₃ conversion v. residence time $T'$
Fig 29. Variation of BCl₃ conversion with feed configuration
Fig. 30: Normal tail gas injection mode.
Fig 31. Effect of tail feed configuration - argon plasma

Fig 32. Effect of tail feed configuration - argon+BCl₃ plasma
Fig 33. Effect of normal tail injection to an argon plasma
Fig 34. Effect of increased \( \text{BCI}_3 + \text{H}_2 \) tail feed distance

Fig 35. Effect of increased \( \text{H}_2 \) tail feed distance
Fig 37. Boron yield v. H₂ concentration

Fig 38. Boron yield v. BCl₃ concentration
Fig. 39. Boron yield v. residence time $T$
Fig 40. Pilot plant results

Boron yield (g/min) vs. BCl₃ feed rate (g/min)
Fig 41. Projected intensity distribution

Fig 42. Radial intensity distribution
Fig 43. Normalised projected intensity distribution

Fig 44. Normalised radial intensity distribution
Fig 45. Temperature variation of argon emission

Fig 46. Temperature distribution of argon plasma
**Fig 47.** Axial distribution of $B^*$ emission

**Fig 48.** $B^*$ emission as a function of $P_{BCl_3}$
Fig 49. Particle size distribution of boron

Fig 50. Particle size variation with $\text{BCl}_3$ rate
Fig 51. Degree of ionisation for argon plasma - 1 atm
Fig. 52: $I^2$ plot for $B^+$ ion v. partial pressure $BCl_3$

Fig. 53: $I^3$ plot for $B^+$ ion v. partial pressure $BCl_3$
Fig 54. $\text{BCl}_3$ equilibrium composition
Fig 55. $H_2/BCl_3$ equilibrium: ratio $1\frac{1}{2}/1$
Fig 56. H₂/BCl₃ equilibrium ratio 4/1.
Fig 57. H$_2$/BCl$_3$ equilibrium: ratio 9/1
pressure - 1 atm.
curve A \ H_2/\text{BCl}_3 = 1.5:1 
curve B \ H_2/\text{BCl}_3 = 4:1 
curve C \ H_2/\text{BCl}_3 = 9:1 

Fig. 58. Equilibrium conversions to solid boron
Fig 59. Mean plasma temperature variation

Fig 60. First order plot for BCl₃
Fig 61. Equivalent half-life plot for excited species

- $\text{BCl}_3 + \text{Argon plasma} \quad T_{1/2} = 0.47 \text{ sec}$
- $\text{Argon plasma} \quad T_{1/2} = 0.28 \text{ sec}$
Fig 62. Equilibrium temperature profiles

A) argon plasma

B) argon + BCl₃ plasma
## APPENDIX 1: Possible Reaction Intermediates

<table>
<thead>
<tr>
<th>Species</th>
<th>Previously observed in:</th>
<th>Possibility of occurring in RF plasma</th>
<th>( \Delta H_f )</th>
<th>Other Information</th>
</tr>
</thead>
<tbody>
<tr>
<td>ArI</td>
<td>HF discharge in argon</td>
<td>Yes, detected spectroscopy</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Ar⁺</td>
<td>Argon discharge tube</td>
<td>&quot;</td>
<td>365 kcal/mole</td>
<td>IonPot=15.68eV</td>
</tr>
<tr>
<td>Ar²⁺</td>
<td>Argon discharge tube</td>
<td>Not detected</td>
<td>1001 kcal/mole</td>
<td>IonPot=43eV</td>
</tr>
<tr>
<td>Ar³⁺</td>
<td>Electron impact</td>
<td>&quot;</td>
<td>1944 kcal/mole</td>
<td>IonPot=84eV</td>
</tr>
<tr>
<td>Ar⁴⁺</td>
<td>Electron impact</td>
<td>&quot;</td>
<td>3323 kcal/mole</td>
<td>IonPot=147eV</td>
</tr>
<tr>
<td>Ar⁵⁺</td>
<td>Electron impact</td>
<td>&quot;</td>
<td>5053 kcal/mole</td>
<td>IonPot=219eV</td>
</tr>
<tr>
<td>Ar⁶⁺</td>
<td>Electron impact</td>
<td>&quot;</td>
<td>7158 kcal/mole</td>
<td>IonPot=310eV</td>
</tr>
<tr>
<td>Ar₂⁺</td>
<td>Mass spec. reaction: Ar+Ar, Ar⁺+e</td>
<td>-</td>
<td>-</td>
<td>Ref 241</td>
</tr>
<tr>
<td>B(gas)</td>
<td>Spark source</td>
<td>Yes, detected spectroscopy</td>
<td>132.8±4 kcal/m</td>
<td>Ground state Config: (^1S_0)</td>
</tr>
<tr>
<td>B I</td>
<td></td>
<td>&quot;</td>
<td>&quot;</td>
<td>-</td>
</tr>
<tr>
<td>B⁺</td>
<td></td>
<td>&quot;</td>
<td>324.1±4.0 kcal/m</td>
<td>IonPot=8.26eV</td>
</tr>
<tr>
<td>B²⁺</td>
<td>From B₂O₄⁺ in RF ion source</td>
<td>Not detected</td>
<td>871.7 kcal/mole</td>
<td>IonPot=25.00eV</td>
</tr>
<tr>
<td>B³⁺</td>
<td></td>
<td>&quot;</td>
<td>1747.5 kcal/mole</td>
<td>IonPot=37.75eV</td>
</tr>
<tr>
<td>B₂</td>
<td>Emission from BCl₃ in N₂ discharge</td>
<td>&quot;</td>
<td>195.0±6.4 kcal/m</td>
<td>G.S.C. = (^3Σ^-_g)</td>
</tr>
<tr>
<td>B₂⁺</td>
<td>Mass spectrum of Diborane</td>
<td>&quot;</td>
<td>500 kcal/mole</td>
<td>Ref 242</td>
</tr>
<tr>
<td>B₃</td>
<td>U.V. spectrum of low press. BCl₃ discharge</td>
<td>&quot;</td>
<td>-</td>
<td>Ref 243</td>
</tr>
<tr>
<td>Cl I</td>
<td>Spectrum of chlorine discharge</td>
<td>Suspected</td>
<td>28.9±1 kcal/m</td>
<td>Excited level (^3Π - ^1Σ)</td>
</tr>
</tbody>
</table>

(continues...)
<table>
<thead>
<tr>
<th>Species</th>
<th>Previously observed in:</th>
<th>Possibility of occurring in RF plasma</th>
<th>$\Delta H_f^{298}$</th>
<th>Other Information</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl$^+$</td>
<td>Mass spectrum of BCl$_3$</td>
<td>Suspected</td>
<td>330.6±0.5 kcal/m</td>
<td>I.P.$\approx$12.95eV GSC=$\approx$P$_2$</td>
</tr>
<tr>
<td>Cl$^{++}$</td>
<td>&quot; &quot;</td>
<td>Not detected</td>
<td>-</td>
<td>I.P.$\approx$23.67eV</td>
</tr>
<tr>
<td>Cl$_2$</td>
<td>Ident. in Chlorine H.P. discharge</td>
<td>Detected</td>
<td>$D_0^0 = 57$ kcal/m</td>
<td>Excited state</td>
</tr>
<tr>
<td>Cl$_2^+$</td>
<td>Discharge tube in Cl$_2$</td>
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<td>265 kcal/mole</td>
<td>I.P.$\approx$13.2eV</td>
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<td>Discharge tube in H$_2$</td>
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COMPLETE SPECIFICATION

High Temperature Chemical Reaction and Apparatus therefor

We, UNITED STATES BORAX AND CHEMICAL CORPORATION, a Corporation organized and existing under the laws of the State of Nevada, United States of America, of 3075 Wilshire Boulevard, Los Angeles, California, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:

This invention relates to a method of effecting a chemical reaction at high temperature, and to apparatus for use in this method.

The method of this invention is in general applicable to any two or more reactants whose reaction takes place only at high temperature, and is particularly useful for two reactants whose product of reaction is a solid. The solid product of the process of this invention is in finely divided form, and by varying parameters of operation of the process the particle size of the product can, within limits, be controlled at will.

An example of the high temperature reaction between two reactants which can be effected by this invention is the reduction of a volatile halide of a metal or metalloid, for example the reduction of a boron halide, with a reducing gas such as hydrogen.

A process for the reaction between a boron halide and hydrogen to produce elemental boron has been previously disclosed. This process consists of forming a plasma of argon, feeding the boron trihalide into the ionized argon, and feeding hydrogen either into the ionized argon together with the boron halide or into the argon before it is ionized so that the hydrogen also is ionized and forms part of the plasma. In this prior process the plasma is formed in a plasma torch, that is the plasma-forming gas is passed between a cathode and an anode across which a low voltage-high current arc is maintained. Thus in the prior process there is used an arc plasma. By injection of boron trichloride into an arc plasma there is obtained elemental boron in particle sizes ranging from about 25 mm. up to 300 mm.

The prior disclosure refers to the production of crystalline boron and consequent need to grind the product, in order to achieve a fine particulat e form.

By the process of the present invention elemental boron can be recovered from boron halide by reduction with hydrogen in a plasma, but a very much finer product is obtained, with a mean particle size of 1 to 2 microns and a range of less than 1 up to about 10 microns. Furthermore, a product purity of substantially above 99% can be obtained. We have found it possible to do this by forming a plasma by radio-frequency coupling instead of by an arc and by control of the location at which the material fed into the plasma contacts it.

According to the present invention there is provided a method of effecting a chemical reaction between at least two reactants which comprises continuously passing a stream of a gas through a reaction zone, forming a plasma of the gas within the reaction zone by radio-frequency coupling, feeding one reactant into the plasma at a point downstream of the centre of the plasma in the direction of gas flow, feeding another of said reactants into said plasma-forming stream or into the formed plasma thereby forming a gas stream containing the product of high temperature reaction, and separating said product from the gas stream.

In the usual form of this process one reactant is present in or constitutes the gas forming the plasma and a second reactant is fed into the plasma. In that case the plasma is preferably formed from a gas mixture passed into the reaction zone which consists of one of the reactants together with a gas which is ionized more readily than said reactants and
is inert to the reactants. Preferably also the other reactant which is fed into the formed plasma is fed in gas form. In an alternative form of this process there is formed a plasma of an inert gas and two reactants are fed into the plasma. A suitable inert gas when one is used is argon.

A coupled plasma can be formed either by an alternating magnetic field, which gives a plasma of the so-called "H" type, or by an alternating electric field established between two conductors, which gives a plasma of the so-called "E" type. While our process might be operated, somewhat inefficiently, with capacitative coupling it is preferred to use inductive coupling and to form an "H" type plasma.

Our process is particularly suitable for the preparation of finely divided elemental boron by reduction of a boron halide such as boron trichloride, e.g. with hydrogen.

Thus in one aspect the present invention provides a process for the preparation of finely divided elemental boron by reaction of a boron halide with hydrogen which comprises continuously passing a first stream of a gas which comprises one of the reactants through a reaction zone, forming a plasma of the gas within the reaction zone by inductive coupling, feeding a second stream of gas which includes the other of said reactants into the plasma at a point downstream of the centre of the plasma in the direction of gas flow thereby forming a gas stream containing elemental fine-sized boron, separating the boron from the gas stream and recovering the boron. In this process for the preparation of finely divided boron, the gas of which the plasma is formed is usually a mixture of an inert gas (e.g. argon) and one of the reactants. Alternatively the first stream of gas, which is ionized, can be just an inert gas, and then the second stream of gas, which is fed into the plasma comprises hydrogen together with the boron halide. If a mixture of inert gas and boron trihalide is used for forming the plasma while hydrogen is fed into the formed plasma, it is possible, (though with danger of extinction of the plasma flame) to reduce the quantity of argon to nil while maintaining the plasma, so that the first gas consists of boron halide while the second gas consists of hydrogen. In each of these ways the boron halide is reduced and hydrogen chloride is present in the product-containing gas stream. The usual boron halide in these processes is boron trichloride.

The invention is not limited to the reduction of a boron halide with hydrogen. Instead of reduction of boron halide, there can be effected reduction with hydrogen of a volatile halide of a metal or silicon; or there can be effected reaction between a volatile halide of a metal or metalloid (by "metalloid" we mean boron and silicon) and a gas such as ammonia, a carbon perhalide, hydrogen sulphide, or a phosphorous halide. Reduction with hydrogen gives rise as product to the elemental metal or metalloid; reaction with the other gases gives rise as product to the nitride, carbide, sulphide or phosphide, respectively, of the metal or metalloid.

Specific examples of these reactions are: boron trichloride with ammonia to form boron nitride; silicon tetrachloride with ammonia to form silicon nitride; aluminium trichloride with ammonia to form aluminium nitride; and boron trichloride with carbon tetrachloride to form boron carbide.

Another class of reactions possible by our process is those between a volatile halide of a metalloid and the halide of a refractory hard metal such as titanium, tungsten or hafnium; this reaction necessitates the use of hydrogen as third reactant which will normally be the plasma. The reaction with a boron halide can be symbolized thus (where X is a halogen and M is a refractory hard metal)

\[ H_2 + BX_3 + M X \rightarrow BM + 4HX \].

The halides of metals as well as of metalloids can be reacted according to our invention; e.g. aluminium trichloride can be reacted with ammonia to give aluminium nitride. High temperature reaction which can be effected by our process is thus the removal of the halogen from volatile halide; of metals or metalloids and its optional replacement by another element. In such reaction, one reactant is present in or constitutes the gas forming the plasma and the second reactant is fed into the plasma.

The process of this invention can be used also for the formation of hydrazine from nitrogen and hydrogen or from ammonia and nitrogen, for the production of hydroxyazine from nitrogen, hydrogen and oxygen, and for the production of hydrogen cyanide from nitrogen and a hydrocarbon.

It will be noted that in our process the interaction takes place only after the plasma has been formed, by feeding the reactant into the plasma at a point downstream of the centre thereof in the direction of gas flow. This facilitates stabilisation of the plasma (that is both formation of a plasma and its maintenance despite minor fluctuations in feed materials) and also makes it possible to control the particle size of the product, as the reactant fed to the plasma absorbs heat and so serves as a quench, the speed of quenching being one of the factors on which particle size depends.

In the process of the present invention, as the gas flows through the reaction zone and is subjected to radio-frequency inductive heating, it is ionized so that a visible fireball
occurs which is quite a sharp zone of brightness, having a definite centre. Downstream of the bright zone the ionized gas cools, forming a progressively less bright tail.

One of the reactants is injected into the tail or into the fireball downstream of its centre.

Desirably the reactant fed into the plasma is delivered at an angle to the axis of gas flow intermediate between the direction radial to the gas flow and the direction axially countercurrent to the gas flow; that is to say while the gas moves downstream the reactant is delivered in an upstream direction.

Rapidity of cooling is an important factor in determining the particle size of the product and for preventing reversion of the product to the starting material.

For the formation of elemental boron by reaction of boron halide some care must be exercised to ensure that the feed meets the gas at an appropriate temperature. This can be readily ascertained experimentally and with the aid of theoretical calculations by adjusting the point at which the feed enters the plasma. When the boron is formed from boron trichloride this temperature should be about 2000°C. During cooling to about 1000°C, there is a tendency for the boron to react with the hydrogen chloride formed and for reversion to the original starting materials to occur, but the quantities of gas are such that this cooling is so rapid that very little equilibrium reversion occurs. For the formation of elemental boron from boron tri-fluoride, the trifluoride should be fed to the hydrogen plasma where it is at a temperature of about 4600°C. Some quenching of the plasma after reaction is then desirable in order to produce a rapid fall in temperature to the temperature of about 500°C, at which substantial reversion no longer takes place. When boron tribromide is used as the feed reactant the reaction temperature can be as low as 900°C and there is no serious problem with reversion on cooling; such low reaction temperatures hardly necessitate use of a plasma. In general, the loss of heat from the inner hot zone of the plasma to the outer, cooler portions of the gas stream provides sufficient cooling for reversion to be substantially no problem without extraneous quenching.

Supplementary cooling of the plasma, e.g. by withdrawal of heat from the tail of the plasma to circulating cooling water which surrounds the plasma-containing apparatus, can be adopted when this is found advantageous.

It is preferred when carrying out a chemical reaction according to this invention to carry the gas stream along a substantially straight path through the induction zone and thence to the separation. Separation is preferably effected centrifugally, e.g. in one or more cyclone separators, since in this way an even back pressure can be established in the gas stream whereby the initiation and maintenance of an even plasma is facilitated.

After the product has been recovered from the gas stream, the gases after any necessary washing to remove unwanted by-products can be recycled to the reaction zone.

It will be seen therefore that in addition to a method for effecting a chemical reaction at high temperature the present invention provides apparatus for use in a preferred mode of operation of the method. The apparatus of the invention comprises a generally cylindrical dielectric reaction vessel having preferably tangential inlet means for gas, a radio-frequency induction coil surrounding a portion of said reaction vessel downstream of the inlet means so as to define therein a plasma-generating zone, and tubular inlet means for a reactant which means are arranged to deliver the reactant into the vessel along a path inclined to the axis of said vessel and on the side of the induction coil remote from said gas inlet.

We will next describe the invention in more detail with particular reference to the production of elemental boron from boron trichloride. Modifications of the process needed for other reactions will be apparent from this specific description.

The apparatus is illustrated in the accompanying drawings, of which Figure 1 is a diagram of the reaction apparatus and associated separators, while Figure 2 is a more detailed sectional elevation of the reaction apparatus and Figure 3 is an end view of the apparatus seen from the left of Figure 2.

Referring first to Figures 2 and 3, the apparatus includes a quartz tube 10 about two inches in diameter and two feet long, closed at one end by a quartz cap 12 integral with the tube and open at its other end where it is connected to a tapering glass tube 14 (glass being cheaper than quartz where resistance to the heat of a plasma is not required). An inlet port 16 in cap 12 is connected by a line 18 to a source of argon; the inlet port is arranged to deliver gas tangentially of the circular tube.

Downstream of the inlet port an induction coil 20 surrounds the tube, coil 20 being connected to a source of radio frequency power. The circumferentially spaced ports 22 are formed in tube 10 about 2 cm downstream of the last turn of coil 20. (The spacing between the coil and the ports can be varied so as to vary the point in the plasma at which a feed admitted through ports 22 contacts the ionized gas, thus varying the temperature at which the reaction takes place and the rapidity of cooling of the plasma.) Ports 22 are connected to respective quartz
4 tube technique permitted the maintenance of a countercurrent to the direction of gas flow through port 16 and as it flows along the tube, a gas outlet 30 which communicates with a second cyclone separator 32 provided with a collector box 34 for fine particles and a gas outlet 36. Outlet 36 communicates with an electrostatic precipitator 38, and the outlet from gas inlet 16 to first cyclone communicates with a collector box 28 for coarse particles

5 Referring now to Figure 1, glass tube 14 extends for about four feet and communicates with a cyclone separator 26. It will be seen that from gas inlet to first cyclone separator 26 gas has to follow a straight path, so that pressure pulses within the plasma are minimized. The fine separator is provided with a collector box 28 for coarse particles and a gas outlet 30 which communicates with a second cyclone separator 32 provided with a collector box 34 for fine particles and a gas outlet 36. Outlet 36 communicates with an electrostatic precipitator 38, and the outlet 40 from which is connected to gas washing apparatus (not shown). In use of the apparatus for the reduction of boron trichloride to boron, the preferred procedure is as follows: argon is fed into the reaction zone through port 16 and as it flows along the tube, radio frequency power supplied to the coil at e.g. about 10 kw. is coupled inductively to the argon so that the argon ionizes to form a visible plasma within the region surrounded by coil 20. To facilitate formation of a plasma a spark may be struck in the argon by a Tesla coil, but it is not essential to strike a spark.

10 When the argon plasma has been formed so that the argon becomes conducting, hydrogen is mixed with the argon feed and the argon-hydrogen mixture is ionized, the power input at the same time being increased appropriately to e.g. 30 kw. If induction technique permitted the maintenance of a hydrogen plasma in the absence of a more readily ionizable inert gas such as argon, it would be possible according to the principles of this invention to feed pure hydrogen (or other reactant gas when a different reaction is intended) into the plasma-forming zone.

15 The operating conditions, (i.e. the relationship of the power input to the constituents of the gas mixture, the disposition of the coil, and the pressure of the gas mixture) can be adjusted to provide a fireball which is confined at the desired location within the tube and does not destroy the tube. Well established principles for this adjustment of operating conditions are described in the Chemical Engineer, No. 203, issued in November 1966.

20 Gaseous boron trichloride is supplied to the plasma through ports 22, being directed counter current to the direction of gas flow which is marked by an arrow in Figure 2. The proportions and flow rates of the gases are adjusted as described below, but when the ratio of boron trichloride to hydrogen exceeds that stoichiometrically necessary for formation of elemental boron, additional hydrogen can be fed into the plasma together with the boron trichloride through the said gas ports. This may be advantageous as an alternative to increasing the amount of hydrogen in the feed gas or to increasing the quantity of feed gas. Temperature within the plasma may vary from a few hundred degrees Centigrade at the outside to 2000°C at the centre. As is well known, exact measurements of temperature within the plasma are of limited practical value as the temperatures vary so rapidly over a minute distance; therefore it is preferred to establish the position of the feed inlet relative to the induction coil not so much by theoretical temperature considerations as by experimental methods. Some boron is deposited on the walls of the quartz tube but the bulk of it is deposited as a fine powder in the cyclone separators. After the boron has been separated from the gas stream, the gas stream is washed to remove hydrogen chloride (unreacted boron trichloride first being condensed out if desired) and then can be recycled. In recycling the hydrogen-argon mixture, care must be taken to replace the hydrogen which has been consumed and to avoid the disturbance of pressure conditions within the reaction zone. Recovered unreacted boron trichloride can also be recycled.

25 The quantities of the various gases fed into the reaction zone can be varied within wide limits so as to optimise the particle size, the yield relative to power input, the rate of production of the product, or the ease of washing and recycling unreacted gases. The argon-hydrogen mixture fed to the plasma-forming zone normally contains at least one part in sixteen of argon in order to ensure plasma stability. In a typical run there are used 5 litres per minute of argon, 9 litres per minute of hydrogen and 16 litres per minute of boron trichloride. By increasing the quantity of hydrogen to e.g. 35-40 litres per minute of boron trichloride, the average particle size in the range 1-10μ, the average particle size being 1.5-2μ (as determined on a Fisher sub-sieve sizer). Fine particle size can be promoted by supplying an inert gas together with the boron trichloride into the plasma. Small quantities of boron trichloride can be included in the gas mixture fed to the plasma forming zone.

30 The finely divided boron produced by this process has the following characteristics: a purity of not less than 99.0%; a surface area as determined by the B.E.T. method in the range 4-7 m²/g; a moisture pickup of 0.5%
The operating conditions and results of some typical runs are as follows:

<table>
<thead>
<tr>
<th>Hydrogen with</th>
<th>Argon</th>
<th>Argon</th>
<th>Hydrogen</th>
<th>Power</th>
<th>Yield</th>
<th>Purity</th>
<th>Particle size</th>
</tr>
</thead>
<tbody>
<tr>
<td>Argon (1/m)</td>
<td>BCl3</td>
<td>(g/m)</td>
<td>(1/m)</td>
<td>(mole/mole)</td>
<td>(kw)</td>
<td>(%)</td>
<td>(%)</td>
</tr>
<tr>
<td>5</td>
<td>40</td>
<td>25</td>
<td>73</td>
<td>13</td>
<td>2.73</td>
<td>16.7</td>
<td>21.5</td>
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<tr>
<td>10</td>
<td>10</td>
<td>81</td>
<td>100</td>
<td>35</td>
<td>2.46</td>
<td>20.3</td>
<td>26.0</td>
</tr>
<tr>
<td>10</td>
<td>12</td>
<td>100</td>
<td>83</td>
<td>31</td>
<td>2.52</td>
<td>19.0</td>
<td>31.4</td>
</tr>
</tbody>
</table>

The gases of columns 1, 2 and 3 are plasma-forming gases fed as a mixture into the torch through inlet “8”; the hydrogen of column 4 is tail hydrogen, fed to the formed plasma through inlets 24.

WHAT WE CLAIM IS:—

1. A method of effecting a chemical reaction between at least two reactants, which comprises continuously passing a stream of a gas through a reaction zone, forming a plasma of the gas within the reaction zone by radio-frequency coupling, feeding one reactant into the plasma at a point downstream of the centre of the plasma in the direction of gas flow, feeding another of said reactants into said plasma-forming stream or into the formed plasma thereby forming a gas stream containing the product of high temperature reaction, and separating said product from the gas stream.

2. A method as claimed in Claim 1, in which one reactant is present in or constitutes the gas forming the plasma and a second reactant is fed into the plasma.

3. A method as claimed in Claim 2, in which the gas stream which is passed into the reaction zone consists of one of the reactants together with a gas which is ionized more readily than said one reactant and is inert to the reactants.

4. A method as claimed in Claim 1, in which there is formed a plasma of an inert gas and two reactants are fed into the plasma.

5. A method as claimed in Claim 3 or 4, in which the inert gas is argon.

6. A method as claimed in Claim 2, 3, 4 or 5, in which the two reactants are respectively (i) a volatile halide of a metal, boron or silicon and (ii) a gas.

7. A method as claimed in Claim 6, in which the gas is hydrogen and the elemental metal, boron or silicon is formed as product.

8. A method as claimed in Claim 7, in which a boron halide is reduced to elemental boron.

9. A method as claimed in Claim 8, in which boron trichloride is the boron halide.

10. A method as claimed in Claim 6, in which ammonia, a carbon perhalide, hydrogen sulphide or a phosphorous halide is used as the reactant gas and there is formed as product the nitride, carbide, sulphide or phosphide of the metal, boron or silicon.

11. A method as claimed in Claim 10, in which a boron halide is the volatile halide.

12. A method as claimed in Claim 6, in which the two reactants are respectively the volatilised halide of boron or silicon and the halide of a refractory hard metal, and hydrogen is also present.

13. A method as claimed in any of Claims 6 to 11, in which the plasma is formed from the gas and the volatile halide is fed into the plasma.

14. A method as claimed in any of Claims 6 to 11, in which the plasma is formed from the volatile halide and the gas is fed independently into the plasma.

15. A method as claimed in claims 8 and 13, in which the plasma is formed from a mixture of hydrogen and an inert gas, and the boron halide is fed into the plasma.

16. A method as claimed in Claim 15, in which a minor quantity of the boron halide is delivered with the plasma-forming gas stream and the remaining quantity is fed into the plasma.

17. A method as claimed in Claim 15 or 16, in which the inert gas is argon and the boron halide is boron trichloride.

18. A method as claimed in any preceding claim, in which inductive coupling is used to ionize the gas and form the plasma.

19. A process for the preparation of finely divided elemental boron by reduction of a boron halide with hydrogen which comprises continuously passing a first stream of a gas which comprises one of the reactants through a reaction zone, forming a plasma of the gas within the reaction zone by inductive coupling, feeding a second stream of gas which is the other of said reactants into the plasma at a point downstream of the centre of the plasma in the direction of gas flow thereby forming a gas stream containing elemental fine-sized boron, separating the boron from the gas stream and recovering the boron.

20. A method as claimed in claim 19, in which the first gas stream comprises argon
and hydrogen and the second gas stream is the boron halide.

21. A method as claimed in any preceding claim, in which the reaction zone is circular cylindrical and the gas stream forming the plasma is delivered tangentially to the boundary thereof.

22. A method as claimed in any preceding claim, in which the reactant fed into the plasma is delivered at an angle to the axis of gas flow.

23. A method as claimed in claim 22, in which the reactant fed into the plasma is delivered at an angle intermediate the direction perpendicular to the axis of gas flow and the direction countercurrent to the axis of gas flow.

24. A method as claimed in any preceding claim wherein the quantity of gas fed into the plasma, the point at which the gas is fed into the plasma and the quantity and temperature of the ionized gas forming the plasma are adjusted to cool the plasma sufficiently quickly to prevent reversion of product.

25. A method as claimed in Claim 24, in which supplementary cooling of the plasma is used.

26. A method as claimed in any preceding claim, in which the gas is caused to flow in a substantially straight path into and through the reaction zone and onwards to a separation zone.

27. A process as claimed in any preceding claim, in which particulate product is separated from the gas stream by centrifugation.

28. A process as claimed in any preceding claim, in which gases separated from the product are re-cycled to form the plasma.

29. A method of effecting a high-temperature chemical reaction according to claim 1, substantially as hereinbefore described.

30. A method of reducing a boron halide to elemental boron in an induction plasma, substantially as hereinbefore described.

31. Elements or compounds prepared by a method as claimed in any preceding claim.

32. Finely divided elemental boron prepared by a method as claimed in claim 19, 20 or 30.

33. Apparatus for carrying out a high temperature reaction using an ionized gas which comprises a generally cylindrical dielectric reaction vessel having inlet means for gas, a radio frequency induction coil surrounding a portion of said reaction vessel downstream of the inlet means so as to define therein a plasma-generating zone, and tubular inlet means for a reactant which means are arranged to deliver the reactant into the vessel along a path inclined to the axis of said vessel and on the side of the induction coil remote from said gas inlet.

34. Apparatus as claimed in claim 33, in which the gas inlet is arranged to deliver gas tangentially to the reaction vessel.
Fig. 1

Fig. 2

Fig. 3
APPENDIX III

The Efficiency of the Plasma Boron Process as a Function of the Operating Parameters.

Terms:

A - argon flowrate (lit/min).
B - boron trichloride flowrate (lit/min).
H - hydrogen flowrate (lit/min).
H' - hydrogen chloride flowrate (lit/min).
Pb - partial pressure of boron trichloride in gas stream at condenser inlet (atmos.).
Tc - effective condensation temperature (°C).
Vb - vapour pressure of boron trichloride at Tc°C.
c - fractions of boron trichloride reduced to boron per pass.
n - ratio of input volumes of hydrogen to boron trichloride.
f c - fraction of boron trichloride condensed per pass.
fl - fraction of boron trichloride lost per pass.

The boron trichloride entering the system can be considered in three separate fractions;

c - that fraction which is reduced to boron.
fc - that fraction which is subsequently condensed and is available for re-use.
fl - that fraction which is lost.

Thus the efficiency of the process is given by

$$\eta = \frac{c}{c+fl}$$  \hspace{1cm} (1)

As 1 volume of boron trichloride requires for reaction 1.5 volumes of hydrogen and produces 3 volumes of hydrogen chloride, then it is apparent that,

Volume of boron trichloride reacted = \(\frac{3}{2}cB\)
Volume of hydrogen reacted = \(\frac{3}{2}cB\)
Volume of hydrogen chloride produced = \(3cB\)

Thus the gas flow into the condensers, \(F_T\) is given by

\[ F_T = [\text{argon}] + [\text{hydrogen}] + [\text{boron trichloride}] + [\text{hydrogen chloride}] \]
\[ F_T = (A)+(H-\frac{3}{2}cB)+(B-cB)+(3cB) \]
\[ F_T = A+nB-\frac{3}{2}cB+B-cB+3cB \]
\[ F_T = A+nB+\frac{5}{2}B+B \]  \hspace{1cm} (2)
Now, the fraction of boron trichloride condensed at any temperature $T_c$ is given by

$$f_c = \frac{P_b - V_b}{P_b} \quad \text{......... (3)}$$

Where $P_b$ is given by

$$P_b = \frac{\text{boron trichloride flow into condensers}}{\text{total gas flow into condensers}} \times 1$$

i.e. $P_b = \frac{B(1-c)}{A+nB+\frac{B+B}{2}} \text{ atm.}$ and from eq. (2)

$$P_b = \frac{B(1-c)}{A+nB+\frac{B+B}{2}} \text{ atm.} \quad \text{......... (4)}$$

From eq. (3), that fraction of the total boron trichloride condensed at $T_c$ is given by

$$f_c = (1-c)(1-V_b)$$

and the fraction lost is given by

$$f_l = 1 - \left\{c + fc\right\} \quad \text{......... (5)}$$

Substituting for $P_b$ from eq. (4) and for $f_l$ in eq. (1),

$$c = \frac{c + (1-c)}{1 - (1-c) + V_b(\frac{B+B+n}{2})}$$

$$1 = \frac{c + (1-c) \left(1 - \frac{V_b}{P_b}\right)}{1 - (1-c) + V_b(\frac{B+B+n}{2})}$$

$$c = \frac{1}{1 + V_b \left(\frac{A+nB}{B+2+n+1}\right)}$$
By substituting for Pb from eq. (4) into eq. (5) an expression for the fraction of boron trichloride lost per pass can also be derived,

\[ f_l = 1 - \left\{ c + (1-c) \left( 1 - \frac{V_b}{P_b} \right) \right\} \]

\[ f_l = 1 - \left\{ c + (1-c) \left( 1 - \frac{V_b}{1-c} \left\lceil \frac{A+B}{B} + n + 1 \right\rceil \right) \right\} \]

\[ f_l = 1 - \left\{ c + 1 - c - V_b \left( \frac{A+B}{B} + n + 1 \right) \right\} \]

\[ f_l = V_b \left( \frac{A+B}{B} + n + 1 \right) \]

Note also that eq. (1) can be rewritten

\[ f_l = c \left( \frac{1}{n} - 1 \right) \]

and that the maximum temperature \( T_c \) at which condensation of boron trichloride will take place is obtained from equation (3) by putting \( f_c = 0 \).

i.e. When \( V_b = P_b \).
PLATE 1: Low Energy Argon Plasma.
PLATE 2: 10 kW Argon Plasma.
PLATE 4: Spectrum of Argon Plasma.
PLATE 5: Spectrum of Argon Plasma.
PLATE 6: Spectrum of Ar/H₂/BCl₃ Plasma.
PLATE 7: Electron micrograph of boron sphere (x 96).

PLATE 8: Electron micrograph of boron sphere (x 520).
PLATE 9: Electron micrograph of boron sphere (x 1000)

PLATE 10: Electron micrograph of boron whisker (x 1050)
PLATE 11: Electron micrograph of boron whisker (x 2000)

PLATE 12: Fractured end of boron whisker (x 2200).

Left: β rhombohedral crystals.
Right: amorphous powder.
Electron Micrographs of Plasma Boron (x 10K)
Electron Micrographs of Plasma Boron.
PLATE 18: Electron micrograph of Plasma Boron (x50K)
(7000Å Dodecagonal Platelet)
Electron Diffraction Pattern of 12-sided Platelet
PLATE 20

Electron Diffraction Pattern of 12-sided Platelet.
Electron Diffraction Pattern of Boron Particles.