A STUDY OF THE TITANIUM TETRACHLORIDE
OXIDATION IN A ROTATING ARC PLASMA JET

by

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Chemical Technology
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ABSTRACT

The object of this work was to determine the kinetics of the titanium tetrachloride oxidation reaction. A fundamental requirement for kinetic studies in high temperature flow systems is the homogeneous initiation of the chemical reaction. This implies the need to supply thermal energy uniformly across a section. The use of a magnetically rotated plasma jet to achieve this condition has been investigated. A new method for the qualitative assessment of thermal mixedness using a probe based on a corona discharge has been developed. This has been used in designing a new reactor based on the rotating arc plasma jet.

The oxidation reaction of titanium tetrachloride has been investigated in this reactor over a temperature range of 970 - 1498°K. Evidence of a slow chlorine reassociation process was discovered, and was best described by:

$$\frac{d[Cl_2]}{dt} = - 0.632 \times 10^{-4} \exp\left(- \frac{29743 \pm 2200}{RT}\right)$$

Taking this into account, the oxidation reaction was found to proceed according to the following rate expression:

$$\frac{d[TiCl_4]}{dt} = - 0.360 \times 10^{-4} \exp\left(- \frac{10030 \pm 1060}{RT}\right)$$

Dilute systems were used in this investigation and the lack of dependence of these rate expressions on the reactant concentrations may not be applicable for more concentrated systems.
ACKNOWLEDGMENTS

The efforts and contributions of many people made possible the completion of this work. Certainly, the technical guidance and support of Professor F. J. Weinberg is unequalled. His unfailing human concern throughout the research period is most appreciated.

Discussions with Dr. A. R. Jones added further insight to many parts of this work, and is gratefully acknowledged.

The professionalism and speed in the fabrication of equipment, as provided by Tony Jones, Colin Smith, Ken Grose, of the glassblowing workshop; and Bert Lucas, Russ Harris, of the main workshop, is greatly appreciated. The efforts of Trevor Agus is duly acknowledged.

My thanks are due to Tioxide International for their financial support, and to Mr. E. R. Place for valuable discussions.

To my wife, Jamie, I give my thanks and appreciation for typing this thesis, and for her continuous support and encouragement.
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<td>Cl₂</td>
<td>Chlorine</td>
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<tr>
<td>O₂</td>
<td>Oxygen</td>
</tr>
<tr>
<td>TiCl₄</td>
<td>Titanium Tetrachloride</td>
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<tr>
<td>TiO₂</td>
<td>Titanium Dioxide</td>
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### Chapter Two

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<tr>
<td>B</td>
<td>Magnetic field, W m⁻²</td>
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<td>f₀</td>
<td>Arc frequency of rotation, Hz</td>
</tr>
<tr>
<td>I</td>
<td>Arc current, Amps.</td>
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<tr>
<td>Uₓ</td>
<td>Linear gas velocity, cm s⁻¹</td>
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<tr>
<td>δ</td>
<td>Arc diameter, cm</td>
</tr>
<tr>
<td>π</td>
<td>Spiral pitch</td>
</tr>
<tr>
<td>r</td>
<td>Ratio of linear velocity to frequency of rotation, cm/arc revolution</td>
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<td>Ar</td>
<td>Argon</td>
</tr>
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<td>a</td>
<td>TiCl₄ flow rate, mole s⁻¹</td>
</tr>
<tr>
<td>b</td>
<td>O₂ flow rate, mole s⁻¹</td>
</tr>
<tr>
<td>c</td>
<td>Ar flow rate, mole s⁻¹</td>
</tr>
<tr>
<td>F anode</td>
<td>Anode cooling water flow rate, Kg s⁻¹</td>
</tr>
<tr>
<td>F cathode</td>
<td>Cathode cooling water flow rate, Kg s⁻¹</td>
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<tr>
<td>ΔHᵣ</td>
<td>Heat of reaction, cal mole⁻¹</td>
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<tr>
<td>I</td>
<td>Arc current, Amp.</td>
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<tr>
<td>J</td>
<td>cal/4.186</td>
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<td>T₀</td>
<td>Reference Temperature (273°K), °K</td>
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Inlet gas temperature, °K

Mean Reaction Temperature, °K

Anode water temperature difference, °C

Cathode water temperature difference, °C

Potential difference across arc, Volts

1 cal/gm °C

Heat capacity of thermocouple material, cal gm⁻¹ °K⁻¹

Thermocouple junction diameter, cm

Heat transfer coefficient, cal/cm² °K s

Thermocouple time constant (D ρ Cs/4h), s

Gas temperature, °K

Thermocouple junction temperature, °K

Mean temperature, °K

Amplitude of temperature fluctuation, °K

Thermocouple material density, gm cc⁻¹

Temperature fluctuation frequency, Hz

Heat transfer coefficient

Thermal conductivity of gas

Nusselt number

Prandtl number

Reynolds number

Reactor wall temperature, °K

Temperature indicated by thermocouple, °K

Actual gas temperature, °K
a  Thermocouple wire absorptivity
\[ \varepsilon \]  Thermocouple wire emissivity
\[ \sigma \]  Stefan Boltzmann constant \( (= 1.356 \times 10^{-12} \text{ cal cm}^{-2} \cdot \text{s}^{-1} \cdot \text{K}^{-4}) \)

Chapter Seven

A  Cross-sectional area, cm\(^2\)
A, B  Reactants
C  Product
\( [A] \)  Concentration of species A, moles s\(^{-1}\)
\( A^T \)  Transpose of the matrix \( A \)
\( (A^T A)^{-1} \)  Inverse of the matrix \( (A^T A) \)
\( [B] \)  Concentration of species B, moles s\(^{-1}\)
\( [C] \)  Concentration of species C, moles s\(^{-1}\)
a  i. Polynomial constant for concentration curve
ii. Stoichiometric coefficient of A
\( a' \)  Polynomial constant for temperature curve
b  i. Polynomial coefficient of \( t \) for concentration curve
ii. Stoichiometric coefficient of B
\( b' \)  Polynomial coefficient of \( t \) for temperature curve
c  i. Polynomial coefficient of \( t^2 \) for concentration curve
ii. Stoichiometric coefficient of C
\( c' \)  Polynomial coefficient of \( t^2 \) for temperature curve
E  Activation energy, cal/mole
K  Pre-exponential constant, units depend on rate expression form: cc/s, mole, or mole/cc.s
m  Number of observations
n  Number of unknowns

xii
P  i. Pressure, atms.
ii. Reaction order with respect to [A]

Q  i. Reaction order with respect to [B]
ii. Volumetric flowrate, cm$^3$ s$^{-1}$

R  Gas constant, 1.9869 cal/mole °K

T  Temperature, °K

t  time, s

U  gas velocity, cm s$^{-1}$

\[ \sum_{i=1}^{m} U_{ii}^2 \] Residual sum of squares

V  Volume of constant mass, cm$^3$

x  Distance, cm

ln  Natural logarithm

\( \rho \)  Gas density, g m$^{-3}$

\( \mu_{x_i} \)  Standard deviation in fitted parameters

\( \sigma_K \)  Standard deviation in K

\( \sigma_{\ln K} \)  Standard deviation in \( \ln K \)

\( C_i \)  Concentration of species, i, mole cc$^{-1}$

\( N_i \)  Number of moles of species, i, moles

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Chapter Eight

\([\text{Cl}_2]\)  Chlorine concentration

E  Activation energy, cal/mole

K  Pre-exponential constant

\([\text{O}_2]\)  Concentration of oxygen, moles cc$^{-1}$

p  Reaction order with respect to TiCl$^4$

q  Reaction order with respect to O$_2$

R  Gas constant, 1.9869 cal/mole °K
T \quad \text{Temperature, } ^{0}\text{K}

Rate \quad \text{Reaction rate, moles cc}^{-1}\text{ s}^{-1}

R_N \quad \text{Rate of chlorine formation or depletion, moles cc}^{-1}\text{ s}^{-1}

R_r \quad \text{Rate of chlorine reassociation, moles cc}^{-1}\text{ s}^{-1}

R_f \quad \text{Rate of the oxidation reaction, moles cc}^{-1}\text{ s}^{-1}

[TiCl_4] \quad \text{Concentration of titanium tetrachloride, mole cc}^{-1}

t \quad \text{time, s}
Titanium dioxide is widely used as a white pigment. The properties which make it valuable include its high refractive index of 2.7 and, in contradistinction to lead salts, its non-toxicity. It occurs naturally in three crystalline forms; anatase, brookite, and rutile. These are substantially titanium dioxide, but usually contain small amounts of impurities, such as iron, which give them a dark colour. Rutile is the thermally stable form and is one of the most important ores of titanium. It is a raw material used for the production of titanium tetrachloride from which pure titanium dioxide is obtained. Tables 1.1 and 1.2 present some physical properties of titanium dioxide and tetrachloride.

The industrial manufacture of pigmentary titanium dioxide is effected by two methods: the sulphate and the chloride processes. Details of both of these processes are given by Barksdale (1) and Kirk-Othmer Encyclopedia of Chemical Technology (2), and Fig. 1.1 represents a flow diagram of the two methods:

The chloride process, which is the one relevant to this work, involves the oxidation of titanium tetrachloride in the gas phase to titanium dioxide and chlorine. This reaction is usually described by the following chemical equation:

\[ \text{TiCl}_4 + \text{O}_2 \rightarrow \text{TiO}_2 \text{(solid)} + 2\text{Cl}_2 \quad \text{Exothermic} \]
Fig. 1.1 Flow Diagram for the Manufacture of Titanium Dioxide Pigments, after Kirk-Othmer
(with permission of Interscience Publishers)
Crystal Modifications:
Anatase, Brookite, Rutile (most stable modification)

Refractive Index:
Anatase: 2.55
Rutile: 2.71

Specific Gravity:
Anatase: 3.84
Rutile: 4.26

Surface Area:
(Rutile): 13.8 m²/gm

Melting Point:
1840 ± 10°C

Heat Capacity:

<table>
<thead>
<tr>
<th>Temp. °K</th>
<th>Cal/mole °K</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>13.153</td>
</tr>
<tr>
<td>1000</td>
<td>17.500</td>
</tr>
<tr>
<td>1500</td>
<td>18.990</td>
</tr>
<tr>
<td>2000</td>
<td>20.393</td>
</tr>
</tbody>
</table>

Physical State:

a. Up to 2100°K, TiO₂ rutile crystal
b. 2100-4000°K, TiO₂ liquid

On heating TiO₂ oxygen is lost, leaving non-stoichiometric TiO₂-x : x depends on the temperature and on the pressure of oxygen.

Table 1.1 Physical Properties of Titanium Dioxide (1, 2, 37)
Appearance: Colourless liquid fumes strongly in air.

Specific Gravity: 
- $0^\circ C$: 1.7604
- $10^\circ C$: 1.74
- $136.41^\circ C$: 1.52

Boiling Point: 136.41°C

Melting Point: -23 to 30°C

Heat of Fusion: 12.90 cal per gram.

Molecular heat of Vapourisation (by Clausius-Clapeyron equation): 8960 cal at 25°C, and 8620 cal at boiling point.

Specific Heat: 
<table>
<thead>
<tr>
<th>Temp. $^\circ K$</th>
<th>cal/mole $^\circ K$</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>34.704</td>
</tr>
<tr>
<td>400</td>
<td>34.936</td>
</tr>
<tr>
<td>500</td>
<td>35.153</td>
</tr>
<tr>
<td>1000</td>
<td>36.237</td>
</tr>
</tbody>
</table>

Equilibrium Data: 

<table>
<thead>
<tr>
<th>Temp. $^\circ K$</th>
<th>Equilibrium Species Present</th>
</tr>
</thead>
<tbody>
<tr>
<td>400-2600</td>
<td>TiCl$_4$(g)</td>
</tr>
<tr>
<td>2600-2800</td>
<td>TiCl$_3$(g)</td>
</tr>
<tr>
<td>2800-3200</td>
<td>TiCl$_2$(g)</td>
</tr>
<tr>
<td>3200-4000</td>
<td>TiCl(g)</td>
</tr>
</tbody>
</table>

Table 1.2 Physical Properties of Titanium Tetrachloride (1, 2, 37)
The process is economically attractive, as the chlorine produced may be recycled for the chlorination of mineral rutilite.

There are several ways of carrying out this reaction, and an extensive literature exists mainly in the form of patents (3-22). What most of the literature omits is information regarding the kinetics of the oxidation reaction; this being of prime importance in optimising the formation of titanium dioxide particles, which for use as a pigment should have a mean size of around 0.25 μm. The present study has the investigation of these kinetics as one of its main objectives.

Numerous ways have been used in attempts at producing a controlled environment for the investigation of reaction kinetics. These involve the introduction of a perturbation in the thermodynamic equilibrium and measuring the variation of temperature and concentration of one or more of the species with respect to time. Such techniques are discussed in great detail by several authors (23, 24, 25), and Table 1.3 summarises the more common of these with typical values for some of their parameters (26). Differences between these techniques lie mainly in the means of introducing the perturbation, and the way in which the reaction is distributed in time. The perturbation must be initiated homogeneously and in a time short compared with the reaction half-life.

For reasons which will become apparent later, the method of interest in this work is that of flow reactors, where thermal initiation is usually used. This can be achieved by passing the reactants through a heated duct
<table>
<thead>
<tr>
<th>Type of System</th>
<th>Reaction Speed</th>
<th>Temperature Range °K</th>
<th>Pressure Range ATM.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Discharge Flow</td>
<td>10</td>
<td>300-800</td>
<td>0.1-1.0</td>
</tr>
<tr>
<td>Photolysis</td>
<td>10</td>
<td>300-800</td>
<td>0.1-1.0</td>
</tr>
<tr>
<td>Shock Tube</td>
<td>$10^{-2}$</td>
<td>1000-10,000</td>
<td>0.1-10</td>
</tr>
<tr>
<td>Static Reaction Vessel</td>
<td>$10^4$</td>
<td>300-1300</td>
<td>0.1-1.0</td>
</tr>
<tr>
<td>Premixed Flames</td>
<td>1</td>
<td>1000-2500</td>
<td>0.1-5</td>
</tr>
<tr>
<td>Stirred Reactors</td>
<td>1</td>
<td>300-2000</td>
<td>1.0-10</td>
</tr>
<tr>
<td>Flow Reactors</td>
<td>1</td>
<td>300-2000</td>
<td>0.1-10</td>
</tr>
</tbody>
</table>

Table 1.3  Summary of Experimental Methods For Kinetics Studies after Branch (26)
wall, or mixing them with a pre-heated inert gas. Thermal addition and equilibrium must be effected uniformly in a time much shorter than the reaction time. The chemical reaction is distributed spacially and, at a particular point, under constant flow conditions, the composition approaches a stationary value. The axial temperature and composition are monitored by means of suitable probes.

In order to obtain unambiguous kinetic information, the flow conditions, i.e. radial and axial profiles of velocity, temperature and composition must be clearly defined. The theoretical analysis of these parameters is discussed, e.g. by Branch (26). However, plug flow, that is with no radial gradients would be an ideal model to choose for obtaining and interpreting kinetic data. This can be approached realistically in the region of developing turbulent flows (26).

A rapid and efficient way of introducing thermal energy into a flowing gas is by means of a high frequency magnetically rotated electrical discharge, as discussed in Chapter 2. This type of plasma jet is used for electrically augmenting combustion reactions (27 - 29). A detailed account of its design and development is given by Cox (35).

The present study investigates the possibility of using such a plasma jet as a flow reactor for chemical synthesis and kinetic studies. The criterion determining its suitability is its ability to distribute the electrical energy input uniformly to the cross-section of the stream of flowing reactants.
The investigation begins by considering the flow of oxygen and titanium tetrachloride in argon through the plasma jet. A theoretical and experimental analysis, given in Chapter 3, shows that a uniform thermal distribution can only be achieved at the expense of having undesirably high gas temperatures. This problem was overcome by the use of a post-arc injection reactor. The presence of uniform thermal distribution was confirmed experimentally by the use of a probe, developed for the purpose, which exploits the dependence of the break-down potential of a corona discharge on local gas density. The design specifications for this reactor, including operating conditions, are given in Chapter 5.

The oxidation of titanium tetrachloride is investigated kinetically using the post-arc injection reactor. The progress of the reaction is followed by monitoring the temperature and chlorine concentration variation along the reactor centreline. The mathematical procedure for the reduction of such data into useful kinetic information is presented in Chapter 7. The experimental results are presented and analysed in Chapter 8. It is discovered from these results that the chlorine reassociation occurs at a much slower rate than has been previously assumed. The analysis of this process is considered essential in order to gain further insight into the oxidation reaction. Rate expressions for the chlorine reassociation process and the titanium tetrachloride oxidation reaction are discussed and presented in Chapter 8.
CHAPTER TWO

THE MAGNETICALLY ROTATED ARC PLASMA JET

2.1 Description of the Rotating Arc Plasma Jet

The direct addition of energy to a gas stream can be achieved efficiently using a magnetically rotated arc. Figure 2.1 is a schematic diagram of the rotating arc plasma jet. The mechanical construction of this device includes a water-cooled copper anode and a tungsten cathode housed in a copper frame. The axial magnetic field is produced by passing direct current through a coil made up of 4200 turns of 22 s.w.g. copper wire covered with a high temperature resistance enamel. The coil is water-cooled to prevent unnecessary overheating. Argon is introduced in the arc zone as shown in Fig. 2.1. A small annulus immediately surrounding the cathode allows the passage of a sheath of argon which helps in cooling the cathode and protects it from direct chemical attack when reactants are present.

The electric power for the discharge is supplied by two SRH222(s) Miller Welder d.c. generators. Each of these is capable of supplying 150 amps. continuously. They can be used singly or coupled in series or parallel depending on the desired application. The discharge is initiated using high frequency voltage pulses supplied by a spark generator.

The current supplied to the magnetic field coil is smoothed d.c. produced by rectifying the mains using
Rotating Arc Plasma Jet

Fig. 2.1
the circuit shown in Fig. 2.2. The voltage is controlled by a Variac. This design arrangement allows the field to be varied over a wide range. Figure 2.3 shows the connection of the various electrical supplies to the plasma jet.

The interaction between the arc current, $I$, and the magnetic field, $B$, leads to the Lorentz force, $B \times I$, which manifests itself in the motion of the arc around the cathode. This phenomenon is described and discussed in detail by Cox (35) and others (32, 36). The frequency of this rotation depends on the magnitudes of both $B$ and $I$ (32).

The gas flowing through the cathode-anode annulus encounters the rotating arc, details of which are discussed in a later section. It is necessary to assert that this arrangement provides a unique method of supplying large enthalpies in an extremely short time. Furthermore, the motion of the arc is of primary importance in distributing this enthalpy in the cross-section of the flowing gas.

2.2 Measurement of Arc Frequency of Rotation

The arc frequency of rotation is a fundamental parameter in the practical application of this plasma jet. It can be measured using optical techniques (32) or a search coil (35). It is more convenient in this arrangement to use the latter.

The arc can be viewed as a cylinder, through which a large current is flowing, and which is in
Fig. 2.2: Rectifier Circuit Diagram
Plasma Jet Electrical Supply

- Miller Welder Units
- Plasma Jet
- Electrical Supply
- Magnetic Field Coil
- Cu-Anode
- W-Cathode
- Spark Generator
- Rectifier
- D.C.
- A.C. Mains
- Miller Welder Units

Fig. 2.3
rotational motion. The current induces a magnetic field around the cylinder, which can be picked up using a search coil located near the region of the arc and in the same plane, as shown in Fig. 2.4. The current induced in the search coil will fluctuate with the same frequency as that of the magnetic field. This, in turn, varies with the frequency of the rotating arc. Thus, if the search coil current is displayed on an oscilloscope, its fluctuation is a direct measurement of the arc rotation. The frequency can either be measured by balancing the search coil signal against a tunable output of a signal generator, or by direct photography of the displayed signal.

The search coil used in this work is a Radio Spares Reed Coil No. 2 having about 7000 turns. The frequencies were measured directly by photographing the display. Figure 2.5 represents graphs of field current against frequency for several arc currents, with an argon flow rate of about 140 cm$^3$ s$^{-1}$.

The graphs indicate that for a fixed arc current, the frequency of rotation is proportional to the field current, i.e. to the magnetic field. A slight non-linearity in the proportionality is also evident. Furthermore, as the arc current increases a slightly smaller value of the field current is required for the same frequency of rotation. Work on this has been carried out (32), with the following empirical expression often quoted:

$$f \propto I^{0.33} B^{0.6}$$
Arc Rotation Measuring Equipment

Fig. 2.4
Fig. 2.5: Rotating Arc Characteristic

- X: I = 66
- O: I = 82
- •: I = 100
- □: I = 120

Field Current: I / Amp.

Arc Frequency: \( \omega \) / Hz
Where $f$ denotes the arc frequency, $I$ is the arc current, and $B$ is the magnetic flux, which is proportional to the field current. The family of curves in Fig. 2.5 show agreement with the empirical relationship in as much as they exhibit a stronger dependence of the arc frequency on the induced magnetic field than on the arc current.

2.3 The Interaction Between the Gas Flow and the Rotating Arc

The gas flowing around the cathode encounters the rotating arc when passing through the discharge gap then leaves the anode in the form of a plasma jet. This interaction results in an imprint of a high temperature spiral in the emerging gas. It is made up of regions that have encountered the arc directly, and hence are at a high temperature, and regions that have not encountered the arc, and these are cooler. Ideally, these regions would be uniformly alternating with a frequency equal to that of the arc, and a separation distance, or pitch, between them related to the magnitudes of the linear gas velocity and arc frequency. However, in practice this interaction can manifest itself in the production of hot and cold gas turbules of varying sizes and distribution. In either case, the emerging gas is not uniformly heated. In order to investigate methods of achieving uniform heating the following model for the interaction process is considered:

Let $U_x$ be the linear gas velocity, cm s$^{-1}$, passing through a zone in which an electric arc is rotating.
with a frequency $\omega$, Hz. The arc is represented, for simplicity, by a rotating solid cylinder. The gas elements progress linearly by a distance, $r$, where:

$$r = \frac{U_x}{\omega}$$

centimetres per arc revolution.

If the arc diameter is represented by $\delta$, cm, then the ratio:

$$\pi = \frac{r}{\delta}$$

is a measure of the spiral pitch. Thus, it can be seen immediately that the value of $\pi$ relates to the thermal uniformity mentioned earlier. For example, when the value of $\pi$ is unity, the gas elements progress linearly by one arc diameter per arc revolution. This further implies that each of the gas elements at a cross-section encounters the arc once as they pass through the arc zone. Therefore, ideally, uniform heating of the gas can be achieved if the ratio $\pi$ is unity, i.e.

making:

$$U_x = \delta \omega$$

On the other hand, non-uniform heating is present if $\pi$ exceeds unity. The gas elements may encounter the arc more than once if $\pi$ is less than unity. However, as will be seen later, this case is not achieved experimentally.

Figure 2.6 represents a theoretical family of constant frequency curves relating the spiral pitch to the gas flow rate, which is presented instead of velocity for practical convenience. The cross-sectional area of
SPIRAL PITCH VS GAS FLOWRATE

\( \omega = \text{Hz} \)
\( \delta = 0.14 \text{cm} \)
\( A = 0.714 \text{ cm}^2 \)

Fig. 2.6
the anode jet is $0.7 \text{ cm}^2$. A value of $1.4 \text{ mm}$ for the arc diameter based on work by Cox (33), was taken for the theoretical calculation.

In practice, using the rotating arc plasma jet, it has been shown (35) that for a particular gas flow rate and arc current, the frequency can be increased only up to a limited value since arc instability sets in. In an attempt to explain this, Cox suggested that this arose when the arc begins to catch up with its own wake. Furthermore, the onset of this instability is an indication of uniform gas heating. Using the present work definitions, this uniform heating criterion corresponds to the condition when the spiral pitch is unity.
CHAPTER THREE

THE ADDITION OF TITANIUM TETRACHLORIDE AND OXYGEN TO THE ROTATING ARC PLASMA JET

3.1 Introduction

The reaction between titanium tetrachloride and oxygen takes place in accordance with the following equations:

\[
\text{TiCl}_4 + O_2 \rightarrow \text{TiO}_2 + 2\text{Cl}_2 \quad (1) \\
\text{(rutile)}
\]

\[
\text{TiCl}_4 + O_2 \rightarrow \text{TiO}_2 + 2\text{Cl}_2 \quad (2) \\
\text{(anatase)}
\]

\[
\text{TiO}_2 \quad \text{Ti} \rightarrow \text{TiO}_2 \quad \text{rutile}
\]

Depending on the amount of oxygen used, it is possible to produce other oxides of titanium from this reaction (4). Antipov (3) has investigated the oxidation reaction, and reports that it proceeds in the kinetic region if the temperature range is 600 - 1100°C. Furthermore, if the oxidation temperature is 1000 - 1100°C then pigment-grade titanium dioxide can be obtained with 95 - 97% particles smaller than 1 μm. Literature and patents (1, 3 - 22) reveal that the above temperature is widely used for the formation of pigment titanium dioxide by the chloride route. The objective of this work is to investigate the possibility of using the rotating arc plasma jet for the oxidation of titanium tetrachloride.
3.2. Preliminary Experiments

Figure 3.1 represents the apparatus flow sheet for the oxidation of titanium tetrachloride in the plasma jet. All gases are dried using silica-gel filled tubes, and their flows accurately monitored using variable area flow meters. An argon stream, dried by passing through two consecutive packed beds of silica-gel, for extra drying, bubbles through liquid titanium tetrachloride maintained at a constant temperature. The titanium tetrachloride-laden argon stream leaves the bubbler and immediately mixes with the other streams in an electric heater, in order to prevent possible condensation of the tetrachloride. The argon and reactants stream then flows in the compartment around the cathode, see Fig. 2.1, and encounters the rotating arc. The product stream is quenched using cold air injection through side arms in a quartz tube. The products are then filtered for titanium dioxide particles and chlorine scrubbed with sodium hydroxide solution.

The above system is designed for flexibility in the input feeds of the reactants and diluent argon. Thus, by varying the bubbler liquid temperature and the argon flow rate the amount of titanium tetrachloride picked up can be varied.

Preliminary experiments to test the behaviour of the system showed that the argon plasma can only be stabilised in the presence of the reactants if the electric power is appreciably increased, and the concentration of titanium tetrachloride and oxygen in the main
Fig. 3.1: TiCl₄ Oxidation System Flowsheet
argon stream remained very low. The addition of polyatomic molecules, such as these, in the region of the arc leads to the dissipation of arc energy due to dissociation. This causes extinction of the arc unless the power supplied is sufficient to accommodate these processes.

The molar flows of the reactants which gave a stable plasma were in the region of \(9 \times 10^{-5}\) moles s\(^{-1}\) for oxygen and \(4 \times 10^{-5}\) moles s\(^{-1}\) for the titanium tetrachloride, making up no more than 1\% of the total feed stream.

These flows lead to considerable damage to the inner surface of the anode, after a few minutes of the experimental run. The cathode erosion was also appreciable, as indicated by the changes in the size of its tip.

From these preliminary runs, samples of particles were taken from the deposit on the anode wall, and various positions inside the quench tube. Figures 3.2, 3.3, and 3.4 are electron micrographs of some of these samples. A chemical analysis revealed the presence of 12\% copper in samples taken from the anode wall. They also indicated that there was no significant change in the type, quality, and particle size, of the order 0.02 \(\mu\)m, between the samples taken from different parts of the quench tube. Some of the characteristics of these samples may be generated by the sampling technique, and the resultant micrographs may be more of what is happening at the wall and the effect of sample preparation techniques on the material.
Fig. 3.2: Particles samples from anode inner wall.

Mag. = 20,000X
Fig. 3.3: Particles sample from quartz quenching duct.
Mag. = 20,000X
Fig. 3.4: Particles sample from quartz quenching duct.

Mag. = 100,000X
In these runs, the electric power transferred to the gas is calculated by an enthalpy balance around the anode to be about 60% of the total input.

Thus, it can be concluded from these results that the rotating arc plasma jet can be used to supply energy for the oxidation reaction under consideration. The reactant throughputs depend on the input power and the stability of the rotating arc.

3.3 Conditions for Achieving Low Mean Gas Temperatures in the Plasma Jet

The aim of this section is to investigate and establish the limits for the production of a mean reaction temperature around 1100°C in the apparatus. Detailed experiments were carried out in order to achieve this objective. The following is a brief account of the procedure employed:

Initially, the temperature of liquid titanium tetrachloride in the bubbler was set at a constant value of 50°C. The sheath argon flow rate was set at about 40 cm$^3$ s$^{-1}$. It was expected that large throughputs of gas would be used in these runs, thus the magnetic field coil current was chosen near its maximum range of 1.6 - 1.8 amps. The flow of cooling water supplied to the anode and cathode were monitored using rotameters. The change in the water temperature was measured using mercury-glass thermometers. When the water flows were stable, the main plasma argon flow rate was selected and the arc was initiated. The current was then reduced to the minimum output delivered by the
power generators, which were connected in series. An argon carrier stream bubbling through liquid TiCl$_4$ was precalibrated for TiCl$_4$ content using a cold trap.

Oxygen and argon carrier stream flows were selected such that the ratio $O_2$:TiCl$_4$ = 2:1. When the system reached a steady state, all relevant parameters, e.g. arc current, arc voltage, cooling water temperatures, etc., were recorded. This procedure was repeated for several plasma argon flows with a series of different reactant concentration.

Using the experimental results, the mean reaction temperature was calculated using a theoretical model for an enthalpy balance around the arc region, as shown in Fig. 3.5 below:

![Enthalpy balance model around the arc zone](image)

Fig. 3.5 Enthalpy balance model around the arc zone
The following assumptions were made:

i. Perfect mixing in the radial plane.

ii. Complete and instantaneous reaction.

iii. Effects of dissociation of the various polyatomic species on the general enthalpy balance are neglected; this can only be justified in dilute reactant concentrations.

iv. Negligible downstream or upstream radiation losses from the arc.

v. The heat capacities for species at the reaction temperature were taken at the mean value between 3000 - 6000°K (37). However, significant error must be expected in any such calculation much above 6000°K.

The stoichiometry of the reaction was taken to be represented by equation (1) of section 3.1. This was solved simultaneously with the enthalpy equation to give:

\[ \frac{IV}{J} + \left[ a \, Cp_{TiCl_4} + b \, Cp_{O_2} + c \, Cp_{Ar} \right] (T_1 - T_o) = \\
\left[ a \, Cp_{TiO_2} + 2a \, Cp_{Cl_2} + (b-a) \, Cp_{O_2} + c \, Cp_{Ar} \right] (T_2 - T_o) + \\
a \cdot \Delta H_R + \phi \]

where: \( \phi = (F_{cathode} \cdot \Delta T_{cathode} + F_{anode} \cdot \Delta T_{anode}) \times 10^3 \)

The mean reaction temperature, \( T_1 \), defined in this calculation, is solved for using the experimental data. Figure 3.6 is a graph of \( T_1 \) vs. total gas flow and indicates the presence of two regimes of stable plasma:

i. Argon plasma with reactants: It was possible to stabilise the plasma in the presence of reactants up to a total argon flow of 370 cm\(^3\) s\(^{-1}\). The measured arc frequency was 1200 Hz. Referring to Fig. 2.6 the value of...
**Fig. 3.6: Calculated Mean Gas Temperature**

- : Ar
- : Ar + R = 9.8 / 4.8
- : Ar + R = 5.4 / 2.6 (moles s\(^{-1}\) x 10\(^{+5}\))
- : Ar + R = 7.5 / 3.8

R = O\(_2\) / TiCl\(_4\)
is found to be about 2. The mean reaction temperature is calculated to be about 2500°K.

A value of 2 for $\pi$ necessitates further investigation of the mixing conditions for complete specification of the reaction environment. However, even if it is considered to be a reasonable approach to the ideal value of unity, the calculated temperature is too high for our requirement.

ii. Argon plasma without reactants: A stable plasma of pure argon was achieved with flow rates up to 700 cm$^3$ s$^{-1}$. At this flow rate, and an arc frequency of 1200 Hz, Fig. 2.6 gives a value of 6 for the spiral pitch. This value indicates appreciable deviation from the conditions of uniform heating. The calculated gas temperature at this flow rate is about 1600°K. This temperature appears to be suitable for the oxidation reaction. However, in order to achieve uniform distribution under these conditions of flow the applied magnetic field would have to be significantly increased in order to achieve the necessary arc frequency of rotation of about 7000 Hz. This is beyond the capability of this equipment.

Figure 3.7 represents the variation of the power input in the plasma as the throughput varies for pure argon, and argon with reactants. The striking feature of these graphs is the increase in power when reactants are present. It must be noted that the power supply was set at the minimum power settings. Thus, the unit adjusts its voltage-current values accordingly. Values of reactant concentration above those stated in Fig. 3.6 lead to
Fig. 3.7: Min. Power Consumption

Electrical Power / KWatt

Argon Flow / moles s\(^{-1}\) \times 10^2

Ar + Reactants

[Key to Symbols: See Fig. 3.6]
instability in the plasma and finally arc extinction. It would be possible to stabilise a plasma in the presence of higher concentrations by manually increasing the input power to the arc, but as already seen this leads to an increase in the mean reaction temperature.

It may be concluded that uniform thermal distribution in the reactant stream may be achieved at the expense of having high mean temperatures. However, it must be remembered that the mean temperatures calculated were based on a theoretical model representing the arc zone. Thus, it is possible that the reactants encounter even higher temperatures as they flow through this region. Furthermore, in order to achieve a uniform thermal distribution at reasonable temperatures large gas throughputs must be used with arc rotational frequencies far beyond the capability of this device. The following two chapters deal with experimental methods for assessing the degree of thermal mixedness, and the development of the post-arc injection anode.
4.1 Introduction

The investigation of the flow parameters, i.e. velocity, temperature, and composition, within a reactor can be carried out theoretically or experimentally. A theoretical approach is outlined by Branch (26) in which he concludes that for developing flow with chemical reaction, wall effects do not reach the centreline until several inlet duct diameters downstream. Furthermore, these become important sooner for laminar flow, whereas for turbulent flows these profiles remain flatter through the developing region. This leads to the possibility of treating the core of the developing turbulent flow as plug flow. Batten (38), on the other hand, has treated this investigation purely experimentally. He succeeded in designing a plug flow reactor by using coloured water flow to simulate gas flow and photographing its progress within the reactor. The method of investigation in this work is experimental but differs from that of Batten due to the nature of the system involved.

The design of a reactor implementing the rotating arc plasma jet involves the investigation of the effects of variables such as the reactor geometry, gas throughputs, and arc frequency of rotation on the enthalpy distribution downstream. In this chapter, experimental methods
are established which lead to practical estimation of the degree of unmixedness.

4.2 **Optical Methods**

These provide a unique way of measuring gas temperature or its fluctuation, as they do not disturb the system under investigation. A detailed account of interferometry, shadowgraphy, and schlieren techniques and their applications to various systems is given by Weinberg (39). These three methods vary greatly in sensitivity. For small temperature gradients interferometry is appropriate, whereas for large temperature gradients, e.g. flames, shock waves, schlieren and shadowgraphy serve best. However, these methods all integrate over the length of the light beam, and give average results. By use of a transparent cylindrical reactor duct, they can be exploited to investigate gas temperature fluctuations at a cross-section downstream of the rotating arc. Interferometry was ruled out, since the expected temperature gradients are large and of high frequency.

Schlieren methods were investigated first. The practical applications are discussed elsewhere (39-41), and Fig. 4.1 shows the optical arrangement for this investigation.

The reactor duct was made of ordinary quartz, due to its high temperature properties. However, the photograph of Fig. 4.2 indicates poor light transmission through the duct wall. This was the same both with and
Fig. 4.1: Schlieren System
without a schlieren stop. The reason is deflections caused by inhomogeneities in the quartz material, which were large enough to be cut off by the lens aperture. A Spectrasil, high purity quartz, duct improved transmission only slightly as evident in Fig. 4.3. Figures 4.4 and 4.5 show how the addition of a schlieren stop demonstrates the presence of gas temperature variations as seen in the emerging stream, whereas the Spectrasil duct fails to transmit.

Since the objective is to study deflections caused by hot turbules, which would be masked by those of the surrounding duct wall, these methods were considered unsatisfactory in assessing thermal mixing.

4.3 The Use of Thermocouples

It was thought that thermocouple junctions might be used to investigate the fluctuations in the temperature of a flowing gas. Fine wires can be used without significant disturbance to the system. The method differs from optical techniques in that it monitors the temperature at a local position in the cross-section of the reactor duct. The feasibility of this method is studied by a theoretical analysis of the response of thermocouples to high frequency temperature fluctuations.

Thermal equilibrium between the solid thermocouple junction and the flowing hot gas can be written as:

\[ \left( \frac{D \rho_s C_s}{4h} \right) \cdot \frac{dT_s}{dt} = T_g - T_s \]  

(1)
Effects of Quartz Material on Schlieren Analysis

Fig. 4.2: Ordinary Quartz

Fig. 4.3: Spectrasil Quartz

Without Plasma Flow

Fig. 4.4: With Schlieren Stop

Fig. 4.5: Without Schlieren Stop

With Plasma Flow
The frequency response is the solution of the above equation when $T_g$ is of the form:

$$T_g(t) = \bar{T} + \Delta T \cos \omega t$$ \hspace{1cm} (2)

If $K = (D \rho_s C_s) / 4h$, and steady state conditions prevail, then the solution of equation (1) is:

$$T_s(t) = \bar{T} + \frac{\Delta T}{\sqrt{1 + K^2 \omega^2}} \cdot \sin \left\{ \omega t + \tan^{-1} \left( \frac{1}{K\omega} \right) \right\}$$ \hspace{1cm} (3)

The signal amplitude is:

$$\frac{\Delta T}{\sqrt{1 + K^2 \omega^2}}$$

It can be seen that if $K$ is taken as a constant and $\omega$ is zero, $(1 + K^2 \omega^2)^{-1/2}$ is unity and the amplitude of the response is equal to $\Delta T$. The response decreases accordingly as $\omega$ increases. Further analysis is demonstrated in the following two cases:

Case 1: It is possible to calculate the diameter of the junction if the amplitude is to be within 10% of $\Delta T$. A value of 1000 Hz for $\omega$ is of relevance in the plasma jet study, and $K$ can be expressed in terms of the junction diameter, using practical values for its other parameters, as:

$$K = 50 \cdot D$$

$D$ denotes junction diameter, cm.
Solving \((1 + K^2 \times 10^6)^{-1/2} = 0.9\) for \(K\) leads to a value of \(9.7 \times 10^{-6}\) cm for the diameter. It is practically not feasible to construct a thermocouple of such a small junction.

Case 2: A practical case is considered here in which a junction diameter is specified at 0.01 cm. This gives a value of 0.5 for \(K\), and for \(\omega\) at 1000 Hz, \((1 + K^2 \omega^2)^{-1/2}\) has a value of \(2 \times 10^{-3}\). This implies that the thermocouple response to a temperature fluctuation of 200°C at 1000 Hz is 0.4°C. This is equivalent to an e.m.f. fluctuation of 2 \(\mu\)V for a Pt - Pt/13% Rh thermocouple. This further implies that it is required to measure a change of 2 \(\mu\)V in 10 mV, which would correspond to a possible mean gas temperature of 1000°C. The practical difficulties in such a measurement are self evident. Figure 4.6 shows the output e.m.f. from a 25 \(\mu\)m thermocouple junction, made out of Pt - Pt/13% Rh, displayed by an oscilloscope as a function of time. The thermocouple was located in a gas stream that has encountered the rotating arc. In this case the arc frequency of rotation was about 400 Hz, whereas the displayed thermocouple frequency response is about 16 Hz.

It may be concluded that even though this method looks attractive in view of its simplicity in application, the limitations are such that it would only be feasible as a method of analysis in temperature fluctuations of very low frequencies.
Thermocouple Response to High Frequency Temperature Fluctuations

\[0.001^\circ\text{ Pt — Pt/13\%Rh}\]

\[i = 0.4\text{ Amp.}\]
\[i = 0.6\text{ Amp.}\]

C.R.O. Settings: \(T = 20\text{ ms/cm}\), \(V = 0.1\text{ mV/cm}\); \(Ar\) Flow\(=167\text{ cm}^3\text{s}^{-1}\)

\[i = 1.5\text{ Amp.}\]
\[i = 1.7\text{ Amp.}\]

Fig. 4.6
4.4 The Corona Probe

Temperature fluctuations may be observed through the associated ionization in the gas. A Langmuir-type probe, Fig. 4.7, was made and tested in hot argon gas emerging from the plasma jet. It was found that such a probe indicates fluctuating current signals corresponding to varying ion concentration in the gas. This method was found to be useful only when the gas contained high ion concentration, i.e. close to the plasma. Thermal ionization at the temperatures of interest, about 1100°C, is not sufficient.

It was felt that local ionization in a corona discharge may indicate such temperature variations at the desired reaction temperature. This type of discharge is brought about as a result of the ionization of gas surrounding a conductor, which occurs when the potential gradient exceeds a certain value but is not sufficient to cause sparking. Detailed mechanisms and properties of the corona discharge are discussed by von Engel (42). However, one of its fundamental properties is that the corona current is inversely proportional to the local gas density (42), which is related to the local temperature. Figure 4.8 shows a device exploiting this property, in which a d.c. high tension unit is used to provide the required potential across the tips of two platinum electrodes. These are housed in quartz tubes in order to prevent electrical break-down along their lengths. The separation distance between their tips is usually kept at 0.8 cm. By making the end of the positive
Fig. 4.7: Langmuir Type Probe Circuit

Fig. 4.8: Corona Probe Circuit
electrode into a sphere, the corona is produced at the needle-like tip of the negative electrode. The corona current is monitored using an oscilloscope. As shown, the coupling between the oscilloscope and the probe circuit incorporates a capacitor, which prevents high frequency transients, e.g. high voltage surges, from reaching the oscilloscope.

4.4.1 Preliminary Experiments Using the Corona Probe

Experiments involving the use of the probe in flows downstream of the rotating arc reveal the following: In regions where arc ionization does not persist, as indicated by the Langmuir probe, the observed frequencies of the corona current fluctuations are of the same order of magnitude as those of the rotating arc. Figure 4.9 shows traces of the response for increasing arc frequencies, as represented by the field coil current, i. It clearly indicates that the response frequency increases as the arc rotation is increased. When the probe is taken out of the gas stream, the fluctuations subside, indicating that the response is not due to a possible magnetic pick-up from the rotating arc. Furthermore, if the electrodes are positioned in stagnant gas, the corona discharge, as observed using a telescope, occurred at an applied voltage of about 7 KV. However, when the gas is set in motion, the corona changes into a spark discharge. The applied potential has to be reduced to about 2.5 KV for the restoration of the corona,
Corona Probe Response / Plasma Jet

T = 5
V = 0.5

i = 0.5 Amps.

C.R.O. Settings: T = 2 ms/cm
V = 0.5 mV/cm

T = 2
V = 0.5

i = 1.0 Amps.

i = 1.8 Amps.

Fig. 4.9
and any further increases in the gas velocity produces no noticeable change in the discharge characteristics.

Further experiments were carried out by locating the probe electrodes in the products stream of a town gas burner operated at various throughputs. The laminar flow case results in a d.c. output signal from the probe circuit, indicating no fluctuations. Figure 4.10 shows a trace of the response when it is positioned at the edge of a laminar flame. Figures 4.11, 4.12, and 4.13 show traces corresponding to increasing flame turbulence. These experiments demonstrate the relevant features of the corona probe and its type of response to various degrees of temperature fluctuations.

4.4.2 Current, Voltage, and Temperature Characteristics of the Corona Probe

A number of experiments were carried out to investigate the dependence between the gas temperature, the voltage, and current of the corona probe. The electrodes were located in the gas at a particular cross-section in a quartz duct downstream of a Bunsen burner. This supplied hot gas, which attained steady laminar flow as it reached the probing position. The gas temperature was measured by a thermocouple located at the same level as the corona probe. By adjusting the gas throughput, temperatures between 200 - 800°C were obtained. For each value of the applied potential, the temperature was varied in intervals of 100° within the above range, and the corresponding current, read off a deflection galvanometer. Figures 4.14, 4.15, and 4.16 represents
Corona Probe Response / Flames

Fig. 4.10 : Laminar Flame Edge

Fig. 4.11 : Low Turbulence

C.R.O. Settings: $T=10\,\text{ms/cm}, V=20\,\text{mV/cm}; HT = 3\,\text{KV}$

Fig. 4.12 : Medium Turbulence

Fig. 4.13 : High Turbulence
Fig. 4.14: Corona Probe Characteristics - A

- - - Probe
Gas Flow

Current / µA

Temperature / °C × 10⁻²

5KV
4KV
3 KV
3.5KV

Instability
Fig. 4.15: Corona Probe Characteristics - B

- Gas Flow
- Probe

Current ($\mu$A) vs. Temperature ($^\circ C \times 10^{-2}$)

Voltages: 5 kV, 4 kV, 3.5 kV, 3 kV, 2.5 kV, 2 kV, 1.5 kV, 1 kV
Fig. 4.16: Corona Probe Characteristics

Corona Probe Characteristics - C

Gas Flow

5 KV, 4 KV, 3.5 KV

Current / $\mu$A

Temperature / °C $\times 10^{-2}$
families of curves corresponding to these results for various orientations of the electrodes in the gas stream. The orientation shown in Fig. 4.14 is the one commonly used.

These graphs indicate that the current measured is proportional to the local gas temperature provided that the applied potential does not exceed a value which changes the corona into a spark discharge, as indicated by the upper family of curves in the above figures. However, within the region of the corona discharge, the higher the applied potential the lower the temperature to which the probe is sensitive. Thus, in using this instrument, the applied voltage should be selected at an optimum level determined by the required temperature range, and the stability of the corona discharge.

The corona probe represents a device which has been shown to provide a more faithful response to high frequency temperature fluctuations than the thermocouple. In the following chapter its use in assessing thermal mixedness is demonstrated in detail.
CHAPTER FIVE

THE USE OF THE CORONA PROBE IN

ASSESSING THERMAL MIXEDNESS

5.1 Introduction

The conditions and limitations of achieving uniform thermal mixedness in a reacting stream using the rotating arc plasma jet were outlined in Chapter 3. This chapter deals with the use of the corona probe to investigate the conditions further and the development of the post-arc injection anode reactor.

5.2 Analysis of Thermal Mixedness Using the Corona Probe

A series of experiments were carried out using the probe to determine temperature fluctuations at different cross-sections downstream of the rotating arc for various gas flow rates and system geometries.

For a particular geometry, the probe was inserted through a 1/4" hole in one of the segments making up the duct wall, as shown in Fig. 5.1. The segmented wall made possible several probing positions. The electric power was kept at a minimum and the plasma was stabilised at a frequency of about 1200 Hz. The gas flow rate was selected at values ranging between 50 - 460 cm$^3$ s$^{-1}$. For each value of the gas flow rate, triplicate traces of the probe response were taken. This was repeated with the probe located at a different segment. Table 5.1 represents a summary of the cases considered.
Fig. 5.1: Segmented Duct-Plasma Jet-Corona Probe
Figure 5.6 represents axial temperature decay curves for several gas flow rates obtained when the reactor geometry shown in Fig. 5.3 was used. These are included to supplement the following analysis of the results. Graphs for the other cases are similar.

It can be seen, when examining the traces in Figs. 5.2 - 5.5, that the probe response for low gas flow rates is indicative of minimum temperature fluctuations. This is not necessarily due to uniform thermal mixedness. Figure 5.6 indicates that low gas temperatures are associated with these flow rates rendering the corona probe insensitive to such fluctuations.

Investigation of the probe response at higher flow rates indicates the presence of high frequency temperature fluctuation. The frequency spectrum embodies the arc frequency of rotation. Uniform thermal mixedness is seen to prevail for some flow conditions at positions 3 or 5, as indicated by the flatness of the probe response. However, it does not prevail along the entire length of the reactor for any configuration used. In some instances, uniform thermal distribution can be seen to develop into a badly mixed one, for example, Fig. 5.2
Fig. 5.2
2 cm Anode - 2.6 cm Duct / Corona Probe Response

Plasma Jet

Fig. 6.3

T = 2 ms/cm  V = 1 mV/cm  F = cm³/s⁻¹

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0.6 cm Anode – 4.8 cm Duct/Corona Probe Response

T = 5 ms/cm
V = 1 mV/cm
F = cm³ s⁻¹

Fig. 5.4

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Fig. 5.5
Fig. 5.6: Centreline Temperature Curves in Segmented Duct

F = Gas Flowrate [cm$^3$s$^{-1}$]
at gas flow rates above 50 c.c./s. between positions 3 and 5. This may be due to the mixing of a lower temperature boundary layer with the main stream.

In general, probing at position 2 has been avoided due to the persistence of ionization in the gas, as shown in Fig. 5.2. In this case, the probe gives a signal even in the absence of an applied high tension. The decay of ionization along the length of the reactor is shown in Fig. 5.7 for different gas flow rates. It can be seen that such interference does not persist to a significant level beyond the second segment.

It can be concluded from this section that the present arrangement of using the plasma jet as a flow reactor is not successful in achieving uniform thermal distribution even when the geometry of the system is widely varied. This conclusion, coupled with those of Chapter 3, indicates the need for a new design configuration.

5.3. The Injection Anode Reactor

The design of a reactor based on the rotating arc plasma jet that resolves the problems encountered with the previous approach is thought to be one in which the reactants are introduced in the post-arc region, avoiding direct contact with the arc itself. Use is made of the plasma rotation in mixing the enthalpy with the feed stream. As will be seen later, in order to achieve uniform thermal distribution a nozzle arrangement is required.
0.6 cm Anode - 2.6 cm Duct / Ionisation Pick-Up by the Corona Probe

Fig. 5.7

T=5 ms/cm   V=1 mV/cm   H-T=0   F=cm²/s
Several anode designs were considered, and the one that was most suitable is shown in Fig. 5.8. The gas injection section is incorporated in the anode body. The carrier stream is injected in the high temperature zone through 12 0.8 millimeter diameter holes, each inclined at an angle of 45° to the plasma stream. An injection velocity of about 16 m s⁻¹ can be achieved when a carrier flow rate of 100 cm³ s⁻¹ is used. This represents a highly stirred stage, in which enthalpy and mass are mechanically mixed by the dissipation of the angular momentum of the swirling plasma. A reactor duct was coupled to the injection anode, and the thermal distribution at different cross-sections was examined using the corona probe.

A straight reactor duct was considered first. Various flow rate combinations of the plasma and carrier argon streams were used with a range of arc frequencies. The probe response was observed at different positions downstream as that corresponding to a relatively unmixed temperature in all cases. A typical run is shown in Fig. 5.9. This also indicates that the response is of a low frequency spectrum, suggesting possible destruction of the temperature spiral encountered in the previous arrangement.

It was thought that the addition of a nozzle after the anode might help in improving the enthalpy distribution in the emerging gas. A stainless steel converging-diverging nozzle was made first. This lead to large heat losses to the nozzle wall, and in most cases the
Fig. 5.8
Injection Anode - Straight 1.4 cm Duct / Corona Probe Response

Fig. 5.9

T = 5 ms/cm  \( V = 1 \text{ mV/cm} \)  \( F_1 = 100 \)  \( F_2 = 35 \)  \( H.T = 1 \text{ KV} \)

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temperature of the gas at the exit was no more than 200°C. This nozzle was considered unsuitable.

A divergent nozzle proved promising since the temperature of the gas leaving it was of an acceptable magnitude. The nozzle is made out of stainless steel, the base of which is water-cooled. It is 5 cm in height and the divergence half angle is about 27°. A straight duct couples to this nozzle completing the reactor configuration.

The results of the probe analysis indicate that for an arc frequency of about 700 Hz and a plasma argon stream flow rate of 40 cm³ s⁻¹, uniform thermal mixedness prevails in all cross-sections for an argon carrier flow rate ranging between 80 - 120 cm³ s⁻¹. Figure 5.10 shows these results for a carrier stream flow rate of 100 cm³ s⁻¹. The temperature profiles at these cross-sections are also shown. It must be noted that the corona probe response at position 1 is affected by the presence of ions in the gas stream and is only included for demonstration, and completeness of the analysis.

The position of the cathode tip with respect to the injection holes requires some attention. The tip must be located approximately 1 cm below these holes. The temperature of the gas emerging from the anode depends on the electric power in the arc and the position of the tip. The closer the tip to the injection holes, the higher the temperature. However, the conditions of uniform thermal mixing are affected by the position of the cathode tip. The temperature profile accompanying
Injection Anode + Expansion Nozzle / Corona Probe Response

Fig. 5.10

\[ T = 5 \text{ ms/cm} \quad V = 1 \text{ Mv/cm} \]

\[ F_1 = 100 \quad F_2 = 40 \quad H.T = 1 \text{ KV} \]

\[ \frac{cm^3}{s} \]

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uniform thermal mixing is as shown in Fig. 5.10. These profiles are also included in Fig. 5.11, together with those obtained when the reactor duct is thermally lagged, which shows an improvement in the distribution, and those established when the cathode tip is above the injection holes. In this latter case, the profiles indicate swirling flow. Thus, in using this reactor for kinetic studies, temperature profiles such as those of A and B in Fig. 5.11 should be achieved first, and probing for any kinetic parameter should not be made within the expansion nozzle region due to the ambiguity in the mixing condition.

This configuration represents a flow reactor in which thermal environment is assessed experimentally to be uniform in the cross-section along its entire length. This is used in studying the kinetics of the oxidation reaction of titanium tetrachloride in the following chapters.
A: Temperature profile for unlagged reactor duct.

B: Temperature profile for lagged reactor duct.

C: Temperature profile when cathode tip is located above injection holes.
6.1 Introduction

The investigation of the chemical reaction between titanium tetrachloride and oxygen involves the measurement of reaction parameters such as temperature, composition, and, in this particular case, titanium dioxide particle size, as they vary with distance along the reactor duct. This chapter deals with the experimental methods used in obtaining such data, and the analytical methods employed.

6.2 Temperature Measurement

The use of thermocouples for gas temperature measurement is reviewed in many works (44,45), in which associated problems are discussed and methods of calculating the various necessary corrections can be found. The most important of these corrections are those for conduction, convection, and radiation losses. For a thermocouple mounted in a gas stream without steep concentration gradients and of a relatively low velocity, as in the present case, radiation losses become the main source of error. The following is an expression for calculating such correction:

\[ T_g = T_s + \frac{\sigma h}{h_s} (\epsilon T_s - \frac{h}{T_w}) \]
The gas temperature required, $T_g$, depends on the temperature indicated by the thermocouple, $T_s$, and the wall temperature, $T_w$. The emissivity of the bead, $\epsilon$, can be obtained from tables (46), and the value of the absorptivity, $a$, is taken to be that for $\epsilon$ at the wall temperature (47).

The heat transfer coefficient, $h$, can be found with good accuracy from (48):

$$\text{Nu} = \frac{hD}{k} = 0.42 \text{ Pr}^{0.2} + 0.57 \text{ Pr}^{0.33} \text{ Re}^{0.5}$$

The thermocouple temperature is determined from graphs of e.m.f. vs. temperature plotted from tabulation (46).

6.3 Particle Size and Gas Concentration Measurement

There are many problems associated with the introduction of a sampling probe in the reactor duct for the purpose of obtaining a representable sample of products: The flow pattern of the reaction stream may be altered due to the physical presence of the probe; the difference between the actual sampling position and the position of the probe orifice due to the sampling velocity; the quenching efficiency and the possibility of the probe material acting as a catalyst, are some of the more important ones. These are discussed in detail by many authors (26, 49, 50), and Chedaille and Braud (50) also include a discussion of problems associated with sampling techniques in particle-laden gas streams.
Figure 6.1 shows the sampling probe employed in the kinetic investigation of the titanium tetrachloride-oxygen system based on the suggestions and designs reported in the above references, and the need for speed in obtaining such samples. This latter design requirement is discussed in Chapter 8. The device provides simultaneous sampling for gas composition and particle size. It consists of two sections; a quartz probe and a conditioning chamber. As shown, quenching is achieved by expansion. The conditioning chamber assists in further quenching by sudden expansion which results in mixing the core flow within the probe with the cooler boundary layer. Gas samples are drawn from the conditioning chamber by connecting an evacuated flask of known volume at the indicated position. When the probe is located at a particular point within the reactor a sample is drawn using a suction pump in order to fill the conditioning chamber. The pump is then isolated from the conditioning chamber by closing the valve shown, and the sample flask valve is opened, allowing the flask to fill up to atmospheric pressure. The sample flask volume is larger than that of the conditioning chamber, hence more sample is withdrawn from the gas stream during this operation. This indicates that sampling conditions vary as the flask fills up. However, comparison of gas composition measured using the expansion probe and a water-cooled probe, for the same run, were within experimental error. Furthermore, the advantage in using the expansion probe is its higher surface temperature which prevents any possible condensation of titanium tetrachloride.
Particle & Gas Sampling Probe

Thermocouple Insert

Gas Sample Flask Connection

100 mm

25 mm

Conditioning Chamber

To Pump & Filter

Valve

E.M. Grid Holder in Sampling Position

E.M. Grids

PTFE Screw Connection

E.M. Grid Holder

E.M. = Electron Microscope

Quartz Probe O.D. = 7 mm

Probe Orifice ≈ 1 mm

Fig. 6.1

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Particle sampling involves the introduction of an electron microscope grid, mounted on a glass rod, as shown in Fig. 6.1, in the gas stream during the gas sampling procedure. Whether the particles sampled are a true representation of those present in the main stream depends on the particle size, shape, and density, and on the fluid density, and the patterns of the stream lines in the neighbourhood of the probe (50). For a mean particle size of less than a micron, which is that expected for titanium dioxide particles, the particles behave like fluid molecules whatever the rate of suction (50). Particle samples taken are analysed for size and general appearance.

The sampling probe is mounted on a metal frame which may be moved vertically and horizontally, enabling accurate positioning within the reactor duct.

6.4 Gas Analysis

Titanium tetrachloride (vapour), chlorine (gas), oxygen (gas), argon (gas), and titanium dioxide (solid) are the expected species present in a sample taken from the reaction stream. Analytical methods for these species in such a mixture are limited. For example, the use of a mass spectrometer leads to erroneous results due to interference between chlorine and titanium tetrachloride.

Volumetric analysis was considered to be appropriate. This type of analysis is discussed in great detail by Vogel (51) and others (52, 53). In brief, the
analytical method involves the injection of approximately 25 cm$^3$ of a 10% solution of potassium iodide in the gas sample flask using a hypodermic needle through a serum cap covering the flask entry port. The chlorine reacts with the potassium iodide liberating iodine, and titanium tetrachloride reacts with the water yielding hydrochloric acid. Both of these reactions are rapid. This solution is then titrated against standard solutions of sodium thiosulphate and sodium hydroxide for the iodine and hydrochloric acid concentrations respectively. The volumetric analysis is carried out using micro burettes for maximum accuracy. The result of this analysis is the number of moles of chlorine and titanium tetrachloride per unit volume of gas sample.

Information regarding the oxygen composition cannot be obtained using this method. However, the reaction stoichiometry equations may be solved for such unknowns, providing the feed concentration is known.
7.1 Introduction

The experimental results presented in Chapter 8 are in the form of graphs of chlorine concentrations and temperatures vs. axial distance. The reduction of such data into useful kinetic information is presented in this chapter, based on a general procedure discussed by Branch (26).

7.2 Assumptions

The mathematical analysis includes the determination of the concentration-time histories from the concentration-distance measurements and evaluating the rate data from these. The assumptions employed in this analysis are as follows:

i. Steady flow of an ideal gas is considered in the reactor with constant cross-sectional area and constant pressure. The assumption of an ideal gas is justified since the reactant concentrations are less than 1% in the argon stream.

ii. The sampling process is assumed to provide negligible disturbance to the flow, temperature, and concentration profiles upstream of the sampling point. This can be justified to a good approximation since axial gradients are not very steep.

iii. Plug flow is assumed to hold through the sampling length. The results of the corona probe
iv. The temperature field measured in argon alone is assumed to be the same after reactant injection. This is justified since dilute concentrations are used.

7.3 Concentration-Time Domain

The concentration-distance measurements are transformed into concentration-time domains by considering the following mass continuity equation for a flowing stream of pure argon:

\[(\rho UA)_o = (\rho UA)_x = \text{constant} \tag{1}\]

Where \(x\) refers to parameters measured at a particular sampling point, and \(o\) refers to the feed point. \(U\) is the gas linear velocity, \(\rho\) is the density, and \(A\) is the cross-sectional area, which is constant for the reactor duct. Denoting the volumetric flow rate of argon at the feed by \(Q\), equation (1) can be written as:

\[U_x = \frac{Q}{A_x} \left( \frac{\rho_o}{\rho_x} \right) \tag{2}\]

\(A_x\) is constant within the sampling region.

Using the State equation for a perfect gas, \(PV = NRT\), and for a constant pressure, equation (2) becomes:

\[U_x = \frac{Q}{A} \left( \frac{T_x}{T_o} \right) \tag{3}\]
Equation (3) gives the gas velocity at each sampling position. The residence time between any two sampling points is obtained from a plot of $U^{-1}_x$ vs. distance using the following expression:

$$\text{Residence time} = \frac{1}{2} \left( \frac{U^{-1}_{x_1} + U^{-1}_{x_2}}{x_2 - x_1} \right) \quad (x=x_1 \text{ to } x=x_2) \quad (4)$$

### 7.4 The Rate Expression

The rate of formation or disappearance of chlorine can be calculated from the concentration-time domain. The explicit expression for the rate may be derived as follows:

$$C_i = \frac{N_i}{V} \quad (5)$$

Where $N_i$ represents the number of moles of species $i$, and $V$ is the volume of a constant mass. Differentiating equation (5) with respect to time:

$$\frac{dC_i}{dt} = \frac{1}{V} \frac{dN_i}{dt} - \frac{N_i}{V^2} \frac{dV}{dt} \quad (6)$$

The proper rate is given by:

$$\frac{1}{V} \frac{dN_i}{dt} = \frac{dC_i}{dt} + \frac{N_i}{V^2} \frac{dV}{dt} \quad (7)$$

or

$$\frac{1}{V} \frac{dN_i}{dt} = \frac{dC_i}{dt} + C_i \frac{d\ln V}{dt} \quad (8)$$

by using equation (5).
Using the State equation, the volume change of the system can be expressed as:

\[ \frac{d\ln V}{dt} = \frac{d\ln N}{dt} + \frac{d\ln T}{dt} - \frac{d\ln P}{dt} \]  

(9)

For reactions in which the number of gas moles, \( N \), does not change, e.g. the titanium tetrachloride oxidation reaction:

\[ \frac{d\ln N}{dt} = 0 \]

and for a constant pressure system:

\[ \frac{d\ln P}{dt} = 0 \]

resulting in the following expression for the reaction rate:

\[ \frac{1}{V} \frac{dN}{dt} = \frac{dC_i}{dt} + C_i \frac{d\ln T}{dt} \]  

(10)

The first term on the right hand side, \( \frac{dC_i}{dt} \), can be obtained by fitting the experimental results to a polynomial of the form:

\[ C_i(t) = a + bt + ct^2 \]  

(11)

from which:

\[ \frac{dC_i(t)}{dt} = b + 2ct \]  

(12)
The temperature term is calculated by a similar procedure, i.e.

\[ T(t) = a' + b't + c't^2 \]  

(13)

and

\[ \frac{d \ln T(t)}{dt} = \frac{1}{T(t)} \left[ b' + 2c't \right] \]  

(14)

7.5 The Arrhenius Rate Expression and the Method of Solution

For the purpose of illustrating the method of solution, the following reaction is considered:

\[ aA + bB \rightarrow cC \]

The rate of reaction can be written in terms of each species as:

\[ \frac{1}{a} \frac{d[A]}{dt} = \frac{1}{b} \frac{d[B]}{dt} = \frac{1}{c} \frac{d[C]}{dt} \]  

(15)

and the rate expression can be represented by:

\[ \frac{d[A]}{dt} = - \text{Rate Constant} \times [A]^P [B]^Q \]  

(16)

where:

\[ \text{Rate Constant} = K e^{-E/RT} \]  

(17)

P and Q are the orders of reaction with respect to \([A]\) and \([B]\). \(E\) is the activation energy, \(R\) is the gas
constant, \( T \) is the temperature, and \( K \) is a pre-
exponential constant.

The parameters in equations (16) and (17) that are
usually measured by experiment are \([A]\), \([B]\), and \( T \).
The rate, \( \frac{d[A]}{dt} \), is obtained by the procedure outlined
in section 7.4. The unknown reaction parameters \( E \),
\( K \), \( P \) and \( Q \) are obtained using a least square fit method
discussed below. Equations (16) and (17) can be
written as:

\[
\frac{-d[A]}{dt} = K[A]^P[B]^Q e^{-E/RT} \tag{18}
\]

This is linearized as follows:

\[
\ln \left\{ \left| \frac{d[A]}{dt} \right| \right\} = \ln K + p\ln[A] + q\ln[B] - \frac{E}{RT} \tag{19}
\]

There are \( m \) equations of this form when \( m \)
observations on \( n \) unknowns are made. The method of
solving these is illustrated using matrices:

\[
\begin{align*}
B &= A \cdot X \quad m > n \quad \text{(20)}
\end{align*}
\]

where:

\[
A = \begin{bmatrix}
1 & \ln[A]_1 & \ln[B]_1 & -1/RT_1 \\
1 & \ln[A]_2 & \ln[B]_2 & -1/RT_2 \\
\vdots & \vdots & \vdots & \vdots \\
1 & \ln[A]_m & \ln[B]_m & -1/RT_m \\
\end{bmatrix}
\]
A is a rectangular matrix. It is possible to solve this overdetermined set of equations by multiplying both sides of equation (20) by the transpose of A:

\[ \mathbf{A}^T \cdot \mathbf{B} = \mathbf{A}^T \cdot \mathbf{A} \cdot \mathbf{X} \]  

(21)

\( \mathbf{A}^T \cdot \mathbf{B} \) and \( \mathbf{A}^T \cdot \mathbf{A} \) are square matrices, and the solution is the least square fit (54) given by:

\[ \mathbf{X} = (\mathbf{A}^T \cdot \mathbf{A})^{-1} \cdot \mathbf{A}^T \cdot \mathbf{B} \]  

(22)

The standard error in the fitted parameters is calculated from (55):

\[ \mu_{x_i} = \left\{ \frac{\sum_{i=1}^{m} U_{ii}^2}{D_{ii} \cdot \frac{i-1}{m-n}} \right\}^{1/2} \]  

(23)

Where \( \mu_{x_i} \) is the standard error in the fitted parameters, \( \sum_{i=1}^{m} U_{ii}^2 \) is the residual sum of squares \( \left( = \sum_{i=1}^{m} (\mathbf{B} - \mathbf{A} \cdot \mathbf{X}')^2 \right) \), with \( \mathbf{X}' \) denoting the solution matrix, and \( D_{ii} \) is a diagonal element of \( (\mathbf{A}^T \cdot \mathbf{A})^{-1} \).
It should be noted that the linearization procedure, equation (19), introduces \( \ln K \) as a parameter to be fitted rather than \( K \). The standard deviation in \( K \) is related to that in \( \ln K \) by (65):

\[
\sigma_K = K \sigma_{\ln K}
\]

Thus, a small standard error in \( \ln K \) results in large errors in \( K \).

The above mathematical procedure is used in the next chapter in analysing the data of the oxidation reaction of titanium tetrachloride.
CHAPTER EIGHT

THE KINETICS INVESTIGATION OF THE OXIDATION REACTION

ITS RESULTS, ANALYSIS, AND DISCUSSION

8.1 Introduction

Titanium tetrachloride and oxygen were fed through the injection anode reactor, and the progress of the reaction was followed by measuring the concentration, particle size, and temperature variation along the axis. The experimental procedure is outlined below, together with some qualitative observations. The results are presented in a later section with their analysis and discussion.

8.2 Reactor Wall Material

A recrystallized alumina duct was used to contain the oxidation reaction. This was chosen for its chemical inertness to chlorine and titanium tetrachloride. The duct wall was thermally lagged and its temperature was measured using a thermocouple embedded in its outer surface.

8.3 Experimental Procedure

This was based on operating the injection anode plasma jet reactor with uniform mixing conditions as outlined in Chapter 5. The arc was initiated after the flow rates of the different argon streams, the magnetic field current, and the electric power were set. The system was allowed to reach thermal equilibrium and the gas temperature was then recorded at different
axial positions. The radial temperature profile was checked for consistency with those associated with good thermal mixing. Following this, titanium tetrachloride and oxygen were introduced into the carrier stream. The flow rate of the argon used to bubble through liquid titanium tetrachloride was subtracted from the carrier flow rate in order to retain the same flow conditions. Samples were then taken for concentration and particle size measurement at various axial positions. Relevant parameters, such as arc power, magnetic field current, gas flow rate, etc. were recorded, and the arc was switched off. A sample of the cold gas feed was taken a few minutes later for measurement of titanium tetrachloride content.

8.4 Qualitative Experimental Observations

8.4.1 Temperature Measurements

The effect of the stability and smoothness of the arc rotation on the local gas temperature, monitored at a position downstream of the mixing zone, may be significant. These qualities cannot be quantified as such; however, they may be related to the associated audible pitch. It is observed that instabilities in rotation characterized by a change in this is usually related to a variation in the monitored temperature. However, when argon alone is flowing, pitch variation usually does not occur. In most cases considered, the oxygen addition does not result in noticeable variation. However, the addition of titanium tetrachloride may lead
to a significant change after a short period of running time. Such variations during the sampling procedure affect the apparent reaction rate significantly. This is discussed further in relation to the sampling procedure and the results obtained.

8.4.2 Concentration Measurements

In view of the above, rapidity of the sampling procedure is necessary in order that the temperature field remains the same as that measured. This is one of the requirements in the design of the sampling probe discussed in section 6.3.

The quantitative analysis of these gas samples revealed significant inaccuracy in reproducing the titanium tetrachloride concentration in the presence of chlorine. However, it was possible to measure to within 1% accuracy the titanium tetrachloride concentration in the feed stream. The chlorine concentration measured was not affected by the presence of titanium tetrachloride, and was accurately reproducible to within 1%.

8.5 Experimental Results, Their Analysis and Discussion

8.5.1 Experimental Results

The investigation of reaction kinetics requires stable temperature fields if unambiguous results are to be obtained. In this reactor arrangement it is possible in principle to use high reactant concentration unless the arc stability is adversely affected by one of
the reactants. However, dilute concentrations were employed in order to minimise the effects discussed in section 8.4.1. A large number of experiments were carried out, but only a few were selected for the kinetics investigation. The running conditions of these are shown in Table 8.1 in which reference is made to the corresponding graphs of chlorine concentrations and temperatures against distance. The mathematical procedures outlined in Chapter 7 were used to reduce such data into forms suitable for kinetics analysis. Computer programmes were written in order to perform the various computations. These programmes are listed in Appendix 1.

The analysis was initiated by an attempt to fit the following rate expression to the aggregate of the data collected:

$$\frac{d[TiCl_4]}{dt} = -K [TiCl_4]^p [O_2]^q \exp \left( -\frac{E}{RT} \right)$$

(1)

The concentrations of titanium tetrachloride and oxygen were calculated using the stoichiometry equations as:

$$[TiCl_4] = [TiCl_4]_{feed} - \frac{1}{2}[Cl_2]$$

$$[O_2] = [O_2]_{feed} - \frac{1}{2}[Cl_2]$$

(2)
<table>
<thead>
<tr>
<th>Run No.</th>
<th>TiCl$_4$</th>
<th>O$_2$</th>
<th>Power (KWatts)</th>
<th>Rotation (Hz)</th>
<th>Flowrate (cm$^3$ s$^{-1}$)</th>
<th>Total Gas Fig. No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.41</td>
<td>1.3</td>
<td>2.4</td>
<td>800</td>
<td>160</td>
<td>8.1</td>
</tr>
<tr>
<td>G2</td>
<td>0.45</td>
<td>1.7</td>
<td>2.2</td>
<td>700</td>
<td>120</td>
<td>8.2</td>
</tr>
<tr>
<td>G3</td>
<td>0.37</td>
<td>1.7</td>
<td>2.6</td>
<td>700</td>
<td>120</td>
<td>8.3</td>
</tr>
</tbody>
</table>

Table 8.1 Experimental Results for the Oxidation Reaction
Fig. 8.1: Temperature and Chlorine concentration variation at reactor centreline, Run 1.
Fig. 8.2: Temperature and Chlorine concentration variation at reactor centreline, Run G2.
Fig. 8.3: Temperature and Chlorine concentration variation at reactor centreline, Run G3.
Equation (1) was solved for the average values of $p$, $q$, $E$ and $K$. Table 8.2, below, shows these results with their standard deviations, together with those obtained when equation (1) was fitted to the data of run G2:

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Aggregate Data</th>
<th>Run G2</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E$</td>
<td>$42.2 \pm 48.3$ Kcal/mole</td>
<td>$28.2 \pm 156.7$ Kcal/mole</td>
</tr>
<tr>
<td>$p$</td>
<td>$-9.7 \pm 8.2$</td>
<td>$+51.2 \pm 45.4$</td>
</tr>
<tr>
<td>$q$</td>
<td>$-5.6 \pm 6.8$</td>
<td>$-559.1 \pm 589.4$</td>
</tr>
<tr>
<td>$K$</td>
<td>$0.3 \times 10^{-115}$</td>
<td>$0.6 \times 10^{-113}$</td>
</tr>
</tbody>
</table>

Table 8.2 Values of the Parameters of the Rate Expression Obtained by the Least Square Fit to the Aggregate Data and Run G2

These variations are very much greater than one could possibly reconcile with any experimental errors. They make no sense and they cannot be correlated in any obvious way. It was concluded that it was not possible fundamentally to correlate all the results by the kinetic equation (1), and further investigation into the mechanism was necessary.

A wider range of feed concentrations and temperatures was considered as part of a closer look into the mechanism. An experimental run with lean oxygen concentration in the feed was carried out. The result of this is shown in Fig. 8.4. The striking feature of this graph is that the chlorine concentration decreases with distance, which is not possible according to the basic reaction scheme, and it indicates the occurrence of another process.
Fig. 8.4: Temperature and Chlorine concentration variation at reactor centreline, Run G6.
This was considered as evidence that chlorine must be removed by some other mechanism, and that the only likely one is its reassociation which had hitherto always been assumed to occur in thermodynamic equilibrium at the local temperature. In order to proceed with the analysis of the oxidation reaction it therefore became necessary to investigate any recombination reactions first.

8.5.2 Chlorine Reassociation Process

Experiments were carried out to investigate this process by feeding titanium tetrachloride without oxygen into the carrier stream. Table 8.3 shows the conditions for these runs which were designed to cover the temperature range employed in the oxidation reaction. Graphs of the corresponding chlorine concentrations and temperatures against distance are shown in Figs. 8.5 and 8.6. Table 8.4 gives the results of calculating the equilibrium species concentrations at the temperatures shown for a titanium tetrachloride concentration similar to that of run G7. Values for the equilibrium constants were obtained from tabulation (37).

Comparison of the measured chlorine concentration, runs G7 and G9, with those calculated assuming equilibrium conditions indicate considerable departure from equilibrium. It must be stressed that, hitherto, the reactions involved in the dissociation have always been considered so fast that the equilibrium concentrations would be reached virtually instantaneously. At these temperatures no appreciable amount of chlorine due to dissociation
<table>
<thead>
<tr>
<th>Run No.</th>
<th>$[\text{TiCl}_4]$ mole c.c.$^{-1}$ $\times 10^7$</th>
<th>Power (KWatts)</th>
<th>Arc Rotation (Hz)</th>
<th>Flowrate (cm$^3$ s$^{-1}$)</th>
<th>Total Gas Fig. No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>G7</td>
<td>0.80</td>
<td>2.0</td>
<td>700</td>
<td>150</td>
<td>8.5</td>
</tr>
<tr>
<td>G9</td>
<td>0.62</td>
<td>2.5</td>
<td>700</td>
<td>140</td>
<td>8.6</td>
</tr>
</tbody>
</table>

Table 8.3 **Experimental Results for the Chlorine Recombination Process**
**Fig. 8.5:** Temperature and Chlorine concentration variation at reactor centreline, Run G7.
Fig. 8.6: Temperature and Chlorine concentration variation at reactor centreline, Run G9.
<table>
<thead>
<tr>
<th>T°K</th>
<th>TiCl₄</th>
<th>TiCl₃</th>
<th>Cl₂</th>
<th>Cl</th>
<th>Ti</th>
</tr>
</thead>
<tbody>
<tr>
<td>1500</td>
<td>0.758 x 10⁻⁷</td>
<td>0.390 x 10⁻⁸</td>
<td>0.939 x 10⁻¹⁰</td>
<td>0.371 x 10⁻⁸</td>
<td>0.114 x 10⁻¹⁶</td>
</tr>
<tr>
<td>1400</td>
<td>0.782 x 10⁻⁷</td>
<td>0.149 x 10⁻⁸</td>
<td>0.548 x 10⁻¹⁰</td>
<td>0.138 x 10⁻⁸</td>
<td>0.388 x 10⁻¹⁸</td>
</tr>
<tr>
<td>1300</td>
<td>0.792 x 10⁻⁷</td>
<td>0.490 x 10⁻⁹</td>
<td>0.282 x 10⁻¹⁰</td>
<td>0.434 x 10⁻⁸</td>
<td>0.833 x 10⁻²⁰</td>
</tr>
<tr>
<td>1200</td>
<td>0.796 x 10⁻⁷</td>
<td>0.135 x 10⁻⁹</td>
<td>0.124 x 10⁻¹⁰</td>
<td>0.110 x 10⁻⁸</td>
<td>0.102 x 10⁻²¹</td>
</tr>
<tr>
<td>1100</td>
<td>0.797 x 10⁻⁷</td>
<td>0.301 x 10⁻¹⁰</td>
<td>0.446 x 10⁻¹¹</td>
<td>0.212 x 10⁻¹⁰</td>
<td>0.627 x 10⁻²⁴</td>
</tr>
<tr>
<td>1000</td>
<td>0.797 x 10⁻⁷</td>
<td>0.512 x 10⁻¹¹</td>
<td>0.119 x 10⁻¹¹</td>
<td>0.281 x 10⁻¹¹</td>
<td>0.168 x 10⁻²⁶</td>
</tr>
</tbody>
</table>

The following reactions were considered:

TiCl₄ ⇌ TiCl₃ + 1/2 Cl₂

Cl₂ ⇌ 2Cl

No. of moles of argon diluent = 0.208 x 10⁻⁴

Values for Kp were obtained from Tables (37).

Table 8.4 Number of Moles of Species at Equilibrium with 0.797 x 10⁻⁷ moles TiCl₄ at Various Temperatures
reactions would be expected. This must throw doubt on every previous kinetic investigation in slow systems at these temperatures.

The approach to equilibrium may be via several reactions, and the following are possible examples:

\[ \frac{3}{2} \text{C}_2 \text{Cl}_2 + \text{TiCl}_4 \rightleftharpoons \text{TiCl}_4 \]
\[ \text{C}_2 \text{Cl}_2 + \text{TiCl}_4 \rightleftharpoons \text{TiCl}_4 \]
\[ \frac{1}{2} \text{C}_2 \text{Cl}_2 + \text{TiCl}_3 \rightleftharpoons \text{TiCl}_4 \]

Whichever of these reactions applies, the concentration of the relevant reactants can be expressed to some power of the chlorine concentration and thus the rate is expressed in the following general form:

\[ \frac{d\left[\text{Cl}_2\right]}{dt} = -K \left[\text{Cl}_2\right]^p \exp\left(-\frac{E}{RT}\right) \] (3)

In order to find the best value for the reaction order, \( p \) was selected between 0.1 and 3 at intervals of 0.1. The resultant values for the activation energy, together with their standard deviations, are plotted against \( p \) in Fig. 8.7. It can be seen from Fig. 8.7 that as the reaction order decreases the values of the activation energy for runs G7 and G9 overlap each other. Furthermore, they attain almost the same value at zero reaction order. Therefore, it is concluded that the rate is independent of the chlorine concentration, and
Fig. 8.7: Reaction order versus activation energy, Runs G7 & G9.
accordingly equation (4) below is the appropriate form for the rate law:

\[
\frac{d[Cl_2]}{dt} = -K \exp(-\frac{E}{RT})
\]  

(4)

In view of the above conclusion, runs G7 and G9 were combined, and the following overall rate expression is obtained:

\[
\frac{d[Cl_2]}{dt} = -0.6324 \times 10^{-4} \exp\left(-\frac{9743 \pm 2200}{RT}\right)
\]  

(5)

The standard deviation associated with the pre-exponential term, K, is \(\pm 0.61 \times 10^{-4}\). However, such a large deviation is as a result of the linearization procedure of the rate equation, section 7.5, in which ln K is presented as a parameter to be fitted, and as explained a small error in this results in a large standard deviation in K. A graph of ln \(\left\{\frac{d[Cl_2]}{dt}\right\}\) vs. \(1/T\) is shown in Fig. 8.8 for the above rate expression, and the rate data obtained from experiments. This indicates the uncertainty of the experimental data in the determination of the Arrhenius rate constant.

Thus, the reassociation process is reasonably well represented by a reaction rate expression which is independent of reactant concentration. This is likely to be a result of the dilute system considered. At such high dilutions the third body concentration, that is argon, is high and constant. The collisions between the
Rate = $0.632 \times 10^{-4} \exp\left(-\frac{9743 \pm 2200}{RT}\right)$

**Fig. 8.8:** Plot of Log(Rate) vs 1/Temperature, Runs G7 & G9.
reactants are probably successful in producing a stable product only if the energy made available by their combination can be removed within a very short time by collision with the usually required third body.

The recombination process, having been found to be adequately represented by an overall expression, is used in the following section in the analysis of the oxidation reaction.

8.5.3 The Rate of the Oxidation Reaction

The chlorine reassociation process explains why it was not possible to correlate all the results of the oxidation reaction runs by the rate expression given by equation (1) of section 8.5.1. The investigation of the oxidation of titanium tetrachloride is continued taking into account the chlorine reassociation rate described by equation (5).

The rate of chlorine formation or depletion, \( R_n \), computed from concentration-time domains relating to the oxidation reaction runs, may be expressed in terms of recombination rate, \( R_r \), and the reaction rate \( R_f \), as:

\[
R_n = R_r + R_f \quad (6)
\]

and since \( R_r \) is always negative:

\[
R_f = R_n + R_r \quad (7)
\]
It is assumed that in the presence of oxygen the rate of chlorine recombination may be represented by equation (5). However, it must be noted that the absolute values of the chlorine concentration involved in the recombination reactions in the presence and the absence of oxygen need not be the same. Difference in these values does not affect the above assumption since the rate of recombination is independent of the chlorine concentration.

The rate of reaction, $R_f$, was calculated at each data point for the oxidation reaction runs. Information regarding the absolute value of the chlorine concentration formed as a result of the oxidation reaction can not be obtained since it involves the integration of the reaction rate, $R_f$, which leads to an unknown integration constant, i.e.

$$C_{12}(t) = C_{12}(t_0) + \int_{t_0}^{t} R_f \, dt \quad (8)$$

where $C_{12}(t_0)$ is the integration constant. Thus, the data available for the kinetics investigation of the oxidation reaction consist of the rate of reaction at each temperature. In view of this, and the success of a similar procedure in the analysis of the recombination reactions, the concentration term was omitted from the rate expression chosen for the oxidation reaction. This is justified a posteriori by the results obtained. The form of the rate expression chosen is given by:
\[
\frac{d [\text{TiCl}_4]}{dt} = -1/2 \frac{R_T}{R} = -K \exp \left( -\frac{E}{RT} \right) \tag{9}
\]

The following rate expressions were computed for runs G2 and G3 which were selected a priori for their high oxygen concentration, since any complications due to chlorine reassociation would have been minimised.

Run G2: \[
\frac{d [\text{TiCl}_4]}{dt} = -0.124 \times 10^{-4} \exp \left( -\frac{7050 \pm 440}{RT} \right) \tag{10}
\]

Run G3: \[
\frac{d [\text{TiCl}_4]}{dt} = -0.210 \times 10^{-4} \exp \left( -\frac{9050 \pm 1300}{RT} \right) \tag{11}
\]

Figures 8.9 and 8.10 indicate the uncertainty of the experimental points in determining the rate expression parameters, when graphs of \(\ln \left\{ \frac{d [\text{TiCl}_4]}{dt} \right\} \) vs. \(1/T\) are plotted. It is evident from these graphs that the data points are best represented by an expression of the form given by equation (9).

The similarity between expressions (10) and (11) indicates that one is dealing with a real mechanism common to these reactions and therefore were combined to give the following overall rate expression:

\[
\frac{d [\text{TiCl}_4]}{dt} = -0.36 \times 10^{-4} \exp \left( -\frac{10,030 \pm 1060}{RT} \right) \tag{12}
\]

and Fig. 8.11 indicates the mathematical fit to these data points.

Antipov, et al (3) reports a value of 18.3 Kcal for 'apparent activation energy'. However, the
\[
\frac{d[TiCl_4]}{dt} = -0.124 \times 10^{-4} \text{Exp}\left(-\frac{7050 \pm 440}{RT}\right)
\]

**Fig. 8.9:** Plot of Log(Rate) vs 1/Temperature, Run G2.
\[ \frac{d[\text{TiCl}_4]}{dt} = -0.210 \times 10^{-4} \exp\left(-\frac{9050 \pm 1300}{RT}\right) \]

**Fig. 8.10:** Plot of Log(Rate) vs 1/Temperature, Run G3.
\[
\frac{d[TiCl_4]}{dt} = -0.360 \times 10^{-4} \exp\left(-\frac{10,030 \pm 1060}{RT}\right)
\]

**Fig. 8.11: Plot of Log(Rate) vs 1/Temperature, Runs G2 & G3.**
possibility of chlorine reassociation was not considered. Furthermore, in view of the above rate expression, no attempt at inferring reaction mechanism will be made.

8.5.4 Error Estimation In the Reaction Rate

The error equation derived from the rate expression is given by:

\[
\frac{d}{dt} \left( \frac{R_1}{R_2} \right) = \frac{E}{RT} \cdot \frac{dt}{T}
\]  

(13)

A graph of \( \frac{E}{RT} \) vs. \( T \) is shown in Fig. 8.12 for a value of 10,030 cal/mole for the activation energy. It indicates that errors in the temperature measurement of about 1 - 2%, which are not uncommon in the present study, result in an error of 3 - 10% in the reaction rate.

8.5.5 Observations on Particles

These were on a qualitative basis regarding the particle size, shape, and agglomeration. They fall into two categories depending on the sample source:

i. From the gas phase: Micrographs of these particles are shown in Figs. 8.13, 8.14, and 8.15 for run G2, and at several sampling positions. Higher magnifications resulted in considerable particle drift, and thus were avoided. These micrographs were examined using a calibrated eye-piece. Particle sizes of the order of 0.02 µm are observed, however agglomerates are more common than individual particles. Some of the agglomerates may have been formed as a result of particles
\[ \frac{\text{d}(\text{RATE})}{\text{RATE}} = \frac{E}{RT} \frac{\text{d}T}{T} ; \ E = 10,030 \pm 1060 \text{ Cal. Mole}^{-1} \]

**Fig. 8.12: RELATION BETWEEN TEMPERATURE & RATE ERRORS**
Fig. 8.3: Particles sample taken from the gas phase from run G2 at a distance 1cm away from the expansion nozzle mouth.

Mag. = 16800X
Fig. 3.14: Particles sample taken from the gas phase from run G2 at a distance 3cm away from the expansion nozzle mouth.
Mag. = 16800X
Fig. 8.15: Particles sample taken from the gas phase from run G2 at a distance 5cm away from the expansion nozzle mouth.
Mag. = 16800X
impact on the electron microscope grid during the sampling procedure.

ii. From the Reactor Wall: These samples were taken from different positions within the reactor. Figures 8.16, 8.17, 8.18, 8.19, and 8.20 are representative of these. Particle sizes of about 0.06 - 0.20 μm are observed, and various shapes may be seen. Furthermore, there is no evidence of chain formation. However, this again may be as result of the sample preparation procedure.

The mean particle size of pigment-grade titanium dioxide is about 0.25 μm. Comparison between the above two categories indicates that particles close to those of pigment-grade TiO$_2$ are found in the sample taken from the wall. The particles sampled from the gas are very much smaller than 0.25 μm, and their size variation with sampling position is not observed. Flocculation and surface chemical reaction are two processes responsible for particle growth (7, 56). Reactant concentration and gas temperature are the obvious parameters influencing such processes. Thus, the lack of variation of particle size with sampling position may be explained in terms of the high reactant dilution, which makes the encounter of oxygen, titanium tetrachloride, and a titanium dioxide particle difficult. A purely physical process, i.e. flocculation, may be responsible for the observed particle chains.

The highly dilute system was intended for the study of kinetics and would not normally be expected to lead to
Fig. 8-16: Particles sample from the wall of the injection anode mixing region.
Mag. = 100,000X
Fig. 3.17: Particles sample from the wall of the expansion nozzle region.
Mag. = 100,000X
Fig. 8.8: Particles sample from the wall of position 1. 
Mag. = 100,000X
Fig. 8.19: Particles sample from the wall of position 2.

Mag. = 100,000X
**Fig. 3.20:** Particles sample from the wall of position 3. 
Mag. = 100,000X
pigment grade particles, because of the rare encounter between molecules. Nevertheless, it seemed of interest to examine the particles in terms of the above criteria. Furthermore, in order to produce pigmentary particles from dilute systems one has to allow them to agglomerate as for example on the wall.
The study of titanium tetrachloride oxidation in a plasma jet revealed a number of interesting and unexpected features, which necessitated changes both in the experimental programme and in the analysis for the reaction kinetics.

Initially, the thermal distribution in a gas stream that has encountered the rotating arc was investigated theoretically. This resulted in a criterion which stated that uniform thermal distribution in the cross-section is established when the gas progresses linearly by one arc diameter per arc revolution. In attempting to achieve relatively low mean gas temperatures suitable for the oxidation reaction of titanium tetrachloride, this criterion led to the conclusion that within the capability of the present plasma jet design the attainment of uniform thermal distribution is invariably associated with temperatures far exceeding those required. Accordingly, a new reactor design was sought for.

A new instrument was developed as a result of the need for a more direct method for the investigation of thermal mixedness. The instrument is based on the corona discharge, and was found to be capable of responding to the high frequency temperature fluctuations encountered in such plasma jet flows. The corona probe was utilised in developing the post-arc injection reactor, and in
establishing its running conditions. It was concluded that this reactor was capable of producing a well defined reaction environment suitable for kinetics investigation.

The progress of the oxidation reaction of titanium tetrachloride was followed by measuring the chlorine concentration and temperature variation with distance. In attempting to analyse such data kinetically, it was discovered that the chlorine reassociation was much slower than had been supposed, and it was necessary to investigate this in order to allow the determination of the true rate of the oxidation reaction.

The rate of the chlorine reassociation process was best described by an expression which is independent of the reactant concentration. This is probably a result of the high dilution of the reactants by an inert gas. The oxidation reaction was also best described by an expression which lacked dependence on the reactant concentration, and in view of this, no attempt at inferring reaction mechanism was made. The activation energy in each case was deduced, though the lack of dependence on concentration may not apply in more concentrated systems.

The major contributions of this work, apart from determining the activation energies of the relevant reaction steps, probably lie in the development of the corona probe and the discovery of the slow rates of chlorine reassociation in the oxidation reaction of titanium tetrachloride. The former is an instrument
which ought to be used more generally for the assessment of gas temperature distribution especially in systems in which mixing of temperature dissimilar streams is encountered. The latter throws doubt on every previous kinetic investigation of this reaction in slow systems at these temperatures, and leads to the derivation of the true rate of the oxidation reaction. These contributions lay open paths for more detailed study of this and similar systems.
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47. Private Communication with Dr. A. R. Jones, Chemical Engineering Department, Imperial College.


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APPENDIX 1

COMPUTER PROGRAMMES

Fig. A.1: Flow Diagram for Exagramme Rate.
Program Rate

C THIS PROGRAM CALCULATES THE RATE OF A FUNCTION BY
C FITTING A SECOND ORDER POLYNOMIAL TO THE DATA POINTS
C AND COMPUTES THE DERIVATIVES.
C IT IS SHOWN HERE COMPUTING THE CONCENTRATION RATE.
C INPUT DATA: PARAMETER VALUES TIME NO. OF DATA
C POINTS
C OUTPUT: COEFFICIENTS OF THE SECOND ORDER POLYNOMIAL
C AND THE DIFFERENCE BETWEEN THE FITTED DATA POINTS
C AND THE COMPUTED ONES.
C A SECOND OUTPUT INCLUDES A LIST OF THE INPUT DATA
C POINTS AND THE RATE.

PROGRAM MAIN(INPUT,OUTPUT,TAPE5=INPUT,TAPE6=OUTPUT)
REAL TICL4(150),AR(150),T(150),TIME(150),AR2(3),AR3(*3,3),HOLD1(3),HOLD2(3),HOLD3(3)
REAL AR1(4,3),R(150)
READ(5,1) N
1 FORMAT(I5)
READ(5,2)(TICL4(I),AR(I),T(I),TIME(I),I=1,N)
2 FORMAT(4G12.4)
DO 3 I=1,N
 AR1(I,1)=1.0
 AR1(I,2)=TIME(I)
3 AR1(I,3)=TIME(I)*TIME(I)
 CALL RMINGWAR1IN,3,AR2,AR3)
DO 4 I=1,3
 SUM1=SUM2=SUM3=0.0
 DO 5 J=1,N
 SUM1=SUM1+AR1(J,I)*AR(J)
 SUM2=SUM2+AR1(J,I)*TICL4(J)
5 SUM3=SUM3+AR1(J,I)*T(J)
 HOLD1(I)=SUM1
 HOLD2(I)=SUM2
 HOLD3(I)=SUM3
 WRITE(6,8) HOLD1,HOLD2,HOLD3
8 FORMAT(3(1X,G12.4)/)
 WRITE(6,50)
50 FORMAT(/)
 DO 6 I=1,N
 ARCALC=HOLD1(I)+HOLD1(2)*TIME(I)+HOLD1(3)*TIME(I)*TIME(I)
 TICL4CA=HOLD2(I)+HOLD2(2)*TIME(I)+HOLD2(3)*TIME(I)*
 *TIME(I)
 TICL4CA=HOLD3(I)+HOLD3(2)*TIME(I)+HOLD3(3)*TIME(I)*TIME(I)
 ARDIFF=AR(I)-ARCALC
 TIDIFF=TICL4(I)-TICL4CA
 TDIFF=T(I)-TICL4CA
6 WRITE(6,7) TIDIFF,ARDIFF,TDIFF
SUBROUTINE RMINGM(A,N,M,B,C)
C THIS PROGRAMME IS WRITTEN BY MR. HORSNELL. IT IS PART
C OF THE OPTICS LIBRARY, AND IS INCLUDED WITH KIND
C PERMISSION.
REAL A(N,M),B(M),C(M,N)
DO 1 J=1,M
DO 1 K=1,N
T=0.
DO 2 I=1,N
  T=T+A(I,J)*A(I,K)
1  C(J,K)=T
CALL SMINXN(C,M)
DO 3 J=1,N
DO 5 K=1,N
T=0.
DO 4 I=1,M
  T=T+C(K,I)*A(J,I)
3  A(K,K)=B(K)
2  CONTINUE
RETURN
END

SUBROUTINE SMINXN(A,N)
REAL A(N,N)
INTEGER IN(50)
IA=0
DO 1 J=1,N
  IN(J)=0
1  IN(J)=0
DO 8 I=1,N
  T=0.
  DO 3 J=1,N
    IF(IN(J).EQ.1) GO TO 3
    DO 2 K=1,N
      IF((IN(K).EQ.1.OR.T.GE.ABS(A(J,K))) GO TO 2
  IR=J
8 CONTINUE
132
IC=K
T=ABS(A(J,K))
2 CONTINUE
3 CONTINUE
IN(IC)=IN(IC)+1
IF(IR.EQ.IC) GO TO 5
DO 4 L=1,N
T=A(IR,L)
A(IR,L)=A(IC,L)
4 A(IC,L)=T
IA=1
5 T=A(IC,IC)
A(IC,IC)=1.
DO 6 L=1,N
6 A(IC,L)=A(IC,L)/T
DO 8 K=1,N
IF(K.EQ.IC) GO TO 8
T=A(K,IC)
A(K,IC)=0.
DO 7 L=1,N
7 A(K,L)=A(K,L)-A(IC,L)*T
8 CONTINUE
IF(IA.EQ.0) RETURN
M=N/2
DO 9 I=1,M
L=M-I+1
DO 9 K=1,N
T=A(K,L)
A(K,L)=A(K,L)
9 A(K,L)=T
RETURN
END
Read Input Data

Multiple Linear Regression

Print $K, E$

End

Fig. A.2: Flow Diagram for Programme Main.
Programme Main

C THIS PROGRAM SOLVES THE SYSTEM OF EQUATIONS SHOWN
C IN CHAPTER 7. THE CASE SHOWN HERE IS THAT FOR
C OBTAINING THE LEAST SQUARE FIT FOR RUNS G2 AND G3,
C IN CHAPTER 8.
C DATA= COMPOSITION TEMPERATURE RATE
C M AND N MUST BE SPECIFIED AFTER THE DIMENSION
C STATEMENT.
C M= NUMBER OF DATA POINTS
C N=NUMBER OF PARAMETERS TO BE FITTED
C EQUATION: RATE=K*EXP(E/RT).
C OUTPUT= PRE-EXPONENTIAL TERM ACTIVATION ENERGY
C AND THE STANDARD ERRORS IN THE FITTED PARAMETERS
C AND THE VALUE FOR THE RATE COMPUTED USING THE FITTED
C PARAMETERS AND THE INPUT TEMPERATURES.
C

PROGRAM MAIN(INPUT,OUTPUT,TAPE5=INPUT,TAPE6=OUTPUT)

DIMENSION A(50,10),B(50,11),X(10,11),U(50,11),SUM(11),
  *W(10,21),WT(50),STDERR(10)
DIMENSION TICL4(150),AR(150),T(150),R(150)

M=9
N=2
RG=1.9869
WT(1)=-1.0
INVRS=1

DO 10 I=1,M
  READ(5,5) TICL4(I),T(I),R(I)
  5 FORMAT(3G12.4)
10 CONTINUE

DO 15 I=1,M
  B(I,1)=ALOG(R(I))
  A(I,1)=1.0
  A(I,2)=-1.0/(RG*T(I))
15 CONTINUE

IP=N+1
DO 40 I=1,M
  DO 40 J=2,IP
    B(I,J)=0.0
40 CONTINUE

CALL GLSP(A,M,N,B,IP,X,U,SUM,WT,INVRS,STDERR)
X(1,1)=EXP(X(1,1))
WRITE(6,2)
2 FORMAT(1H1/1HT/60X,12HPROGRAM MAIN/60X,12(1H-)//42X,
  *1HK,24X,1HE)
WRITE(6,3) (X(I,1),I=1,N)
3 FORMAT(20X,2(40X,G12.4)///)
STDERR(1)=STDERR(1)*X(1,1)
WRITE(6,6) (STDERR(I),I=1,N)
6 FORMAT(20X,2(40X,G12.4)///)

135
WRITE(6,7)
7 FORMAT(30X,15HCALCULATED RATE,10X,10HINPUT RATE,/)  
    X(1,1)=ALOG(X(1,1))
    DO 90 I=1,M
    CALC1=EXP(X(1,1))*EXP(-X(2,1)/(RG*T(I)))
    RCALC=CALC1
    WRITE(6,8) RCALC,R(I)
8 FORMAT(30X,G12.4,12X,G12.4)
90 CONTINUE
     STOP
END

C SUBROUTINE GLSP PERFORMS THE MATRIX MANIPULATIONS
C RESULTING IN THE LEAST SQUARE FIT SOLUTION.
C IT IS WRITTEN BY M.C.BRANCH (26). IT IS NOT
C INCLUDED IN THIS THESIS.