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Preparation of Catalyst Supports

Using Chemical Vapour Deposition

by

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A Thesis Submitted for
The Degree of Doctor of Philosophy
of
The City University, London

The Department
of
Chemistry

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Dedication

To M and P

To wszystko byto bolace

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Abstract

The purpose of this project was to determine the suitability of employing the technique of chemical vapour deposition for the production of refractory oxide supports, for use in catalytic gas detectors. These are usually prepared by successive thermal decompositions of an appropriate salt solution. Chemical vapour deposition is an attractive alternative as the oxide bead is deposited in a single continuous process, thus minimizing contamination problems.

Attempts were made first to coat platinum coils with alumina using aluminium isopropoxide as the starting reagent. Various coil temperatures, flow rates and deposition times were used, but dense, coherent, thick deposits could not be produced. Extensive amounts of impurities were incorporated into the product and dendritic-type growth was observed when the preparation of thick deposits was attempted.

Attention was then turned to the production of titania from titanium tetrachloride. Dense, blue/grey polycrystalline rutile titania was produced between the temperatures of 480 and 800°C using three oxygen concentrations. A Fortran IV computer programme was constructed in order to predict the maximum growth rates obtainable under mass transport control. Good agreement was obtained between experimental and theoretical maximum growth rates and a temperature of ~800°C, indicating that the boundary layer model used in the calculations was applicable and that mass transport was rate controlling at this temperature.

At lower temperatures the experimental growth rates and calculated percentage conversions showed that rate-control involved both mass transport and surface kinetics. On the basis of evidence, the reaction was assumed to be first order, and the growth rate by surface kinetics alone was

calculated. A value for the "true" energy of activation was thus obtained. The surface mechanism appears to conform to Rideal-Eley kinetics with oxygen dissociatively adsorbed on titania and reacting with gaseous titanium tetrachloride. The rate-controlling step for reaction in the gas phase is considered to be dissociation of the first chlorine from titanium tetrachloride; results obtained in this work are compared with other data in the literature in the light of this assumption.

In summary, the technique of chemical vapour deposition appears to be a highly satisfactory method for the preparation of gas detectors using titania as support. For preparation of alumina supports, the method is not effective.

List of Symbols

b	Sutherland constant	$\text{g.cm}^{-1}\text{s}^{-1}\text{K}^{-1}$
b_i	Langmuir constant for ith species adsorbed on a surface	
c	Molar density of mixture	g.cm^{-3}
c	Root mean square speed	cm.s^{-1}
C_i	Concentration of i	g.cm^{-3}
$\hat{C}_p$	Heat capacity at constant pressure	$\text{J.K}^{-1}\text{mol}^{-1}$
D''_i	Effective average diffusion coefficient	cm^2s^{-1}
D_{AB}	Binary diffusion coefficient	cm^2s^{-1}
E_a	Heterogeneous activation energy	kJ.mol^{-1}
E_H	Homogeneous activation energy	kJ.mol^{-1}
G	Growth rate	cm.s^{-1}
$\Delta G^{\ominus}_f$	Free energy of formation	kJ.mol^{-1}
$\Delta G^{\#}$	Free energy of formation of a critical sized cluster	kJ.mol^{-1}
ΔG_v	Free energy of formation of TiO_2	kJ.cm^{-3}
$\Delta G^{\ddagger}$	Free energy of activation	kJ.mol^{-1}
h	Planck constant	
h	Heat transfer coefficient	$\text{J.cm}^{-2}\text{K}^{-1}$
J_i	Molar flux	$\text{mol.cm}^{-2}\text{s}^{-1}$
k	Thermal conductivity	$\text{J.cm}^{-1}\text{s}^{-1}\text{K}^{-1}$
k	Reaction rate constant	s^{-1}
kg	Mass transfer coefficient	$\text{mol.cm}^{-2}\text{s}^{-1}$
L	Avogadro constant	mol^{-1}
M_i	Molecular weight of i	g
N	Number of molecules in a cluster	
N_i	Molar flux of i relative to a fixed set of stationary co-ordinates	$\text{mol.cm}^{-2}\text{s}^{-1}$
Nu	Nusselt number = hd/k	
Nu_{AB}	Sherwood number = $\text{kg.d/c.D}''_A$	
p_i	Partial pressure of i	atm
P	Total pressure	atm
$(pf)_A$	Partial film pressure factor for diffusion of A through B	atm
Q_i	Heat of chemisorption of i	J.mol^{-1}
r_{crit}	Radius of critical sized cluster	cm

R	Gas constant	$\text{cm}^3 \text{atm. K}^{-1} \text{mol}^{-1}$
R	Rate of reaction	$\text{mol. cm}^{-2} \text{s}^{-1}$
R_o	Cold resistance	Ω
R_t	Resistance at temperature t	Ω
Re	Reynolds number = $dV\rho/\mu$	
S	Sutherland constant	K
Sc	Schmidt number = $\mu/\rho D''_A$	
T	Temperature	K
$\bar{u}$	Mean speed	cm. s^{-1}
v_{AZ}	Mass average velocity of A in Z direction	$\text{g. cm}^{-2} \text{s}^{-1}$
V_Z	Molar average velocity for a multicomponent mixture in Z direction	$\text{mol. cm}^{-2} \text{s}^{-1}$
V_{N_2/O_2}	Volume of N_2/O_2 respectively	cm^3
V_{TiO_2}	Molar volume of TiO_2	$\text{cm}^3 \text{mol}^{-1}$
x'	Arithmetic mean average mole fraction	
x''_i	Effective mole fraction of ith component	
x_{is}	Mole fraction at surface	
x_i	Mole fraction in bulk stream	
X	Quantity of reactant in gas phase	g
Z	Collision frequency	s^{-1}

Greek

α	Temperature coefficient of platinum	$^{\circ}\text{C}^{-1}$
β	Diffusion velocity constant	$\text{mol. cm}^{-2} \text{s}^{-1}$
δ	Boundary layer thickness	cm
θ	Fractional coverage	molecules cm^{-2}
λ	Mean free path	cm
μ	Viscosity	$\text{g. cm}^{-1} \text{s}^{-1}$
μ'_g	Chemical potential in gas phase	kJ. mol^{-1}
μ'_s	Chemical potential in solid phase	kJ. mol^{-1}
ν	Rate of surface reaction	mol. s^{-1}
ρ	Mass density	g. cm^{-3}
σ	Collision cross-section	nm
ϕ	Ratio of mass transfer rates	
Ω_D	Collision integral	

INTRODUCTION

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1.0 Importance of Catalytic Gas Detectors

Catalytic gas detectors are frequently used in the detection of flammable gases or vapours in various industrial environments, such as coal mines and in liquid storage tanks, where dangerous levels of methane and other gases can build up and approach explosive concentrations. Equipment for monitoring such gases ranges from small portable instruments to large multi-point-sampling systems which continuously monitor gas concentrations throughout the plant and which contain alarms that are automatically activated at certain pre-set concentrations.

The most important part of these devices is the sensing element itself. The simplest and oldest form of catalytic sensing element involves a coil of platinum wire. A flammable gas, such as methane is oxidised on the surface of the platinum and the heat produced is measured directly using the platinum coil as a resistance thermometer. Unfortunately, at the temperature at which the rate of oxidation is sufficiently high (between 900°C and 1000°C) the metal evaporates at an appreciable rate from the surface of the wire. This produces changes in the geometry of the coil, which in turn alters the instrument output signal. Eventually the coil burns out. These difficulties can be overcome by using a pellistor which consists of a refractory bead such as alumina or titania in which the platinum coil is imbedded. This bead can be coated with any desired catalyst, thus not restricting one's choice of catalyst to platinum or its alloys.

Pellistors are usually prepared by successive thermal decompositions of the appropriate metal salt solution on the wire. A saturated drop of (say) aluminium nitrate is applied dropwise to the coil and subsequently thermally

decomposed at 900°C using the coil as a heater. This process is repeated a number of times until a bead of alumina of the correct dimensions has been produced. The catalyst is deposited on the bead in a similar manner.

Although this preparative method has been used quite successfully for a number of years there are some problems. The materials must be extremely pure, and contamination by dirty apparatus or polluted atmospheres must be avoided. In addition, the physical form of the bead and the catalytic surface can be affected by the temperatures and times of heating. As a result, the stability of pellistors produced in this manner can vary considerably, and accurate reproducible behaviour may be difficult to obtain.

An alternative process for the production of refractory oxides involves the use of chemical vapour deposition (C.V.D.). The refractory oxide bead is deposited in a single process thus minimising contamination problems, as successive applications of deposit are not required. In addition, C.V.D. results in uniform deposits on supports of relatively complex shapes, and is applicable to a wide range of materials.

The main object of this work was to investigate the suitability of chemical vapour deposition as a means of preparing refractory oxide supports which can be used in catalytic sensing elements.

1.1 Catalytic Detectors for Flammable Gases

Instruments are required to measure firedamp concentrations in two ranges, 0 to 100% and 0 to 5%, the latter being the most important. The major flammable component of firedamp is methane, which has a lower explosion limit of 5%.

Other gases such as ethane and propane may also be present, but for mining purposes it is easier to measure the amount of firedamp in terms of just the methane concentration.

Most instruments for the measurement of firedamp concentration are based on catalytic oxidation. The flammable vapour oxidizes on the catalytic surface and the temperature increase is measured as a function of electrical resistance. In principle a number of reactions of a gas can be used for its detection; however, an oxidation reaction is most commonly used as this involves a large heat of reaction. In addition, there is normally a ready supply of oxygen in the atmosphere containing the gas to be measured.

Three basic requirements are needed for a transducer to convert the methane concentration into an electrical signal effectively by oxidation of the gas and measurement of the heat produced.¹ First a suitable surface on which oxidation will occur is required. Secondly, this surface must be able to be heated to a sufficiently high enough temperature to promote an adequate catalytic oxidation rate. Thirdly, a sensitive means of measuring the heat produced must be available.

The most common method for the measurement of the temperature is to use a platinum or platinum-alloy coil as a resistance thermometer in the transducer. The coil is connected to one arm of a Wheatstone bridge. A reference coil is connected to another arm where it acts as a compensating resistance. Both catalytic and compensating arms are affected equally by changes in water vapour concentration, atmospheric pressure and instrument temperature, so the bridge output is virtually unaffected by changes in these factors. The conditions under which catalytic gas detectors are used can vary considerably, so it is extremely important for the instrument to be insensitive to changes in the environment other than the methane concentration.

Concerning the mode of construction, there are two basic types of catalytic flammable gas detectors. One type conveys the gas to the sensor by an aspirating mechanism such as a squeeze bulb. The other type allows the gas to diffuse to the detector through a porous plate.² In both types of instrument transport by diffusion is involved. Detectors are usually calibrated for a particular gas, such as methane, and give a reasonable response for a range of concentrations. If the instrument is used for gases other than for it was calibrated, a correction factor may need to be introduced not only because of the different heat of combustion involved, but because gases of higher molecular weight diffuse more slowly to the catalyst surface and hence give lower readings at the same concentration level. Mass transport is the rate controlling factor, as the catalyst oxidizes any flammable gas immediately it arrives at the surface. Low readings obviously lead to a reduction in safety margins.

Gas detectors react to concentrations either at the end of sampling lines or in the immediate vicinity of the instrument. In many cases the gas concentration is not uniform and layering may occur, the instrument response is then dependent on the position of the sampling point. In addition, low or zero readings can be obtained with very high gas concentrations where there is insufficient oxygen for combustion. Temperature can also be important. If the instrument and gas is above the calibration temperature lower readings can result. If the gas is hot and the instrument at ambient temperature, there is a risk of condensation occurring, especially with the less volatile vapours. Another problem occurs in moving air streams, where cooling effects may develop which also lead to inaccurate results.

In addition to physical factors, susceptibility of the catalyst to poisoning is another cause of low readings.

If the catalyst surface is poisoned, the resulting very low rate of oxidation on the surface becomes rate controlling and the instrument gives low readings. Catalysts can be poisoned by numerous materials such as silicone oils, lead, potassium and phosphates. The poison permanently reduces the rate of oxidation on the catalyst and the sensitivity of the transducer. However, in a system involving flow sampling the majority of these poisons can be removed from the gas sample using activated charcoal.

Thus gas detectors (especially portable ones) should be used as a guide to the conditions present, and should not be regarded as of high accuracy unless adequate research has been undertaken to assess the errors involved.

1.1.1 Principles of Operation of Various Gas Detectors

Infra-red absorption can be used for continuous analysis of gas streams.³ The source of radiation is a platinum-rhodium heating element embedded in an alumina bead which is covered in borosilicate glass. The operating temperature is in the region of 400 to 500°C.

Optical methanometers make use of the difference in the refractive index of methane and air.⁴ If light is passed through a cell containing air and through a test gas, the optical fringes obtained will be different if the refractive index is different. By adjusting a prism one can return the fringes of the test gas to the original position, and thus infer from the deflection of the prism how much the refractive index differs from the reference. This can then be related to the amount of methane present in the test sample by calibration.

Thermal conductivity is a function of the individual gases present and of their relative amounts. The overall thermal

conductivity of a mixture can therefore be used as a measure of composition; for high precision a reference gas is used for comparison. The instrument consists of a fine platinum wire stretched along the axis of a metal or glass cylinder. Two such cylinders are used to form two arms of a Wheatstone bridge. The equilibrium temperature of the wire depends on the thermal conductivity of the gas surrounding it: the higher the conductivity, the lower the temperature and vice versa. If the gas in the test cylinder is the same as the reference then the bridge is balanced, but if the gases are different the equilibrium temperatures and resistances of the wires are different and the bridge is unbalanced. A serious drawback to this type of detector is its non-specificity.

The flame lamp is essentially a naphtha lamp with a flame arrestor to disperse the heat generated by the flame. A flame has a characteristic colour, height and intensity when in air, whilst in flammable gases the nature of the flame changes and the flame burns more vigorously. The temperature can increase by 16% with a 1% increase in methane concentration,⁵ and thus this device is in principle a very sensitive indicator of gas in the atmosphere.

1.1.2 Platinum Wire Transducers

This transducer has all the required properties for both the oxidation of gas and the measurement of the heat provided mentioned in section 1.1. Platinum was initially chosen as its specific resistance and resistance temperature coefficient are high. In addition, platinum has a relatively high mechanical strength, so a platinum wire coil is reasonably stable at high temperatures. It is resistant to corrosion and, specifically, oxidation.

Unfortunately, platinum is a poor catalyst for the oxidation of methane and temperatures greater than 800°C are needed to obtain a sufficient oxidation rate. At these temperatures the metal can evaporate from the wire and thus reduce the cross-sectional area.⁶ This causes an increase in resistance which is shown by an increase in instrument zero reading; eventually the wire burns out.

The geometry of the coil is extremely important. If, for example, two turns are close together the temperature in that region is substantially higher, which reduces seriously the life of the detector. In practice, therefore, a platinum coil has a comparatively narrow working temperature range. Below this range the oxidation rate is rapidly reduced while above it the zero reading increases very rapidly with time. Another disadvantage resulting from the high temperatures needed is that it is not yet possible to make a reference transducer of the same geometry which can operate at the same temperature as the test transducer, therefore instrument compensation is imperfect. To prevent oxidation on the surface of the reference transducer it is poisoned or coated with a non-active metal such as gold or used at a lower temperature than the catalytic transducer.

1.1.3 The Pellistor

The pellistor was developed initially at the Safety in Mines Research Establishment.^{7,8} It was introduced to alleviate the difficulties inherent in the operation of high temperature platinum sensing elements (see above discussion). With the pellistor, one's choice of catalyst is no longer restricted to platinum and its alloys as the catalytic surface is separated from the combined heater and resistance thermometer in the centre of the bead (see Fig. 1.).

The pellistor consists of a coil of platinum wire embedded in a hard pellet of a refractory oxide, usually α -alumina.¹ This enables the geometry of the coil to remain constant and provides an in-built resistance to shock and vibration. It operates at a lower temperature than the simple platinum wire, and results in an almost complete elimination of zero drift. In addition, a nearly perfect reference transducer can be made using this system, differing only from the active pellistor in that no catalyst is applied to the refractory oxide of the reference bead. Any residual catalytic activity the reference bead oxide may have is removed by poisoning the surface with potassium.

The manufacture of pellistors is a simple procedure.⁹⁻¹⁴ A machine-wound eleven-turn, 0.05mm diameter platinum wire coil with a pitch of 0.125mm is cleaned in chromic acid

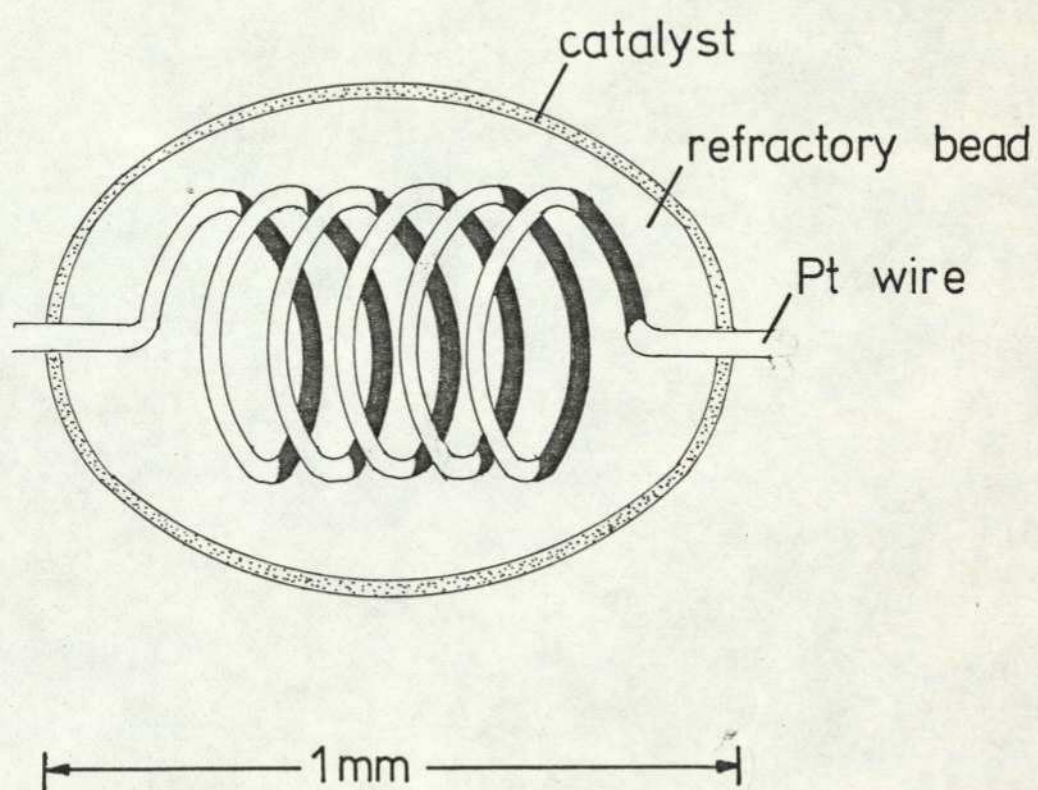


Fig 1. The Pellistor.

and washed successively in water, alcohol and water. The coil is then dipped into an aluminium nitrate solution, and the drop of solution left on the coil is thermally decomposed to alumina by passing a current through the wire. The dipping process is repeated until a bead of alumina of approximately 1mm diameter is formed. Any excess alumina formed on the wire ends of the coil is next removed by boiling in acid in the case of catalytic pellistors, or in potassium hydroxide solution with reference pellistors. The catalyst is impregnated onto the bead in a similar manner, by dipping the bead into a solution of (for example) ammonium chloropalladite and thorium nitrate and then thermally decomposing the salts. The process is repeated until sufficient catalyst has been deposited. The pellistors are then welded to support wires held in either a plastic plug or a glass-metal seal, and the catalyst is heated to 900°C in a 12% methane/air mixture to reduce any palladium oxide to palladium metal.

Palladium/thoria pellistors have been found to be very suitable for use as flammable gas detectors in the temperature range of 500° to 600°C .¹

1.1.4 The Electrical Circuit

The electrical circuit shown in Fig. 2. is based on a Wheatstone bridge made up of both the detecting and reference pellistors and two other fixed resistors. The bridge voltage and the resistances of the pellistors are chosen so that the current needed to reach the operating temperature passes through the pellistor. The out-of-balance signal produced when the bridge is put out of balance by the presence of methane is then sufficiently large to be displayed on a milli-ammeter. Any difference between the detecting and reference pellistors can be reduced by the "trimming" resistor T. The relative values of the fixed

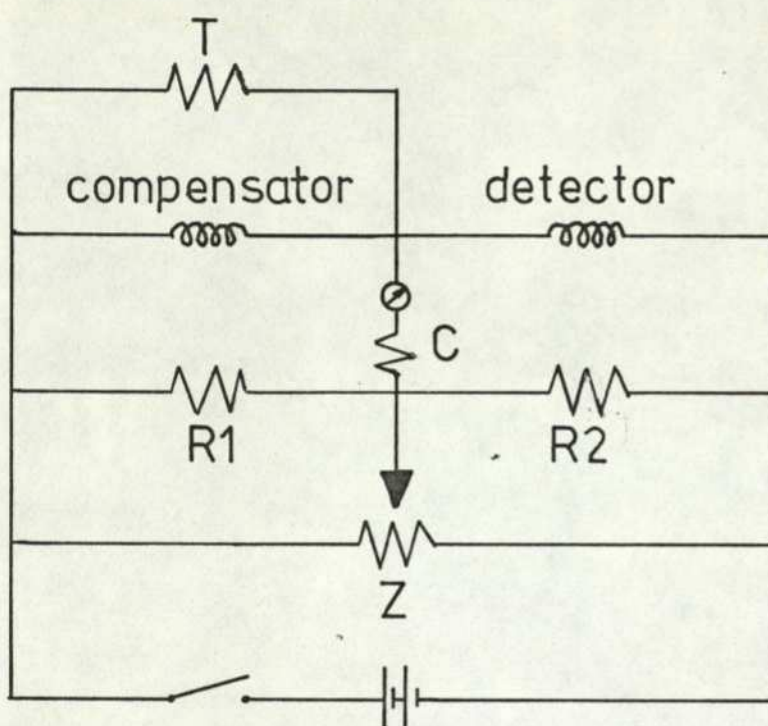


Fig 2 . The Circuit Diagram

Taken from reference 1.

resistors R1 and R2 are selected in order to bring the zero adjustment range into the region of fine control. This zero control is marked as Z in Fig. 2.

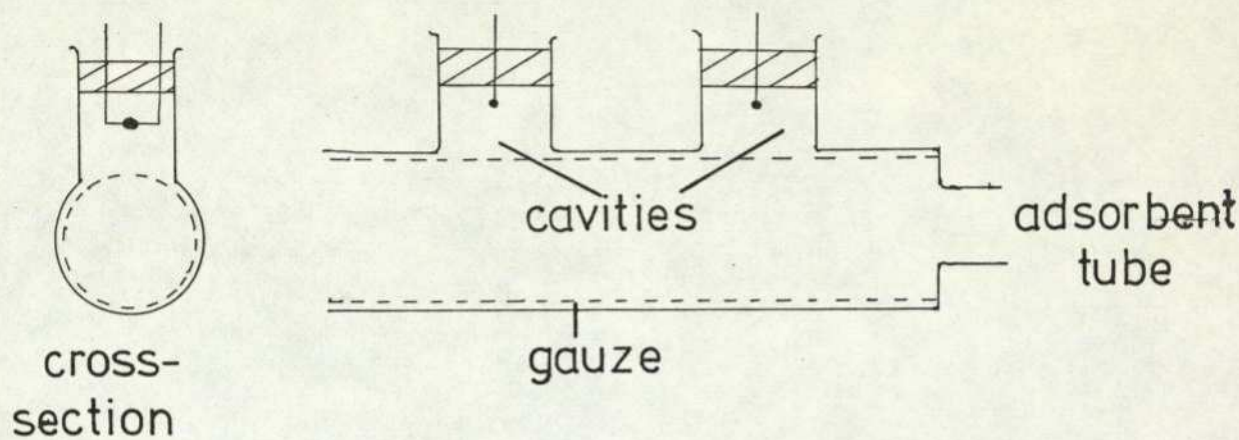
1.1.5 The Gas-Flow System

As discussed above, the gas mixture can be conveyed to the pellistors in two basic ways, either by an aspirated flow, or by pure diffusion flow. In pumped flow (see Fig. 3a.) the sample is drawn through a tube of activated charcoal to remove poisons and through a tube lined with stainless steel gauze which serves as a flame trap. The two pellistors are mounted at the centre of a cavity, which is open at one end to the gauzed cylinder. The gas diffuses through the gauze and convection currents in the cavities bring it to the centre where it diffuses through a boundary layer to the surface of the pellistors. Reaction products diffuse out by the reverse process. If the length of the cavity is equal to its diameter, the convection currents are not affected by orientation and the positioning of the pellistor is not critical.

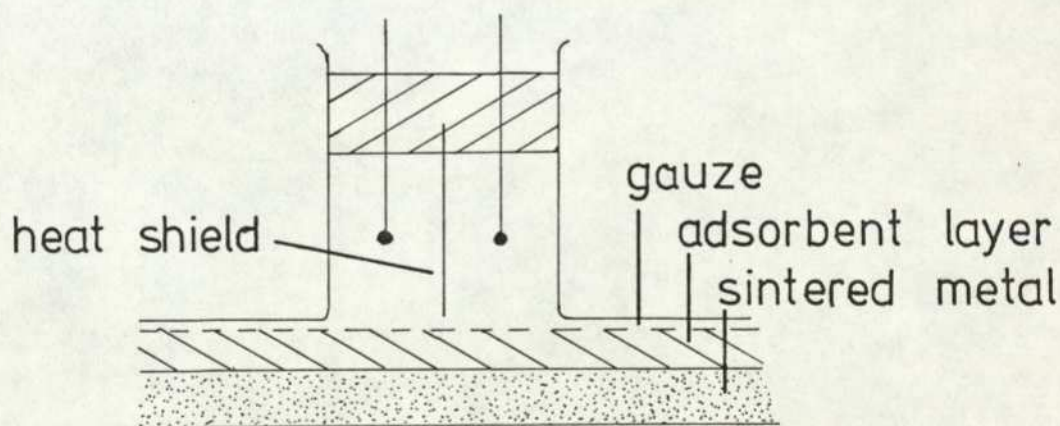
For continuous monitoring of flammable gases a diffusion flow system is used (Fig. 3b.). The sample diffuses into the cavity through a sintered metal disc, which protects the detector from damage and dust, and an adsorbent layer of activated charcoal. A heat shield is placed between the two pellistors in order to prevent thermal interaction.

1.1.6 Other Catalytic Sensing Elements

There are several other types of pellistor available. For the detection of high concentrations of methane (up to 60%) the coil is embedded in a glass bead instead of alumina in order to provide a non-porous base for the catalyst.¹



(a) Pumped flow



(b) Diffusion flow

Fig 3. Flow systems for pellistors.

Taken from reference 1.

A non-porous base is needed at high concentrations as the carbon and hydrogen formed in the partial oxidation reaction can exert large pressures in a porous base and may break and destroy the bead altogether. Attempts have been made to directly coat the platinum coil with catalyst¹⁵ to promote a lower oxidizing temperature. A thermocouple has been embedded in a glass tube externally wound with a catalyst-coated heater wire.¹⁶ In another device all three functions of the catalytic transducer are separated. A machine former of alumina is fitted with an internal heater and externally wound with resistance thermometer wire coated with a catalyst.¹⁷ Sieger¹⁸ have used a similar method: a core of silica fibre is wound with the resistance thermometer and then impregnated with the catalyst.

A platinum wire coil can be coated with a slurry of aluminium hydroxide¹⁹ or a paste of alumina and aluminium nitrate²⁰ then dried and heated by passing a current through the coil to convert the salts to aluminium. Zirconia stabilized with calcium oxide²¹ can also be used for the detection of flammable gases.

1.2 Chemical Vapour Deposition

The basic method is as follows. A volatile compound of the element or substance to be deposited is vaporized, and the vapour is thermally decomposed or allowed to react with other gases or vapours close to the substrate surface, to give non-volatile products which are deposited on the substrate as a coating. This process is shown schematically in Fig. 4.

The volatilized material is transported to the substrate using a pressure and/or a temperature difference, or by a carrier gas. As the vapour condenses on any cool surface it meets, the deposition system must be at least as hot as the vapour source. The reaction zone is generally controlled at a temperature which is much higher than that of the vapour source, but yet considerably lower than the melting point of the deposit.

The advantages of CVD are obvious, in that it is possible to selectively volatilize a material, transport it to a desired place and deposit it in a controlled manner to give a pellistor of predictable morphology. Despite the seeming simplicity of the process, a number of physical and chemical steps are involved in the preparation of a desired deposit at reasonable deposition rates.

1.2.1 The Evaporation Process

Thermal evaporation from a liquid or solid surface is the simplest method for providing a vapour for deposition and it is quite suitable for chemicals which exhibit high vapour pressures and which do not decompose.²² When the vapour pressures are low, a method for increasing the rate of volatilisation must be found, such as sputtering, where the evaporating surface is bombarded with high energy

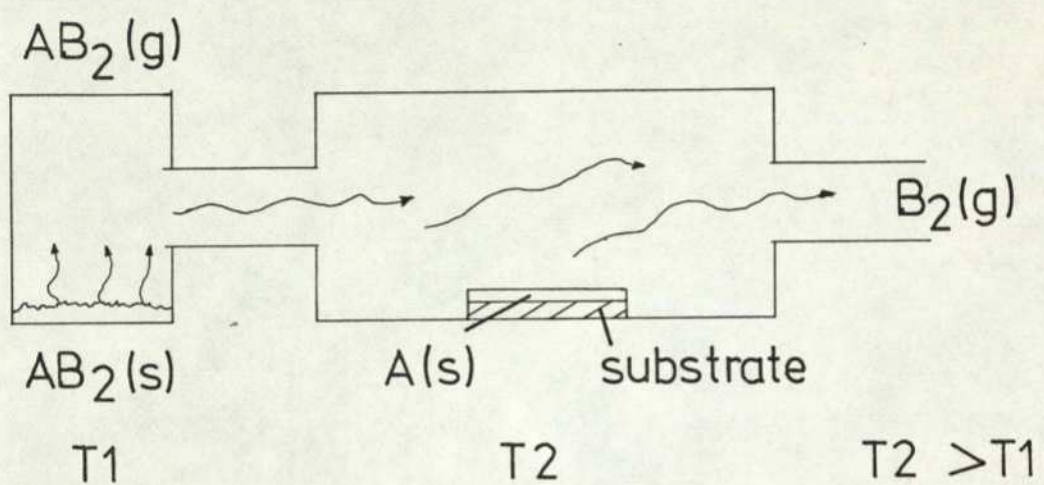


Fig 4 . Schematic diagram of a CVD process.

Taken from reference 30.

ions. These ions lose their kinetic energy by displacing atoms of the material into the vapour phase.

Another method used is chemical evaporation, which relies on the free energy change involved in the formation of a volatile compound. Thermal evaporation and sputtering rely on the transfer of kinetic energy for evaporation. In chemical evaporation a reactive gas is adsorbed on the surface of the material, where it reacts. The volatile product is then desorbed and transported to other parts of the system where it can further react to deposit a modification of the starting material. This method is very useful as it is not limited by the volatility of the material and provides an additional means of varying the composition of the deposits.

1.2.2 Transport Processes

The process of CVD is usually assumed^{23,24} to involve:

- (i) Transport of reactant(s) to the substrate;
- (ii) Adsorption of reactant(s) on the substrate surface;
- (iii) Chemical reaction on the surface;
- (iv) Desorption of product gas(es) away from the surface;
- (v) Transport of gas(es) away from the substrate.

Steps (ii), (iii) and (iv) can be referred to as chemical rate processes and steps (i) and (v) as mass transport processes. Both slow mass transport and slow surface kinetics can lead to resistance to deposition. Usually, however, one mechanism dominates.

The regions labelled A, B and C on Fig. 5. represent respectively rate control by a reaction occurring at or near the surface, rate control by mass transport in the gas stream and rate control by gas phase nucleation.²⁵

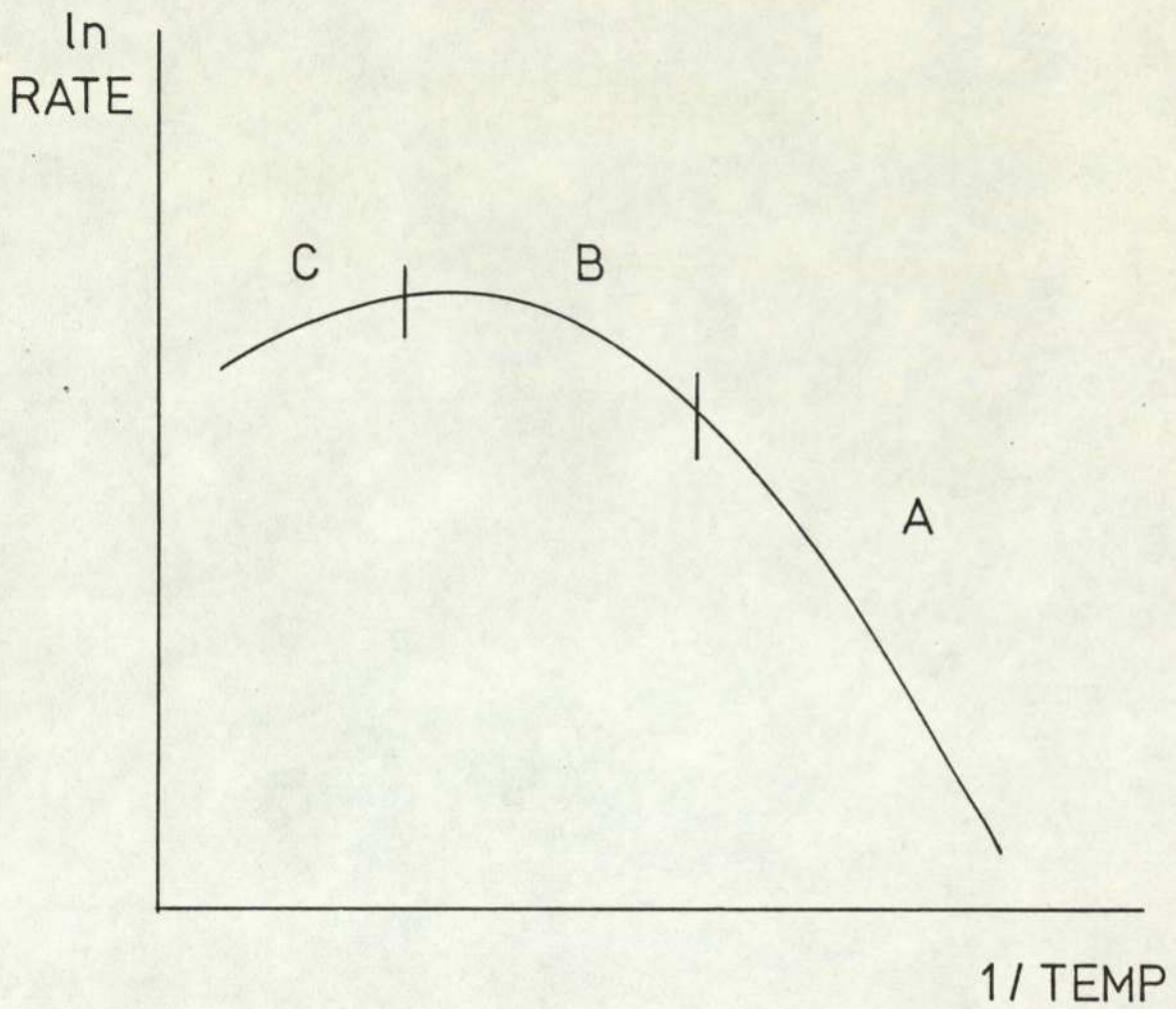


Fig 5. Effect of Temperature on Deposition Rate.

Taken from reference 23.

At low temperatures deposition is limited by the rates of heterogeneous (ie. surface) nucleation and by adsorption effects. Homogeneous nucleation (ie. gas phase) can occur when the reactant gases are excessively heated and super-saturation is high, giving precipitation of the solid reaction product in the gas stream and so leading to a reduction in deposition rate on the substrate. At intermediate temperatures the maximum deposition rate is obtained. Rate control is via interdiffusion of gaseous reactants and products. Mass transport control is indicated by a relative independence of rate on pressure when constant deposition temperature, gas composition and flow rate are used. At high flow rates mass transport control is shown by the deposition rate being dependent on flow rate, all other parameters held constant. At higher flow rates, if the deposition rate is independent of flow rate, rate control is by surface kinetics.

Either a film model or boundary layer model can be used to obtain an equation describing the deposition growth rate when mass transport is rate controlling. It is assumed that the resistance to mass transfer is contained in a relatively thin layer of gas adjacent to the surface of the substrate. Gas phase reactions and surface kinetic rate control are assumed to be absent. In the film model, the physical properties of the film are assumed to be constant over its thickness and only the boundary conditions are needed. In a boundary layer model, the effects of mass transfer and bulk flow on the thickness of the layer are considered. The boundary layer model is dealt with in detail in section 1.3.

1.2.3 Deposition Reactions and Thermal Decomposition

The choice of chemical reaction used in CVD is determined,

for a given vapour, by the conditions used. If the substrate is heated sufficiently the reactant gas(es) can decompose and leave a coating on the substrate. This technique, known as thermal decomposition or pyrolysis, can be classified into high or low temperature decomposition and is considered irreversible. Low temperature decomposition processes occur from slightly above room temperature to about 600°C.²⁶ Typical compounds used include the metal hydrides, borohydrides or carbonyls, most organometallic compounds, unstable metal halides and metal carbonyl halides. Above 600°C high temperature decomposition processes are said to occur, the compounds used being mainly the metal halides, especially the iodides. Compounds used for low temperature deposition can also be used in high temperature processes when the conditions are such that premature decomposition is suppressed, ie. at greatly reduced pressures or in an atmosphere rich in gaseous decomposition products. This technique is sometimes used in order to obtain a particular crystal structure, orientation or size, or to obtain a desired composition or purity of deposit which may be more likely to form at high deposition temperatures.

Many of the compounds mentioned above are capable of depositing more than one non-volatile deposit. For example, carbon from the carbonyls and organometallics may be present in the desired metal product. The extent to which other atoms are incorporated into the deposit depends on the nature of the bond between the two depositing atoms, the various bonds in the compound in the vapour phase and by the overall reaction mechanism.

1.2.4 Hydrogen Reduction

One of the most frequently used types of CVD reaction is hydrogen reduction.²⁶ The reaction is carried out at

elevated temperatures so that the reduction reaction is favoured by a suitably rapid reaction rate or by a favourable thermodynamic equilibrium. The temperature can range from about 100°C to the temperature at which the coating compound dissociates. These higher temperatures are usually in the region of thermal decomposition of the metal halides, except for the metal iodides.

As well as metal halides, other compounds commonly reduced by hydrogen in CVD, are oxyhalides and other oxygen containing compounds.²⁶ In the latter case the extent of contamination of the deposit with oxide depends on the reducibility of the metal oxide with hydrogen. Hydrogen may also be used when pyrolysing metal carbonyls and organometallics. In these cases reduction is not the main objective; the function of the hydrogen is to improve coating characteristics, probably by preventing the co-deposition of small amounts of carbides or oxides.²⁶ The addition of hydrogen can also be desirable to prevent premature deposition during pyrolysis of volatile metal hydrides, and hence permit the use of higher deposition temperatures.

Hydrogen reduction can be likened to a thermal decomposition reaction aided by the removal of one or more of the gaseous decomposition products. Thus the temperature required for decomposition is lower when hydrogen is present than when it is absent, ie. hydrogen can be used with unstable compounds to reduce the CVD temperature.

If the reactant used is not appreciably volatile it has to be vaporized into a stream of inert carrier gas which can be mixed with hydrogen at the deposition zone, thus avoiding reduction in the vaporizer. Addition of a stabilizing gas, such as carbon monoxide or free halogen, into the carrier gas permits the use of more unstable coating compounds.²⁶

1.2.5 Metal Vapour Reduction

Reducing agents other than hydrogen can be used in metal halide decomposition and one can "tailor" the strengths of the reducing agent to the stability of the metal halide coating compound. Hydrogen is too weak an agent to reduce titanium, zirconium or beryllium halides at appreciable rates, but stronger reducing agents such as zinc and magnesium vapours can reduce these halides to yield good metal yields.²⁶ Hydrogen can be used to deposit silicon and boron from their halides, but zinc vapour gives higher yields and faster deposition rates at lower temperatures. Too strong a reducing agent, such as sodium vapour, can cause premature gas phase reduction, producing powdery deposits rather than dense coherent ones.²⁶

The reducing potential of the metal vapour can be deduced from the standard free energy of formation of its metal halide. However, if this halide is less volatile than the reductant metal co-deposition may occur. One usually selects a reducing metal with a standard free energy of formation for the halide which is comparable to that of the metal halide to be reduced. The reducing agent itself can of course contaminate the deposit by producing solid solutions. Contamination and co-precipitation can be avoided by operating at reduced pressure, which also prevents premature reduction of the coating compound.

1.2.6 Other Deposition Reactions

Disproportionation reactions are generally considered reversible within a defined temperature range.²⁷ When the temperature is altered the equilibrium of the reaction is displaced. The reaction involves an element capable of exhibiting different oxidation states, at least two of which must be present in the vapour phase.

Displacement reactions do not necessitate a change in oxidation state; usually the transported element is present in its highest oxidation state. The amount deposited depends on the activity of the reactant and its partial pressure in the gas phase.

The deposition reactions discussed above are summarized in Table A.²⁸

The substrate itself can enter into the deposition process if it can act as a reducing agent for a metal halide vapour, it in turn being converted to a volatile metal halide. The substrate can dissolve the coating compound to form an alloy or solid solution or react exothermically with the coating compound to form a moderately or highly stable compound. A subtle catalytic effect can also be exerted by the substrate. This effect can be very large in some cases so that a deposition reaction may occur in conditions when one would not expect it. This effect is probably present, to a certain degree, in most CVD reactions.

1.2.7 Structure of Deposits

CVD is capable of producing a variety of morphologies, including epitaxial, polycrystalline, amorphous, platelet, whisker-like and dendritic growths. Epitaxy is a regularly orientated growth of a crystalline substance on a crystalline substrate, ie. a deposit with a unique lattice plane parallel to the substrate. Orientated overgrowth occurs when a crystalline substance is deposited on an amorphous one. There are two forms of epitaxy - if the deposit is grown on the same substance the process is defined as homoepitaxy while growth on a different substrate is described as heteroepitaxy. Epitaxy is most commonly used to grow single crystals and also for the production of thin films used in electronics. Imperfections

Table A. (Based on S Audisio L'actualite Chimique. 1978,(7),25)

<u>Type of Reaction</u>	<u>Characteristics</u>
1. <u>Thermal Decomposition or Pyrolysis</u>	
a. $MX_m(g) \longrightarrow M(s) + \frac{m}{2} X_2(g)$ $M_x C,O... _Y(g) \longrightarrow M_YO_{Y-Z}(s)$ $+ C_Y,O_Z... $ eg. $ZrI_4(g) \xrightarrow{1,500^\circ C} Zr(s) + 2I_2(g).$	Decomposition at high temperatures of halogen or oxygen containing compounds.
b. $M(CO)_n(g) \longrightarrow M(s) + nCO(g).$ eg. $Ni(CO_4) \longrightarrow Ni + 4CO.$	Decomposition at lower temperatures than above of carbonyls, hydrides or organometallics.
c. $2MX(g) \rightleftharpoons M(s) + MX_2(g)$ eg. $2GeI \rightleftharpoons Ge\downarrow + GeI_4$	Disproportionation.
2. <u>Reduction or Oxidation Reactions</u>	
a. Hydrogen reduction $BX_m(g) + \frac{m}{2} H_2(g) \rightleftharpoons mHX(g) + B(s)$ eg. $CrF_2 + H_2 \rightleftharpoons 2HF + Cr$	Reduction of metal halides by hydrogen to produce the metal.
b. $BX_m(g) + Y_n C,N,O... (g)$ $\Downarrow \Uparrow$ $M_x C,N,O... (s) + X,Y,C,N... $ eg. $TiCl_4 + 2H_2O \rightleftharpoons TiO_2\downarrow + 4HCl$	Reaction of a metal halide with a gas containing carbon, N_2 , B, Si or O_2 .
3. <u>Displacement Reactions</u>	
$BX_m(g) + A(g) \rightleftharpoons AX_m(g) + B(s)$ eg. $SiCl_4 + CH_4 \rightleftharpoons SiC(s) + 4HCl(g)$	

such as stacking faults, growth pyramids and dislocations have an adverse affect on epitaxial deposits. The occurrence of these imperfections is largely controlled by the substrate surface. Correct surface preparation techniques therefore help to minimize them.

High temperatures, good lattice match between the substrate and deposit and correct concentration ranges favour epitaxial growth. If these conditions are not met polycrystalline or amorphous structures may be produced. Lower temperatures and higher gas phase concentrations of the depositing material favour the production of polycrystalline deposits, where the structure of the substrate has little or no effect. With these conditions there is a high rate of feed of reactant to the surface, but the surface mobility of the adsorbed atoms is low. Many differently orientated nuclei are therefore formed, which upon coalescence produce a polycrystalline deposit.

At even lower temperatures and higher gas phase concentrations more condensation nuclei are formed initially which lead to finer grained deposits, and eventually non-crystalline amorphous deposits result.³⁰ Fig. 6. summarizes the above generalisations. It is apparent that increasing concentration (super-saturation) leads to an increased nucleation rate and increased density of nuclei on the surface. Increasing temperature has the opposite effect.

Polycrystalline deposits often comprise a columnar microstructure.²⁹ This consists of a network of low density material surrounding an array of parallel rod-like high density regions which have a marked degree of preferred orientation. A randomly orientated layer is first formed on the substrate, but deposition proceeds by the more rapid growth of preferentially orientated grains, which in turn inhibit the less favourably orientated ones.³¹

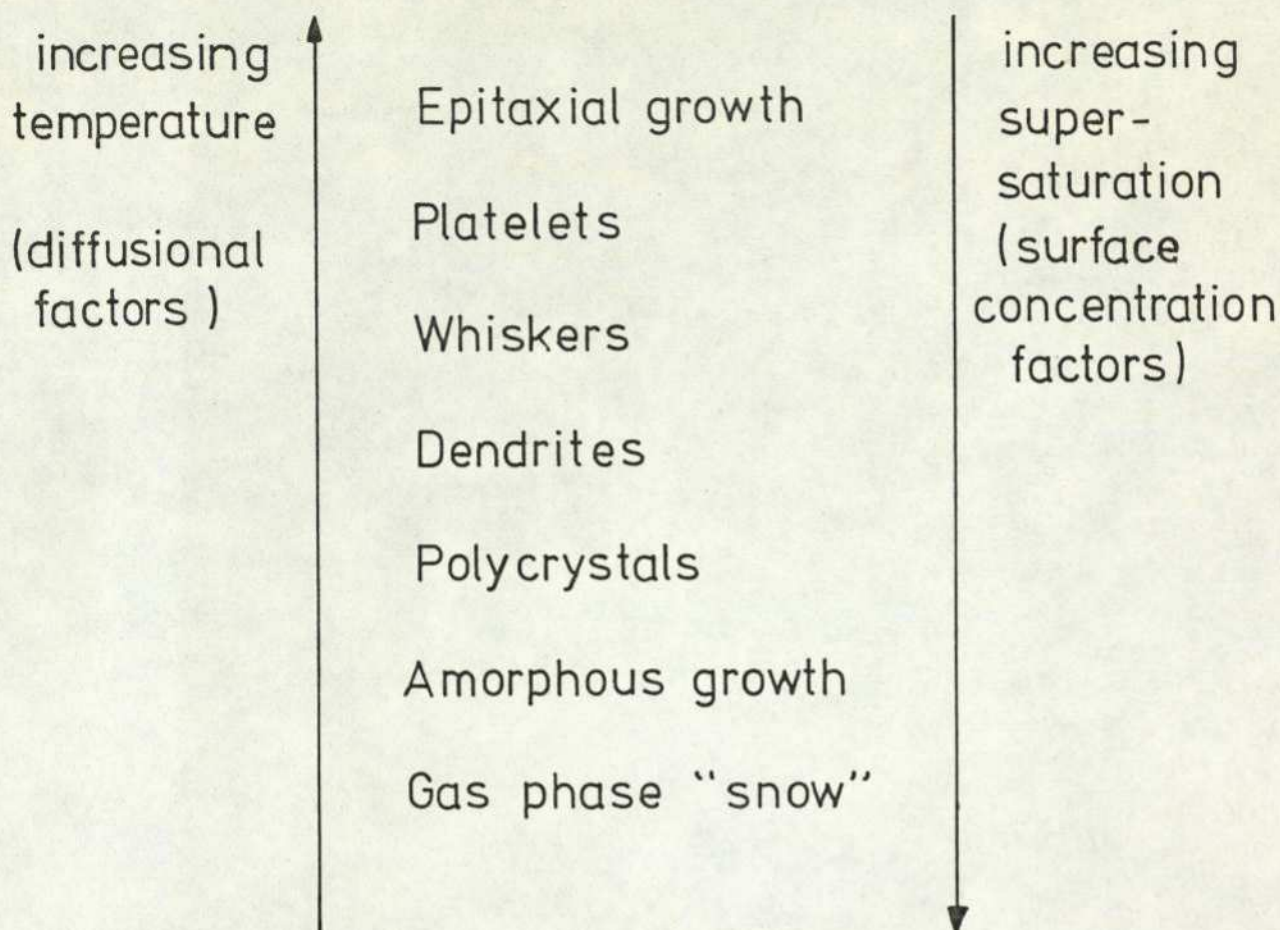


Fig 6 . Effects of Temperature and Supersaturation on morphology of crystals formed by condensation .

Taken from reference 34 .

In extreme cases a single crystal deposit can be formed in the last stages of growth.

Porous deposits may be obtained when the growth rate is controlled by a mass transport process. The tips of the growing crystallites normally extend furthest into the gas phase boundary layer, in which there is a reactant concentration gradient. Thus the reactant concentration and the growth rate is greater at the tips than at the intercrystalline boundaries, resulting in a built-in boundary porosity. In contrast, high density deposits are obtained when the reactant concentration is uniform over the deposit, which occurs when surface kinetics is the rate controlling mechanism.²³

Amorphous deposits, useful in electronic devices, are produced at low temperatures due to limited mobility of the adsorbed atoms. The atoms are not able to move to more energetically favourable sites where nucleation could occur.

Dendrites, botryoids, platelets and whisker growth also occurs in CVD. Both dendritic and botryoidal structures are very porous and irregular in surface coverage. Dendrites usually comprise of a loose agglomeration of crystals, whereas the botryoidal structure resembles a bunch of grapes.

Platelets and whiskers can be considered as two and one dimensional crystals respectively.³⁰ Each crystal face collects its own material, but if one face has a higher acceptance level preferential growth occurs. In platelets one face grows more slowly and one degree of freedom is lost, while with whiskers one plane grows very much faster than the other two and so in effect two degrees of freedom are lost. Molecules are adsorbed onto the sides of the whisker and diffuse to the tip.

All the above structures are formed by heterogeneous nucleation but at sufficiently high levels of supersaturation in the gas phase and a high temperature (not substrate) "homogeneous" nucleation can occur to produce fine powders. This powder formation cannot seriously be considered as homogeneous as nucleation probably occurs on ions, dust particles and impurities in the system.³² Powder formation is undesirable when one requires a continuous solid deposit as it lowers the deposition rate and causes equipment maintenance problems. However, gas phase nucleation is extremely desirable in the production of pigments such as the carbon blacks and the titanium whites.

1.2.8 Adhesion, Coverage, Supply Rate, Purity and Efficiency

As stated above, gas phase reactions can occur with the more unstable coating compounds at some distance from the heated substrate at higher temperatures. This produces non-adherent powder deposits or non-volatile partial decomposition products which may be carried out of the deposition zone before deposition can occur. This difficulty can be eliminated usually by lowering the vaporization temperature, or by reducing the pressure, thus increasing the mean free path of the gas molecules.

Deposit adhesion is also influenced by the extent of inter-diffusion of the deposit and substrate. Inter-diffusion usually improves adhesion, unless an extremely brittle compound is formed at the interface of the deposit and substrate. Chemical attack on the substrate by a gaseous decomposition product can also produce brittle compounds at the interface.³³ Adhesion may be improved if an intermetallic compound is formed which increases the deposit nucleation density. A deposit can be more mobile on the intermediate layer than on the substrate.

The increase in mobility increases the nucleation density and so increases adherence. Deposits with low nucleation density, producing large grain sizes and possible porosity, tend to be non-adherent. With a very large substrate area both adherent and non-adherent deposits can be formed together due to reactant depletion from the gas phase. This can produce stresses between the neighbouring sections which may be large enough to form cracks in the deposit. In addition, after adherence of the deposit to the substrate, it must be able to cope with all the internal stresses and stresses that result when cooling from the deposition temperature takes place, especially if there is a marked difference in magnitude between the thermal expansion coefficients of the deposit and substrate.

A uniform rate of supply of fresh reactant is harder to obtain than uniform substrate temperature. With non-turbulent flow at near atmospheric pressures, the deposit tends to build up in streamlines on the wind-ward side of objects. This is caused by the depletion of reactant gases as they move across the substrate. Non-uniform deposits also occur if the substrate temperature is not constant over the surface, heavier deposits occurring on the hotter portions. Non-uniform temperatures can however be desirable when using certain substrate shapes or reactor chambers in order to give uniform coverage by counter-acting the reactant depletion as it flows over the substrate.

Various methods have been used to counteract the streamlining problem, such as rotating the substrate, suspending it in a relatively large chamber so convection currents and turbulent conditions can be set up, or by tilting it in order to increase projection into the boundary layer. Another means of obtaining uniform coverage, which also gives high deposition efficiency, is to heat only a small part of the substrate whilst keeping the remainder just

sufficiently hot to prevent condensation of the reactant gases. The heated section is then slowly shifted along the entire length of the wire, rod or ribbon (these are the only substrate shapes to which this approach may be applied).

The purity of the deposits naturally depends on the purity of the reagents used. Brittle, rough, discoloured metal deposits can be formed when oxygen, nitrogen, water vapour, oxyhalides and hydrocarbons are present.²⁶ The effects of all these factors can be modified by altering the carrier gas, or by using small amounts of additives.

Deposition rates are a function of the material deposited and of the method used, so the thickness of the deposit can be satisfactorily varied over a wide range. Deposition efficiency (ie. the ratio of material deposited to volatile reactant supplied) varies enormously with the conditions used.

1.2.9 Experimental Requirements

Regardless of the process used in CVD the basic equipment required only consists of the vaporizer and the deposition chamber.

1.2.9a Vaporizer

Transport can occur unaided when the reactant has a high vapour pressure. If a high reactant vapour pressure is not available, transport can be aided by a carrier gas which can either be inert or reducing. Solid or liquid reactants may be vaporized directly into the carrier gas from a bulb or bottle vaporizer. A more elegant design needs to be incorporated, however, if better control over

vaporization rates is desired. Close control of this rate is necessary when deposits of controlled thickness are required, or when alloys or compounds of a particular composition are to be deposited by simultaneous vaporization of reactants from two or more separate vapour sources.

Vaporization from a liquid can be more closely controlled than that from a solid, owing to poor heat transfer effects and the variable area of subliming system in the latter case. Vaporization of liquids from a bubbler virtually saturates the carrier gas with the reactant vapour, especially if the gas-inlet tube ends in a porous glass sinter. The gas stream is not saturated if the residence time in the vaporizer is too short because of a high gas stream flow and/or a low reactant surface area, or if the reactant is picked up in the form of droplets. Use of a porous sinter in a bubbler may generate spray droplets which can then collect on warmer downstream surfaces. Here they can evaporate at a higher temperature than the vaporizer temperature and produce a variable and too concentrated vapour. The droplets may also be carried to the substrate surface itself where they, on decomposition or reduction, tend to nucleate growth defects.

If the liquid is quite volatile at the temperature of vaporization, substantial cooling of the liquid may occur owing to the extraction of the heat of vaporization from the liquid rather than the surroundings. Thus an appreciable temperature gradient may exist between the bulk of the liquid and the interior of the bubbles, making the determination of the actual temperature of vaporization extremely difficult. This temperature difference increases with increasing gas flow rate, causing the degree of vaporization of the liquid to be a non-linear function of the gas flow rate.

By passing the carrier gas over the surface of the liquid

or solid without bubbling, the above difficulties of spray formation and liquid cooling can be avoided. Unfortunately the carrier gas is usually far from being saturated. The rate of vaporization is now diffusion controlled and as the liquid has a known and constant surface area exposed to the carrier gas, a constant gas-film thickness at the interface and a reasonably constant surface temperature, the rate of vaporization will tend to be constant and independent of the gas flow rate.

Thus a constant concentration of reactant tends to be obtained in the bubbling vaporizer while a constant flux is found with the non-bubbling diffusion type. This generalisation applies when medium to low gas flow rates are used and laminar flow conditions are present in the latter case. High carrier gas flow rates are undesirable, producing irregular vaporization rates in both cases.

With solids saturated vapour conditions are sometimes obtained by operating the vaporizer at a temperature close to the melting point of the solid. If vaporization from the liquid phase produces an atmosphere too rich in coating reactant, the carrier gas flow may be split in order to by-pass a proportion of the carrier gas around the vaporizer.

Rather than vaporizing the solid or liquid, the reactant can be generated in situ. This is desirable when the reactant is hygroscopic and/or toxic. However, in this method, the reactant gas stream contains a number of gases rather than the single gas required. For alloy and doped mixed oxide deposition, where mixtures of specified composition are required, simultaneous vaporization from two or more vaporizers may be required.

No matter what means of vaporization and transport is used, the transfer lines must be kept at least as hot as the

source to prevent condensation of the reactant, but not hot enough to cause premature reduction or dissociation.

Numerous kinds of flow-meters can be used to monitor and regulate the reactant flow, such as a rotameter or an electronic type (where the cooling effect of the mass flow of gas on a hot wire is measured). Both systems are convenient to use, but it is important to calibrate the meter separately for each gas used.

1.2.9b Methods of Heating

The primary determinant of the design of the deposition chamber is the method used to heat the substrate. In addition, the design of the chamber is influenced by the geometry, shape and composition of the substrate, by the nature of the coating required and (in the industrial context) by economic factors. Heating of the substrate may be produced by induction, an external furnace, internal resistance, radiation or conduction from an electrically heated hot plate, electron beam bombardment or by a plasma flame.

In common with some of the other methods, induction heating has the advantage of heating the substrate without heating the walls of the reactor. This is desirable as deposition on the wall is then kept to a minimum, thus reducing the frequency of cleaning. In addition, the chance of gas phase nucleation is reduced, since the reactant gas flow temperature is usually much lower than that of the substrate. Induction heating is not really suitable for non-conductive or poorly conducting substances, wires, long tubes or thin sheets. For these cases, other methods are more applicable and give better deposits. When depositing a metal by induction the substrate supports should be so sited so as not to allow the metal to form a closed circuit. With close-

coupled induction coils the walls of the reactor may become hot enough to allow deposition which can cause short-circuiting to occur. Water cooling and looser coil coupling usually prevents this.³⁴

Resistance heating involves passing an electrical current through a conducting substrate of small cross-sectional area, such as a fine metal wire. Temperature control is sometimes difficult as deformations or kinks in the wire can cause hot spots, which increase deposition rate and alter the microstructure of the deposit. Heating by infra-red radiation does not give high temperatures, and for temperatures up to 1,000° or 1,200°C a heat lamp or photographic lamp is more effective. Solar or electric arc radiation concentrated by the use of mirrors can produce temperatures up to 4,000°C. Heating by radiation results in rapid heating and cooling of the substrate, and it can be used with both electrically conductive and non-conductive materials. It is not a suitable method for substrates of high reflectivity, or transparent materials.

Hot-wall-reactors are mainly heated by resistance elements surrounding the unit. Sharp temperature profiles are obtained and temperature control is relatively simple. However, deposition can occur on the walls and, in extreme cases, gas phase nucleation may occur which can prove uneconomical.

1.2.9c Reaction Chambers

As mentioned above the design of the reactor chamber depends on the geometry and shape of the substrate. If the size of the reactor is large compared to the substrate dimensions most of the reactant passes through without reaction. If the reactor is too small, a low velocity gas stream will be prematurely depleted of reactant, which causes uneven

deposits. Ideally the shape of the chamber should correspond to the shape of the substrate. This provides a reasonable gas flow pattern over all the substrate and so promotes a uniform thickness and microstructure.

Low temperature reactors (substrate maintained at a temperature of less than 500°C) are used primarily to produce semiconductors. Heating is usually effected by the resistance method and the pressure is atmospheric. The reactors used can be classified into four basic types:³⁵

1. Horizontal tube displacement flow,
2. Rotary vertical batch,
3. Continuous extended slotted disperser,
4. Continuous laminar flow nozzle.

Horizontal tube displacement reactors (see Fig. 7a) continually supply fresh quantities of carrier and reactant gases, which are usually mixed at the point of entry. The mixed stream passes over the substrates placed on a tilted carrier. This arrangement protrudes the downstream substrates further into the boundary layer and thus minimizes depletion.

Rotary vertical batch reactors (see Fig. 7b) have the substrate wafers rotating above a resistance heater. The chamber can be cylindrical, conical or hemispherical. The incoming gases mix gradually with the partially reacted gas before passing over the substrates. Changes in gas composition can be effected gradually therefore, in contrast to the case of the horizontal reactor, which is desirable if two layers with a graded interface is needed.³⁶ The rotary movement of the substrates ensures maximum uniformity of deposition.

Continuous reactor systems are useful in the large scale production of oxide and glass films. A commercial reactor³⁷

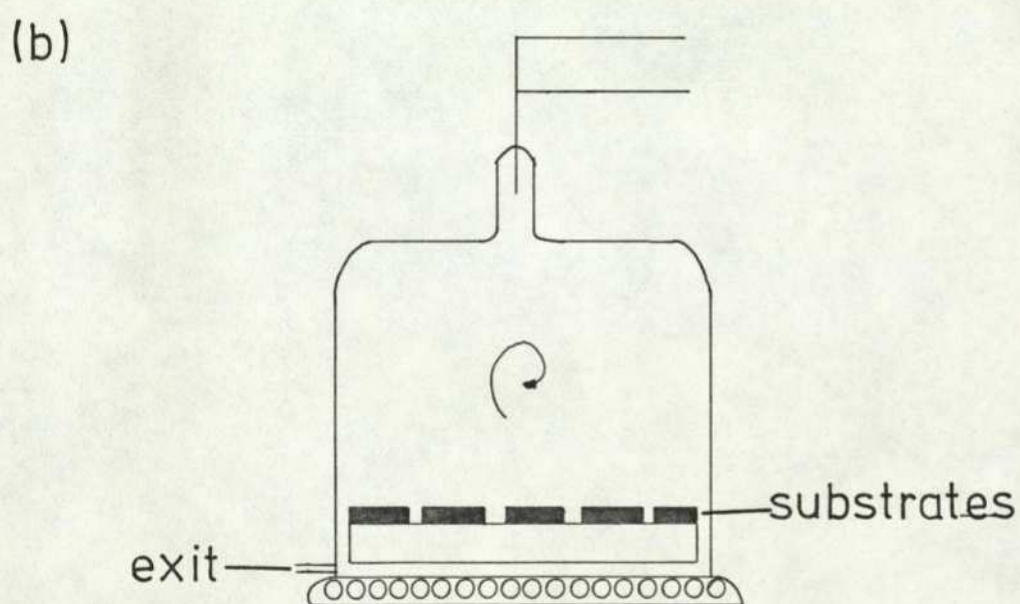
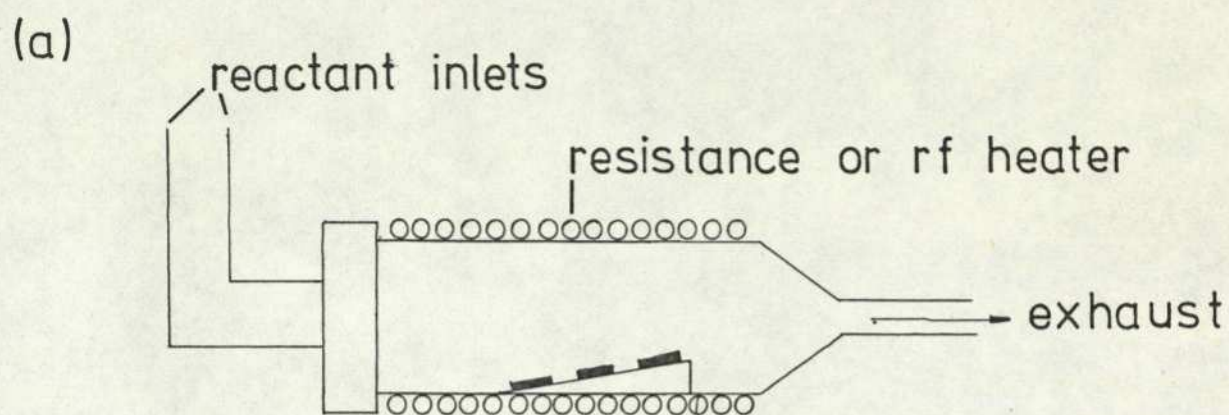


Fig 7. Reactors.

- (a) Horizontal tube displacement flow,
(b) Rotary vertical batch.

Taken from reference 35.

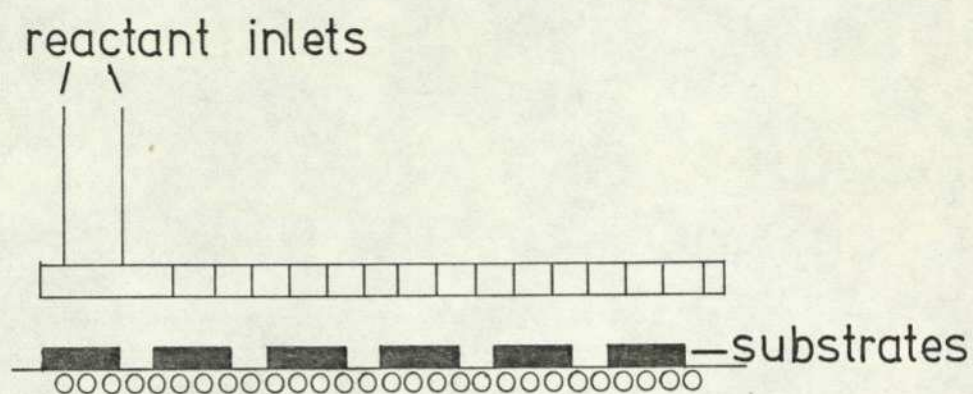
moves the substrate wafers on a conveyor through the reaction zone at constant speed. The reactant gases are pre-mixed, passed through a slotted disperser plate, from which they flow in laminar fashion over the wafers (Fig. 8a). The cross flow dispersion and short wafer to dispenser spacing (1cm) minimizes gas phase nucleation.

In laminar flow nozzle reactors the hydrides and carrier gases are directed through separate laminar flow slots, mixed and reacted in the space between the nozzle and the wafers (2.5mm), forming oxide or glass films (Fig. 8b).

High temperature reactors can be divided into the hot-wall and cold-wall systems mentioned earlier. Hot-wall reactors are used to produce Group III-V and II-VI semiconductors. Cold wall reactors are extensively used for epitaxial deposition of silicon. Fig. 9. shows some reactor types used for these processes. The substrate is the only area, which is directly heated, but the walls of the reactor can be above 500°C when only air cooled, which is nevertheless insufficient to initiate silicon deposition. The walls are water-cooled if silane is used as reactant, but only air cooled when silicon tetrachloride is employed.

In the horizontal and "barrel" reactors r-f heating is most commonly used, though some commercial reactors use high intensity radiation lamps. The incoming gases constantly replace the product gases and so downstream depletion is a problem. By slightly tilting the susceptor the reactor cross-section is decreased and the linear velocity increased. This leads to a thinner boundary layer and hence a faster rate of transport of reactant, which tends to compensate for the downstream depletion. Large amounts of power are required for the above reactors and some 60% of the reactant is wasted.^{30,38} A new reactor has been introduced recently therefore,³⁸ to help improve the efficiency of silicon deposition. Fig. 10. shows a

(a)



(b)

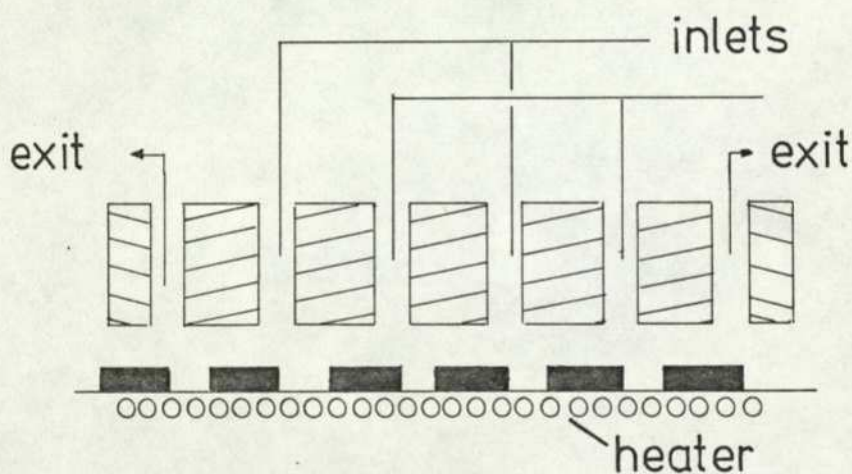


Fig 8. Reactors.

(a) Extend area slotted disperser,

(b) Laminar flow nozzle.

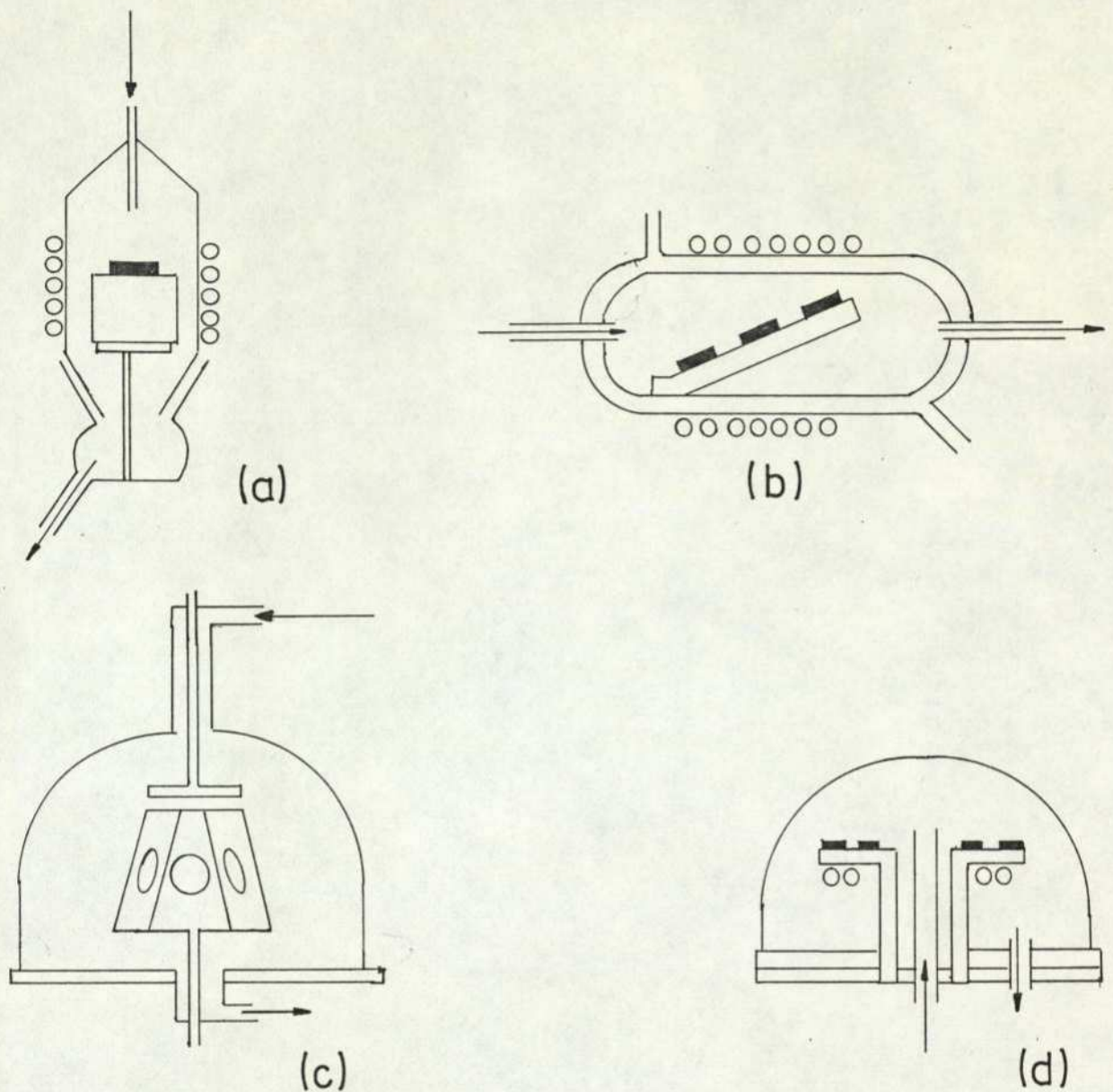


Fig 9 . Reactors .

(a) Single substrate pedestal,

(b) Horizontal,

(c) Barrel,

(d) Pancake type.

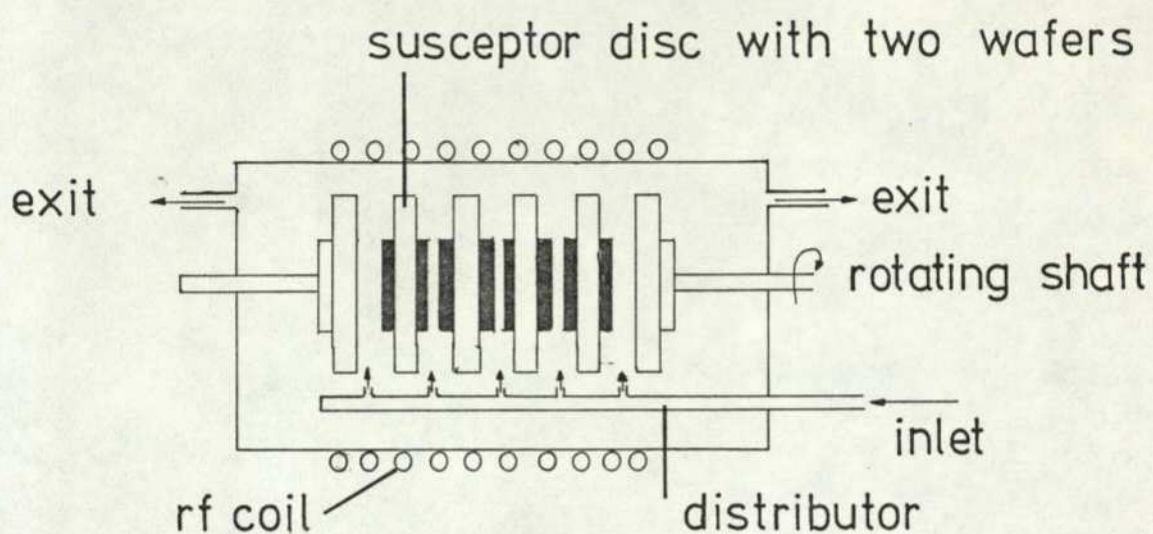


Fig 10 . R.C.A. Rotary Disc Reactor.

Taken from reference 38.

schematic diagram of the RCA rotary disc reactor which combines the capabilities of the atmospheric reactor with the wafer-stack packing of low pressure reactors.

Low pressure CVD reactors are extremely economical in use and give high uniformity of deposition.^{40,41} The substrates are uniformly heated by resistance and can be vertically close packed. Deposits formed on the hot wall are very adherent provided the thickness of the deposit does not exceed 20 μ m. Any particles flaking off do not fall onto the wafer surface due to their vertical arrangement.

The chemical vapour deposition process, as stated earlier in section 1.2.2, consists of a series of steps. The reactants are transported to the substrate, where they adsorb and react on the surface and any gaseous products are then transported back to the bulk gas stream. If the maximum deposition rate is desired, conditions giving rate control by mass transport should be used. (Refer to Fig. 5. section 1.2.2).

When a system contains varying concentrations of two or more constituents there is a tendency for mass to be transferred. The transfer of one component from a region of high concentration to one of lower concentration is called mass transfer.⁴²

Fick's First Law

The amount of a component, either in mass (or molar) units, which crosses a unit cross-sectional area in unit time is termed the mass (or molar) flux. The basic empirical relation defining the molar flux relative to the molar average velocity under steady state conditions is often referred to as Fick's first law. Using the nomenclature of R B Bird et al:⁴³

$$J_{Az} = -D_{AB} \cdot \frac{dc_A}{dz} \quad 1.$$

where J_{Az} is the molar flux per unit cross-sectional area in the z direction.

D_{AB} is the binary diffusion coefficient for compound A diffusing through compound B (sometimes termed the

interdiffusivity) and $\frac{dc_A}{dz}$ is the concentration gradient of A in the z direction.

Equation 1. defines the bulk diffusion of A in the z direction in an isothermal, isobaric system. A more general relation, not restricted by isothermal, isobaric constraints is given by:

$$J_A = -c \cdot D_{AB} \cdot \frac{dx_A}{dz} \quad 2.$$

where c is the molar density of mixture ($= c_A + c_B$) and x_A is the mole fraction of A.

$$\left(= \frac{c_A}{c} \right)$$

In isothermal, isobaric systems, the total concentration c is constant and so equation 2. reduces to equation 1.

An equivalent relation for the mass flux in the z direction is:

$$j_{Az} = -\rho \cdot D_{AB} \cdot \frac{dw_A}{dz} \quad 3.$$

where ρ is total mass density of the mixture,

$\frac{dw_A}{dz}$ is the mass fraction concentration gradient of A, and w_A is the mass fraction of A.

$$\left(= \frac{\rho_A}{\rho} \right).$$

The molar flux in the z direction can be expressed in terms of the molar average velocity:

$$J_{Az} = c_A (v_{Az} - V_z) \quad 4.$$

where v_{Az} is the mass average velocity of A in the z direction,

V_z is molar average velocity for a multicomponent mixture in the z direction.

Equating 2. and 4. one obtains:

$$\bar{J}_{Az} = c_A (v_{Az} - V_z) = -c \cdot D_{AB} \cdot \frac{dx_A}{dz} \quad 5.$$

Rearranging

$$c_A \cdot v_{Az} = -c \cdot D_{AB} \cdot \frac{dx_A}{dz} + c_A V_z \quad 6.$$

But

$$V_z = \frac{1}{c} (c_A v_{Az} + c_B v_{Bz})$$

and using $x_A = \frac{c_A}{c}$, equation 6. becomes:

$$c_A \cdot v_{Az} = -c \cdot D_{AB} \cdot \frac{dx_A}{dz} + x_A (c_A \cdot v_{Az} + c_B \cdot v_{Bz}) \quad 7.$$

As v_{Az} and v_{Bz} are the velocities of A and B in the z direction, $c_A v_{Az}$ and $c_B v_{Bz}$ are the fluxes of A and B in the z direction.

The flux which is relative to a fixed set of stationary axes can therefore be defined as:

$$N_A = c_A \cdot v_A \quad \text{and} \quad N_B = c_B \cdot v_B$$

Substituting this into 7. gives:

$$N_{Az} = -c \cdot D_{AB} \cdot \frac{dx_A}{dz} + x_A (N_{Az} + N_{Bz}) \quad 8.$$

Generalising and writing in vector notation:

$$N_A = -c \cdot D_{AB} \nabla x_A + x_A (N_A + N_B) \quad 9.$$

Therefore N_A , the total molar flux of A, relative to a stationary set of axes is the result of two vector quantities, the concentration gradient contribution $(-c \cdot D_{AB} \cdot \nabla x_A)$ and the bulk motion contribution $[x_A(N_A + N_B) = c_A V]$.

For species A diffusing in a multi-component mixture, the expression equivalent to 9. is:

$$N_A = -c \cdot D_{AM} \nabla x_A + x_A \sum_{i=1}^n N_i$$

where D_{AM} is the diffusion coefficient of A in the mixture.

It is emphasised that the binary diffusion coefficient, D_{AB} , is identical in all equations and either J_A or N_A can be used to describe mass transfer operations.

1.3.2 The Diffusion Coefficient⁴²

The diffusion coefficient or mass diffusivity is basically a proportionating factor in Fick's first law but may be related to the properties of a gas using kinetic theory.

Taking a system containing two near identical types of molecules such as isotopes A and A', consider the rate at which A passes left to right through a unit area in unit time. The unit area is a plane set at right-angles to the z direction, and the concentration of A decreases in the direction of positive z (Fig. 11).

Let the concentration at point 2 be c_A . Then the concentration at 1 is:

$$c_A + \frac{dc_A}{dz} \frac{2}{3} \lambda$$

and the concentration at 3 is:

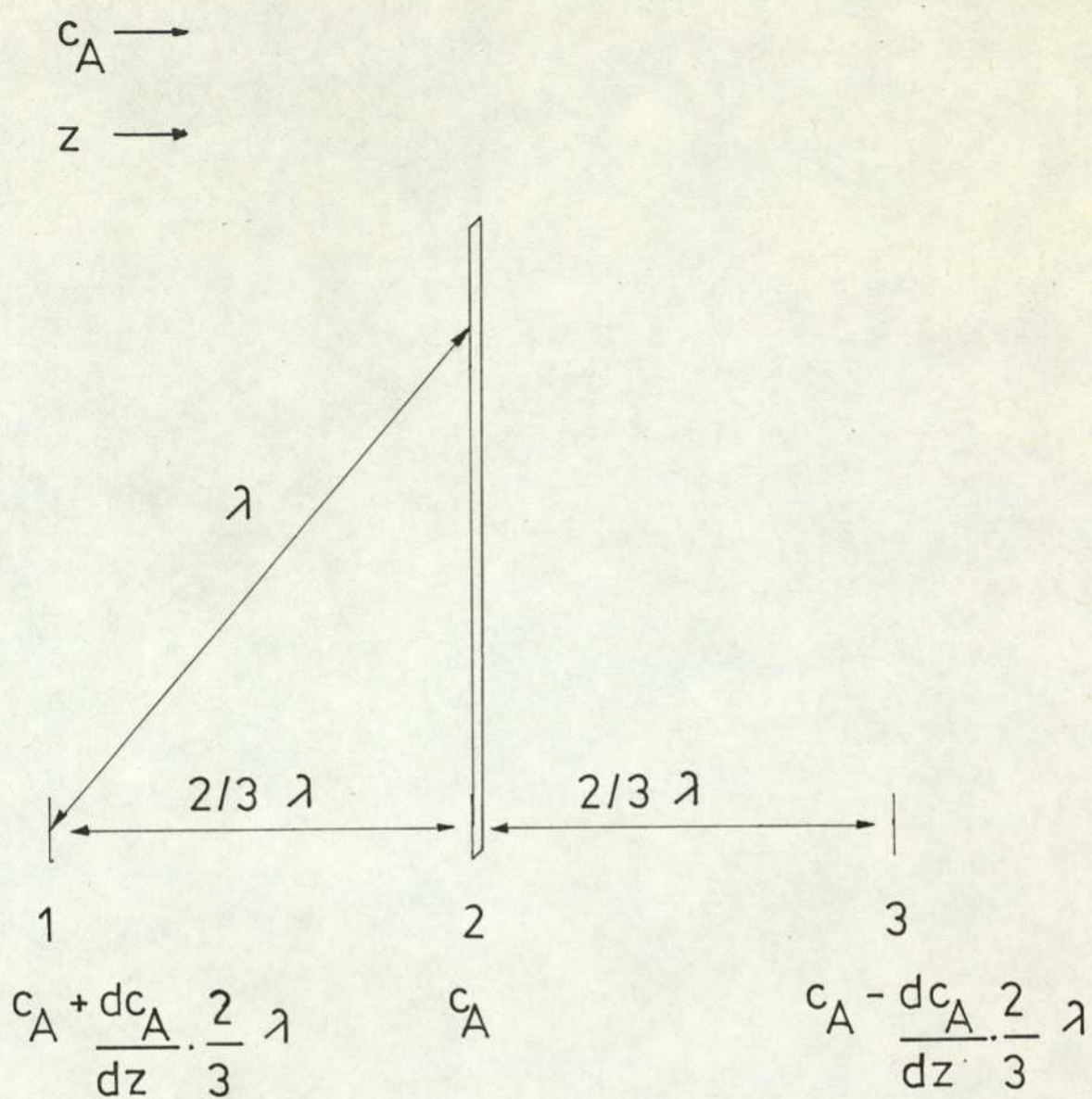


Fig 11.

$$c_A - \frac{dc_A}{dz} \frac{2}{3} \lambda$$

The molecules arriving at the plane have, on average, had their last collision at a distance of $\frac{2}{3} \lambda$, where λ is the mean free path of A in the gas phase. The number of impacts on the plane from left to right is on average $c_A \cdot \bar{u}/4$ (Appendix 1), per unit time and unit area. Therefore the flux from left to right is

$$J(L \rightarrow R) = c_A \cdot \frac{\bar{u}}{4} \quad 10.$$

where c_A is the molecular concentration of A and $\bar{u}$ is the mean Maxwellian molecular velocity.

If points 1, 2 and 3 all have concentration c_A , no net flux would occur, but with the concentrations shown in Fig. 11. one can state that at point 2

$$J(L \rightarrow R) = \frac{\bar{u}}{4} \left[c_A - \frac{dc_A}{dz} \frac{2}{3} \lambda \right]$$

and

$$J(R \rightarrow L) = \frac{\bar{u}}{4} \left[c_A + \frac{dc_A}{dz} \frac{2}{3} \lambda \right]$$

Therefore the net flow from left to right is:

$$\begin{aligned} J_z &= \frac{\bar{u}}{4} \left[\left(c_A - \frac{dc_A}{dz} \frac{2}{3} \lambda \right) - \left(c_A + \frac{dc_A}{dz} \frac{2}{3} \lambda \right) \right] \\ &= - \frac{1}{2} \cdot \frac{2}{3} \lambda \bar{u} \cdot \frac{dc_A}{dz} \\ &= - \frac{1}{3} \lambda \bar{u} \cdot \frac{dc_A}{dz} \end{aligned}$$

Comparing this with Fick's first law gives for the bulk diffusion coefficient

$$D_{AA'} = \frac{1}{3} \lambda \cdot \bar{u}.$$

Substituting in the values for $\bar{u}$ and the mean free path λ :

$$\begin{aligned} D_{A-A'} &= \frac{1}{3} \frac{1}{2^{\frac{1}{2}} \sigma} \frac{kT}{p} \left(\frac{8kT}{\pi m} \right)^{\frac{1}{2}} \\ &= \frac{2}{3} \frac{1}{\sigma p} \left(\frac{k^3 \cdot T^3}{\pi m} \right)^{\frac{1}{2}} \end{aligned} \quad 11.$$

where $\sigma = \pi d^2$, the collision cross-section and p is the absolute pressure in atmospheres.

This equation is really only applicable to a system containing non-polar, monatomic molecules of equal size and mass and having equal average velocities, ie. isotopes. $D_{AA'}$ is thus a self-diffusivity.

More accurate results can be derived for the interaction between non-polar, non-reacting molecules:⁴²

$$D_{AB} = \frac{0.0001858 T^{3/2} \left(\frac{1}{M_A} + \frac{1}{M_B} \right)^{\frac{1}{2}}}{p \cdot \sigma_{AB}^2 \Omega_{D,AB}} \quad 12.$$

where $\Omega_{D,AB}$, the collision integral, is a dimensionless function of temperature and of the intermolecular potential field for one molecule of A and one of B ($\Omega = f\left(\frac{kT}{E_{0,A,B}}\right)$).

There are numerous empirical correlations for the estimation of the diffusion coefficient which are discussed in depth elsewhere,⁴⁴ but the Hirschfelder, Bird and Spotz equation (equation 12) is recommended for use wherever experimental values are unavailable.

1.3.3 Forced Convective Mass Transfer to a Surface

Each chemical system in CVD has its own kinetic parameters but mass-transport characteristics depend mainly on the geometry of the system and are known for most systems

either directly or by analogy with heat transfer processes.⁴⁵

Numerous papers are available in the literature which deal with mass transfer in CVD to flat plates,^{46,47,48,49} cylindrical surfaces^{50,51,52} and in a barrel reactor.⁵³ The theories can easily be applied to spherical surfaces^{45,52} as will be shown.

1.3.3a Theoretical Analysis

The equations for diffusion in an n component ideal gas mixture can be stated as:⁵⁴

$$-\nabla x_i = \sum_{j=1}^n \frac{1}{c \cdot D_{ij}} (N_i x_j - N_j x_i) \quad 13.$$

or

$$-\left(\frac{p}{RT}\right) \frac{dx_1}{d\delta} = (N_1 x_2 - x_1 N_2) (1/D_{12}) + (N_1 x_3 - N_3 x_1) (1/D_{13}) + \dots$$

where δ is the effective film thickness.

For n components there are (n-1) independent variables, as one of the components is dependent upon the others by

$$x_n = 1 - x_{n-1} - x_{n-2} - \dots \quad 14$$

The Stefan-Maxwell equations (above) are a set of simultaneous first-order differential equations. A number of solutions are available to these and ternary solutions have been derived by Benedict and Boas⁵⁵ and Chichelli, Weatherford and Bowman⁵⁶ among others. Unfortunately as the number of components increases, analytical solutions become progressively more difficult to derive, as well as to use, and various approximations

and semi-empirical relations have therefore been used by Wilke,⁵⁷ Carlton and Oxley,⁵¹ Besmann and Spear,⁵⁸ Spear⁵⁹ and Carlsson.⁶⁰

A requirement of the Stefan-Maxwell equations is that a value for the film thickness δ is needed in order to integrate equation 13 between appropriate boundary conditions. The effective film thickness can be obtained by using the Chilton-Colburn "j-factor" analogy⁶¹ between heat and mass transfer,

$$j_H = j_D = f(Re)$$

where Re is the Reynolds number.

The heat transfer correlation for forced convection around a cylinder of diameter d is given by⁶⁴

$$Nu = 0.35 + 0.47 Re^{\frac{1}{2}} \cdot Pr^{\frac{1}{3}} \quad 15$$

and for a sphere

$$Nu = 2.0 + 0.60 Re^{\frac{1}{2}} \cdot Pr^{\frac{1}{3}} \quad 16$$

where Nu and Pr are the Nusselt and Prandtl numbers, respectively.

$$Nu = \frac{h \cdot d}{k}$$

$$Re = \frac{dV\rho}{\mu}$$

$$Pr = \frac{\hat{C}_p \mu}{k}$$

and h = heat transfer coefficient

V = free stream velocity

ρ = density

μ = viscosity
 $\hat{c}_p$ = heat capacity at constant pressure
 k = thermal conductivity.

The corresponding mass transfer correlation is, for a cylinder⁶⁴

$$Nu_{AB} = 0.35 + 0.47 Re^{\frac{1}{2}} Sc^{\frac{1}{3}} \quad 17$$

and for a sphere

$$Nu_{AB} = 2.0 + 0.60 Re^{\frac{1}{2}} Sc^{\frac{1}{3}} \quad 18$$

where Nu_{AB} and Sc are the Nusselt number for mass transfer (Sherwood number) and the Schmidt number respectively.

$$Sc = \frac{\mu}{\rho D''_A}$$

$$Nu_{AB} = \frac{k_g d}{c D''_A}$$

and D''_A = effective average diffusion coefficient of A,
 k_g = mass transfer coefficient.

The effective film coefficient can be defined⁶² as

$$\delta = \frac{d}{Nu}$$

where d = characteristic dimension.

The average mass transfer coefficient, k_g , can be defined in terms of the effective film thickness, according to Wilke,⁵⁷ by

$$k_g = \frac{D''_A P}{RT \delta (pf)_A} \quad 19$$

where D''_A = effective average diffusion coefficient of A.

P = total pressure.

$(pf)_A$ = "partial film factor" for diffusion of A.

The flux of A to a surface is then defined by:

$$N_A = (k_g)_A \cdot P \cdot (x_A - x_{AS}) \quad 20$$

where x_A = Mole fraction of A in the main stream, and

x_{AS} = Mole fraction of A at the surface, assumed to be zero.

The growth rate G is finally defined by:⁶³

$$G = \frac{m_d \cdot N_A}{M_A \rho_d} \quad 21$$

where m_d = molecular weight of the deposit,

M_A = molecular weight of A, and

ρ_d = density of deposit.

Initially the flux (and therefore the growth rate) is calculated between $r = \delta$ and $r = r(\text{surface})$, however, deposition is taking place, thus the characteristic dimension and the effective film thickness are changing with time.

$[\delta = f(d^{\frac{1}{2}})]$. A time t is defined, at which the deposit surface has reached the initial effective film thickness value ie. $[r(\text{surface}) \text{ becomes } (r(\text{surface}) + \delta)]$. One can then use this value to calculate a new film thickness and repeat the above calculations.⁶⁴

The geometry used in this present study is a coil and not unexpectedly no direct correlation has been found in the literature to suit this case. Experimental observations indicate that the coil is best treated as an infinite cylinder initially, with the surface area of the wire used in the coil equal to the surface area of the cylinder.

When the deposit has grown sufficiently so as to obliterate the individual turnings, the best approximation is no longer a cylinder but a sphere of diameter d equal to the pellistor size at any given time.

1.3.3b Definitions and Estimations

Carlton and Oxley⁵¹ do not use the factor $(pf)_A$ in their calculations, but substitute in mean weighted molecular weights of the bulk stream and the film. However, $(pf)_A$ is considered to be a better refinement as it takes into account not only the opposing effect of components diffusing against A but also the "carrying" effect of compounds diffusing in the same direction.

The film pressure factor is defined as:⁵⁷

$$(pf)_A = \frac{P}{\phi_A} (\phi_A - x_A)_{lm} \quad 22$$

where $(\phi_A - x_A)_{lm}$ is the log mean average over the boundary conditions of the film,

$$\text{ie.} \quad (\phi_A - x_A)_{lm} = \frac{(\phi_A - x_{A2}) - (\phi_A - x_{A1})}{\ln \left(\frac{\phi_A - x_{A2}}{\phi_A - x_{A1}} \right)} \quad 23$$

and
$$\phi_A = \frac{N_A}{N_t}$$

N_t = sum of the transfer rates of each component in the +z direction.

For a chemical reaction at a surface with diffusion of components to and from the interface, the ratio of the mass transfer rates for the reaction



becomes

$$\phi_A = \frac{a}{a+b - d-e} \quad 24$$

For equimolar steady state counter-diffusion, assuming a constant diffusion coefficient:

$$\text{Lim}(\text{pf})_A = P$$

$$(\phi_A \rightarrow \infty)$$

The integrated average effective diffusion coefficient, D''_A , given in equation 19 over the diffusion path length, δ , may be determined from⁵⁷

$$D''_A = \frac{1}{\sum_{i \neq A} \frac{x''_i}{D_{Ai}}} \quad 25$$

where x''_i is the effective mole fraction of the i^{th} component, A being excluded from the summation as shown.

Then, for example,

$$x''_B = \frac{(\text{pf})_{AB}}{(\text{pf})_{AB} + (\text{pf})_{AD} + (\text{pf})_{AE} + \dots} \quad 26$$

or, in general,

$$x''_i = \frac{(\text{pf})_{Ai}}{\sum_{i \neq A} (\text{pf})_{Ai}} \quad 27$$

The partial film pressure factors, $(\text{pf})_{AB}$ etc., for diffusion of A into the other gases are given by:

$$(\text{pf})_{Ai} = \frac{P}{\phi_{Ai}} (x'_A + x'_i) (\phi_{Ai} - x'_i) \quad 28$$

where x'_A , x'_i are the arithmetic mean average mole fractions of the components across the film thickness

$$x'_{Ai} = \frac{x'_A}{x'_A + x'_i} \quad 29$$

$$\phi_{Ai} = \frac{N_A}{N_A + N_i} \quad 30$$

D_{Ai} can be evaluated using the Hirschfelder, Bird and Spotz equation discussed earlier in section 1.3.2 (equation 12).

Another problem lies in the estimation of the gas mixture viscosity, which is required for the Reynolds number. Wilke⁵⁷ suggests:

$$\mu_m = \sum_{i=1}^{i=n} \left(\frac{\mu_i}{1 + \frac{1}{x_i} \sum_{\substack{j=1 \\ j \neq i}}^{j=n} x_j \epsilon_{ij}} \right)$$

where

$$\epsilon_{ij} = \frac{\left[1 + \left(\frac{\mu_i}{\mu_j} \right)^{\frac{1}{2}} \left(\frac{M_j}{M_i} \right)^{\frac{1}{4}} \right]^2}{\frac{4}{\sqrt{2}} \left(1 + \frac{M_i}{M_j} \right)^{\frac{1}{2}}}$$

and M_i , M_j are the molecular weights of components i and j .

Finally, the density of the gas mixture can be found from⁴⁹

$$\rho_m = \sum_i x_i \rho_i$$

1.3.3c Effect of Temperature Gradient

For CVD processes in cold wall reactors, especially where the substrate is small compared to the size of the reactor, a steep temperature gradient can exist close to the substrate itself.⁶⁵

The diffusion boundary layer thickness is affected by the temperature gradient at the reaction surface, and the diffusion coefficient itself is strongly temperature dependent. Thus the mass flux to a heated surface is altered with respect to an unheated one. Nevertheless the effect is not too severe - generally reasonable agreement occurs between experiment and theory even if the effect of the temperature gradient is neglected, for the following reasons. If $\frac{dT}{dr}$ is negative (ie. the temperature increases as r decreases) then there is a decrease in the flux of reactant to the surface compared to the isothermal situation and hence a decrease in surface growth rate. This effect is opposed somewhat by the increase in the magnitude of the diffusion coefficient with temperature. For most gases the boundary layer properties are similar and the above two opposing effects often effectively cancel each other out.

The above growth rate calculation assume an absence of surface resistance to deposition. If the actual experimental deposition rate is very much lower than the calculated rate, then surface kinetic control of the rate may be occurring.

Many surface reactions involve interaction between two different species of adsorbed molecules on neighbouring surface sites. The kinetics in such cases is said to conform to the Langmuir-Hinshelwood mechanism.⁶⁶ The extent of surface coverage for each component is usually expressed in terms of fractional coverage θ .

Thus

$$\theta_i = \frac{b_i p_i}{1 + \sum_i b_i p_i} \quad 31$$

where b_i is the Langmuir constant for the i^{th} species adsorbed on the surface. From the statistical mechanical treatment¹¹³

$$b_i = \frac{h^3}{(2\pi m_i)^{3/2} (kT)^{5/2}} \left(\frac{j_{i,\text{int}}^s}{j_{i,\text{int}}^g} \right) e^{(Q_i/RT)}$$

where h is the Planck constant, k the Boltzmann constant, m_i the mass of the i^{th} adsorbed molecule and $j_{i,\text{int}}^s$, $j_{i,\text{int}}^g$ the partition function for the internal degrees of freedom (ie. rotational, vibrational) for the adsorbed (surface) and gaseous forms of molecule i respectively. Q_i is the heat of chemisorption of i on the surface and by convention $Q_i = -\Delta H_i$, p_i is the partial pressure of i above the surface.

The rate of reaction is proportional to the fractional coverage and for two adsorbed species can be expressed by

$$\nu = k \cdot \theta_A \cdot \theta_B$$

or

$$\nu = \frac{k \cdot b_A \cdot b_B \cdot p_A \cdot p_B}{(1 + b_A p_A + b_B p_B)^2} \quad 32$$

where k is the chemical reaction rate constant.

If reactant A is only weakly adsorbed $b_A p_A$ is small, and then

$$\lim_{b_A p_A \rightarrow 0} (\nu) = \frac{k \cdot b_A \cdot b_B \cdot p_A \cdot p_B}{(1 + b_B p_B)^2} \quad 33$$

Here the rate is proportional to the partial pressure of A, but as the partial pressure of B increases the rate increases to a maximum and then decreases.

If reactant B is very strongly adsorbed $b_B p_B > 1$ and

$$\lim_{b_B p_B \rightarrow \infty} (\nu) = \frac{k \cdot b_A p_A}{b_B p_B} \quad 34$$

The rate is now inversely proportional to the partial pressure of B so that, in the catalytic context, B is acting as a poison.

When a reaction occurs between adsorbed A and gaseous B (the Rideal-Eley mechanism) then

$$\nu = \frac{k \cdot b_A \cdot p_A \cdot p_B}{1 + b_A p_A} \quad 35$$

If B can also be adsorbed, but not participate directly but only fills sites A could have occupied

$$\nu = \frac{k \cdot b_A p_A p_B}{1 + b_A p_A + b_B p_B} \quad 36$$

For the latter two equations no maximum occurs in the rate on increasing the partial pressure of either constituent. By careful examination of the experimental data, the appropriate mechanism can be found although ambiguity regarding the details of the mechanism is hard to eliminate. Various papers are available in the literature concerning the surface kinetic mechanism for CVD with uranium carbide,⁶⁷ germanium,⁶⁸ boron on a metal filament,⁶⁹ zirconium oxide, yttrium oxide⁷⁰ and tungsten.⁷¹

The oldest method for the production of alumina by chemical vapour deposition involved hydrolysing aluminium trichloride by the water-gas reaction⁷² in a temperature range between 800° to 1,255°C. The alumina produced between 800° to 1,000°C was grey, microcrystalline and microporous and flaked off the substrate when heated to between 100° and 200°C above the deposition temperature. Gas phase reaction products increased substantially when the deposition temperature was above 900°C. Films produced at 900°C were polycrystalline and became more amorphous as the deposition temperature was lowered.⁷³

Single crystals have been obtained between 1,550° and 1,800°C under low-pressure conditions.⁷⁴ Messier and Wang^{75,76} grew crystals below 1,500°C at 0.5 torr pressure, using water vapour as the reactant gas instead of hydrogen and carbon monoxide. Polycrystalline deposits were formed at 1,400°C, and clear, transparent single crystals at 1,500°C.

Organoaluminium compounds can be used to obtain deposits at lower temperatures. Pyrolysis of tri-isobutyl aluminium in an oxygen atmosphere has been performed^{77,78} and very porous, non-homogeneous thin films were obtained between 250° and 600°C.⁷⁹ Trimethyl aluminium⁷⁸ has also been pyrolysed at 450°C and a growth rate of approximately 10nm min⁻¹ was observed.

Amorphous powders with particle sizes in the sub-micron range have been produced under vacuum at temperatures between 500° and 1,000°C using aluminium isopropoxide as the starting reagent.⁸⁰ Aluminium isopropoxide was also used to produce amorphous alumina films on horizontal quartz substrates, with nitrogen as carrier gas and a deposition temperature of 420°C.⁸¹ The alkoxide was

maintained at 125°C and again a deposition rate of 10nm min^{-1} was obtained using a $10\text{dm}^3\text{min}^{-1}$ flow-rate. The flow-rate had to be increased to $30\text{dm}^3\text{min}^{-1}$ for deposition at 600°C in order to prevent premature decomposition at this high temperature. Overall, the deposition rate was found to be a function of both gas flow and oxygen concentrations. As expected, oxygen aided the decomposition of the molecule. Unfortunately linear velocities are not quoted in the literature so direct comparison is not possible. Oxides deposited at 420°C were optically opaque and very porous, clear, hard transparent films were obtained when the conditions were altered to produce a deposition rate of 6.7nm min^{-1} . The deposition rate was found to be linear with respect to time, and unaffected by the amount of deposit already present on the substrate. The maximum thickness obtained without cracking was $1\mu\text{m}$. Thin platelets of 100nm in diameter were observed on the surface of 50nm and 200nm non-porous thick films, possibly due to the deposition of very fine particles formed by premature decomposition.

Duffy and Revesz,⁸² using the same conditions as Aboaf,⁸¹ obtained films up to 800nm thick. A deposition rate of 10nm min^{-1} was also obtained at 420°C . In some cases rates were reduced to as low as 1.7nm min^{-1} , but no details were given regarding the conditions that produced this change. Uniform films deposited at temperatures up to 700°C were non-crystalline. In contrast, at 925°C the film was polycrystalline.

Deposition between 400°C and 450°C has been carried out with the aluminium isopropoxide source at 120°C .⁸³ A nitrogen flow-rate of $3\text{dm}^3\text{min}^{-1}$ was used through the alkoxide with a nitrogen by-pass of $15\text{dm}^3\text{min}^{-1}$. Deposition rates obtained ranged from 1 to 4nm min^{-1} on silicon and silica substrates, and film thicknesses obtained were between 150 and 500nm . Small amounts of undecomposed organic radicals and/or water molecules may have been

included in the films, but the authors advised further studies to confirm this. Koga et al⁸⁴ increased the deposition rate from approximately 4nm min^{-1} to 45nm min^{-1} by increasing the alkoxide evaporator temperature from 105° to 140°C . Unfortunately no other details of interest are presented in this work.

In a study which conforms more closely to the requirements of this current project McCandless and Withers⁸⁵ coated fine wire substrates with alumina using a CVD technique but they concluded that thick, dense coherent deposits could not be formed from aluminium alkoxides and that only very thin films were practicable. Little further information was given.

A deposition temperature of 500°C with the aluminium isopropoxide maintained at a temperature between 125° and 130°C has been used to coat r-f-heated silicon substrates.⁸⁵ Usually, a deposition rate of about 10nm min^{-1} was obtained and uniform amorphous films up to $1\mu\text{m}$ thick were produced. "Crazing" and "peeling" were found to occur in the thickness range of 0.8 to $1\mu\text{m}$. Films deposited in the presence and absence of oxygen were contaminated with carbon to a level of approximately $0.3\%\text{w/w}$ in both cases.

Hough⁸⁷ used high purity aluminium isopropoxide (abbreviated hereafter as $\text{Al}(\text{O}^i\text{Pr}_3)$) to coat tungsten wires. Deposition rates of nearly $25\mu\text{m min}^{-1}$ were produced at substrate temperatures of 700 to 800°C using a pressure around 1kPa . The coating of amorphous alumina so produced was hard and transparent, but unfortunately very brittle. This lack of mechanical strength apparently resulted from stresses developed while cooling down from the deposition temperature. When depositing alumina under similar conditions upon tantalum wire the deposits did not

develop cracks, and were adherent and tough when handled. Thus the surface morphology reflected the condition of the underlying substrate surface. Hough⁸⁷ was extremely critical of Aboaf's work,⁸¹ suggesting that his compound was not pure enough and perhaps partially decomposed and/or anhydrous conditions were not used, thus explaining the low deposition rates obtained.

Using a vaporizer temperature of 170°C and deposition temperature of 420°C, a growth rate of 20nm min⁻¹ has been obtained, this increased when the oxygen concentration was increased.⁸⁸ Moller and Fabian^{89,90} used a vaporizer temperature of 135°C, and a deposition temperature between 300°C and 500°C to produce deposits between 100 and 400nm thick. A reactant flow of 50dm³ min⁻¹ was used to get a maximum growth rate of 19nm min⁻¹ at 400°C. The growth rate was found to decrease as the substrate temperature was further increased, (10nm min⁻¹ at 600°C). The deposit was found to form "clusters" on the surface.

Al(OⁱPr)₃ has also been used to coat ceramic and glass bodies¹¹² under partial vacuum between temperatures of 371°C and 538°C (vaporizer temperature 232°C). Ammonia vapour was used and found to improve the coating characteristics.

Barybin⁹¹ showed that the pyrolysis of Al(OⁱPr)₃ is a step-wise process involving dissociation of the O-C and Al-O bonds, and the properties of the films so produced depended significantly on the conditions. The best quality films were obtained in a temperature range as narrow as 410°C to 430°C.

Amorphous aluminium and phosphorus mixed oxide films have been obtained at 500°C by mixing aluminium isopropoxide and phosphoryl chloride (POCl₃) vapours.⁹² In another study, trimethyl-siloxy-aluminium diisopropoxide⁹³ has been used to produce a mixed oxide film, and an aluminium

foil has been impregnated with molten $\text{Al}(\text{O}^i\text{Pr})_3$ and then hydrolysed with steam to form alumina.⁷⁷

Aluminium, titanium and zirconium isopropoxides have been hydrolysed⁹⁴ using a deposition temperature of 85°C to produce powdery, amorphous films. Fractures were observed in unannealed films which had been allowed to grow to thicknesses between 300 to 600nm.

A study of the texture of alumina catalysts prepared from different starting materials has been performed.⁹⁵

$\text{Al}(\text{O}^i\text{Pr})_3$ was hydrolysed to a gelatinous alumina mass at room temperature and its gas adsorption properties at 500°C were determined.

The most frequent use of titania is in pigmentation. Titania can be obtained from high temperature oxidation or hydrolysis of titanium tetrachloride vapour to produce very fine powders.⁹⁶⁻¹⁰⁰ Deposition temperatures are typically around 1100°C with total flow rates between 107 and $215\text{cm}^3\text{min}^{-1}$, to produce fine powders.¹⁰¹

Coherent, dense, hard and non-porous thin films have been produced for use in semiconductors by the hydrolysis of titanium tetrachloride or titanium isopropoxide.¹⁰² A reactant flow of $0.2\text{dm}^3\text{min}^{-1}$, and water vapour flow of $1.4\text{dm}^3\text{min}^{-1}$ were mixed 1.5cm away from the germanium, silicon or platinum substrate which was kept at a temperature of 150°C .

Platinum coated quartz has also been used as the substrate at temperatures as high as 900° to 950°C .¹⁰³ Titanium isopropoxide was vaporised at 100°C and a growth rate of 10nm min^{-1} was obtained. Deposition rate depended mainly on reactant concentration and in contrast to alumina deposition, was relatively independent of substrate temperature. Thin amorphous films have been obtained by hydrolysis of $\text{Ti}(\text{O}^i\text{Pr})_4$ at 150°C .^{104,105} Films grown above 550°C show a polycrystalline anatase structure.¹⁰⁶ In addition, deep blue or golden coloured deposits have been grown on amorphous silica between 200° and 800°C .¹⁰⁷ At 200°C amorphous deposits were formed. At 275°C some anatase appeared whilst at 300°C the amorphous material was the minor component. Finally at 400°C only anatase was formed. Titanium isopropoxide has also been pyrolysed in oxygen.¹⁰⁸

Hayashi and Hirai¹⁰⁹ have produced 0.1 to 0.3mm thick films

on single crystal silicon substrates between 100°C and 900°C , by the hydrolysis of titanium tetrachloride vaporized at 20°C . The argon/titanium tetrachloride and argon/water vapour were maintained at 300 and $200\text{cm}^3\text{ min}^{-1}$ respectively. Deposits formed between 100° and 200°C were amorphous, while at 300° amorphous, anatase and rutile structures were observed and finally at temperatures between 400° and 900° the structure was just rutile. When deposited between 400° and 500° a preferred orientation of (301) occurred, and (100) at deposition temperatures of 600° to 900°C . The surface structure consisted of small grains, each grain a well defined crystal whose dimension increased with increase in temperature. At 900°C , small grains were observed to form on the already present large grains. The colour of the deposits depended strongly on the deposition temperature. Between 400° and 900°C deposits were blue and became progressively deeper in colour with decreasing temperature, probably due to oxygen deficiency in the structure. Low temperature deposits (100° to 300°C) were pale brown. Formation of TiO and Ti_2O_3 was not observed.

Ghoshtagore^{110,111} oxidized titanium tetrachloride to produce thin-film rutile titania on silicon wafers over a temperature range of 400° to 1047°C in a horizontal reactor. The reactant was vaporized at 25°C . Deposition rates were not obtained for flow rates less than $5\text{dm}^3\text{ min}^{-1}$ due to non-uniformity of deposits on their substrates. Deposition rates depended on the flow rate, partial pressure of TiCl_4 and oxygen concentration. At all temperatures and partial pressures of TiCl_4 , the growth rate attained a constant value, surface kinetic rate control. For constant TiCl_4 partial pressure, increasing the temperature of the substrate and flow rate prolonged mass transport control. At lower temperatures (less than 827°C) surface kinetics became rate controlling at lower flow rates.

If the partial pressure of TiCl_4 was altered under surface kinetic rate control, the surface reaction was found to be of first order with respect to TiCl_4 at or under 827°C . At temperatures greater than 827°C , the apparent reaction order was greater than 1 and became a function of temperature.

For low oxygen partial pressures the order with respect to oxygen was found to be a half, becoming zero order at an even lower partial pressure. The partial pressure at which zero order kinetics was observed increased with increasing TiCl_4 partial pressure.

Thus

$$v \propto (P_{\text{O}_2})^{\frac{1}{2}} (P_{\text{TiCl}_4})$$

at low values of P_{O_2} for all values of P_{TiCl_4} , and

$$v \propto P_{\text{TiCl}_4}$$

at high values of P_{O_2} and all values of P_{TiCl_4} .

These data indicate that the appropriate mechanism was Rideal-Eley.

Atomic oxygen was adsorbed on the surface and molecular titanium tetrachloride collided with the oxygen adatoms from the gas phase. In the Langmuir-Hinshelwood mechanism both species will be adsorbed, and the rate should pass through a maximum, but since the rate reached a limiting value here the data were more consistent with the Rideal-Eley mechanism. Single silicon crystals were used as the substrate and the rutile deposit had a preferred orientation of (110) when deposited between 357° to 457°C , (101) at 457° to 717°C , (301) between 717° and 852°C and (100) between 852° and 1047°C .

The reasons for the differences in the data produced by the above authors is not clear. The temperature at which rutile TiO_2 was reported to be produced differed in every paper. These differences must be primarily due to the differences in reaction systems, linear velocities and operating techniques.

EXPERIMENTAL

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2.1 Apparatus Design

The apparatus was constructed primarily from 3mm I.D. glass tubing, although 15mm I.D. tubing was used for the gas stream splitter. All taps were constructed from PTFE in order to minimize contamination from grease. GEC-Elliott rotameters were connected via glass-to-metal joints into the apparatus, which were then heated by lagged heating tapes controlled by two "Variacs". Mixing column M3 (Fig. 12) was not heated as this would have affected the calibration of the by-pass rotameter, which enabled a set amount of carrier gas to by-pass the bubbler system and enter the reaction zone. In practice however this by-pass system was little used, as excessive oscillations occurred when it was employed, which prevented the accurate determination of the amount by-passed.

Mixing column M1 was filled with zeolite 5A in order to dry the gas stream before it entered the bubblers. The bubblers themselves were constructed from modified Dreschel tubes with porous P3 sinters.

2.1.1 Details of Reactors

Initial aluminium isopropoxide experiments used a single reactor, the design of which is shown in Fig. 13. The three arms of the gas splitter were joined directly opposite to baffles which were intended to assist the maintenance of an even gas stream composition inside the reactor. Between the baffles six B14 sockets were distributed, into which the PTFE bungs holding the coils could be placed. The coils did not protrude into the main body of the reactor thus giving rise to a static layer of gas round each coil and hence ensuring diffusion control. A large centralised exit tube vented into a fume cupboard. This design ultimately proved unsatisfactory

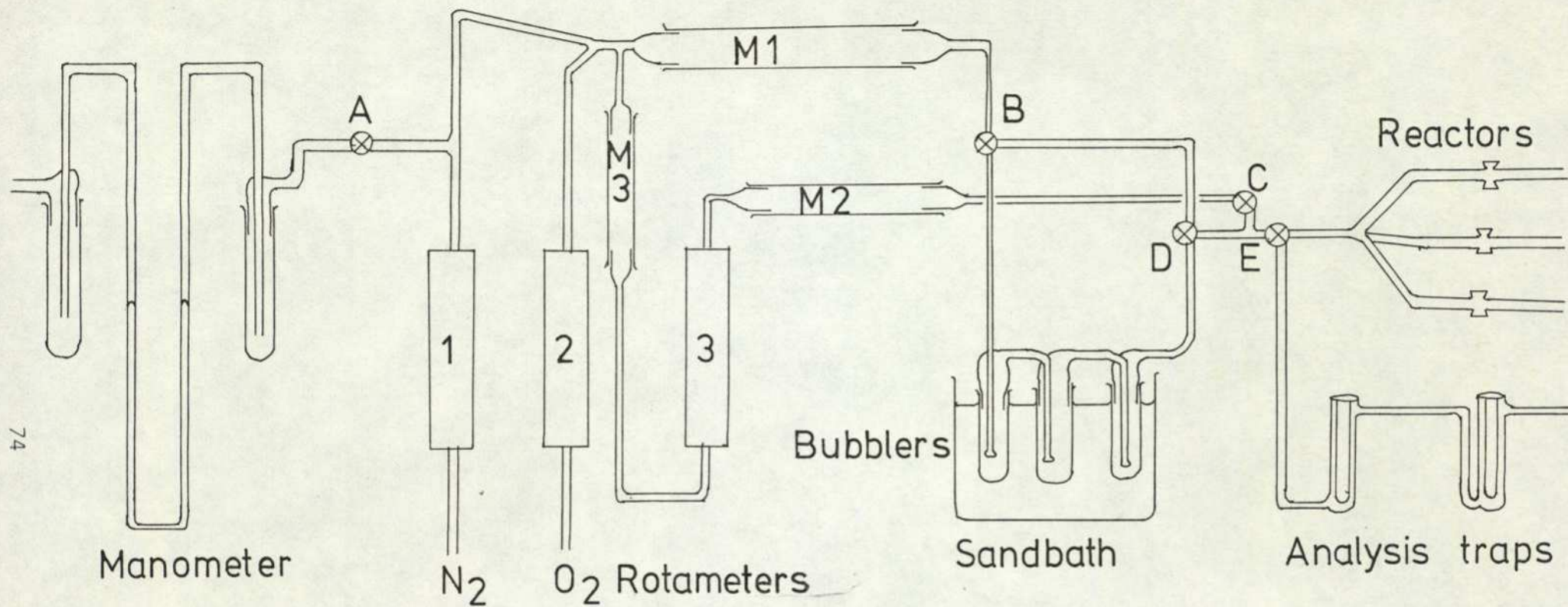


Fig 12. Details of Apparatus.

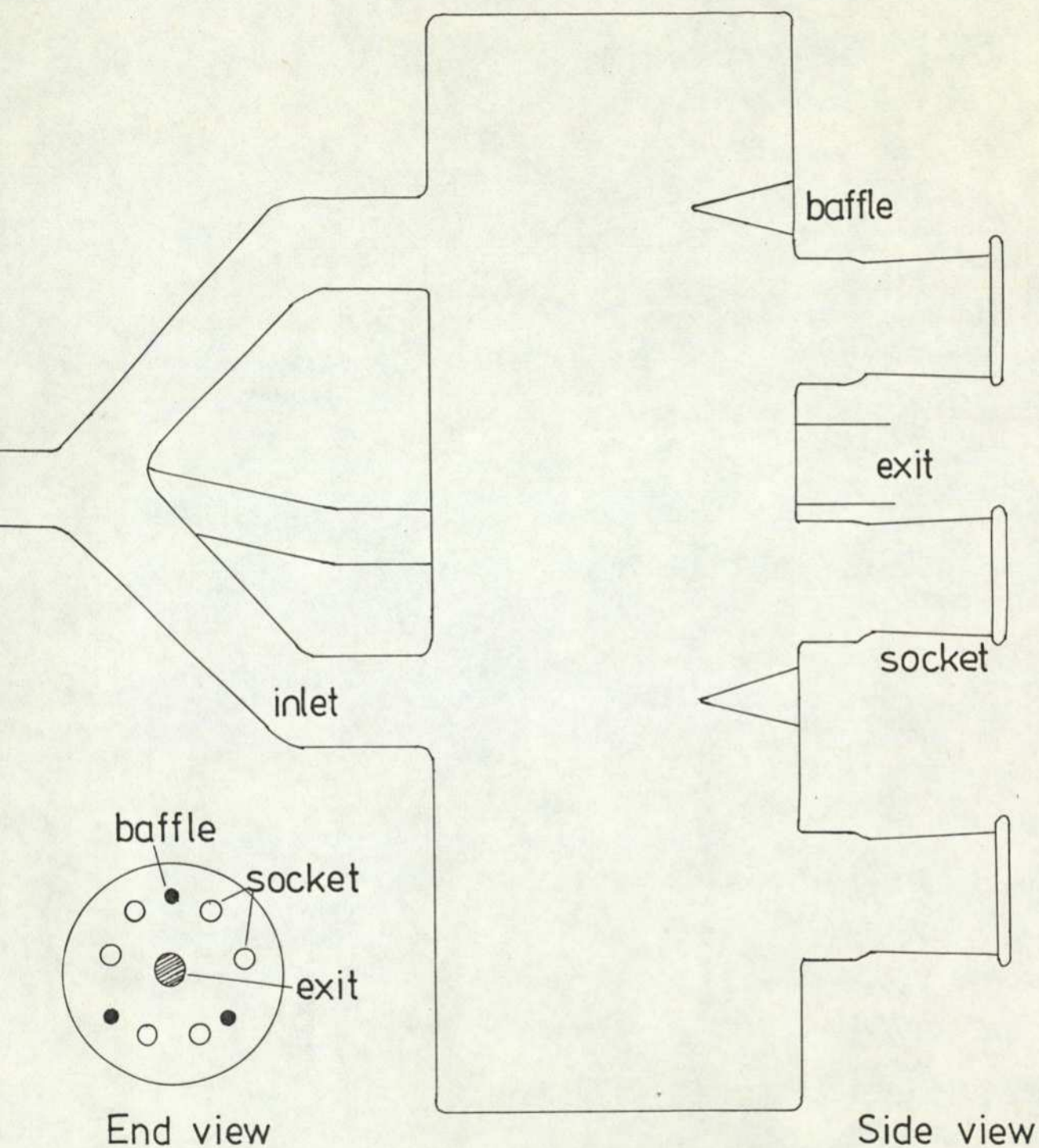


Fig 13.

Views of original reactor.

however as the geometry was such that at high oxygen concentrations the reactant (which tended to build up inside the reactor under all conditions) was explosively ignited by the hot coils, causing the reactor and most of the apparatus line to shatter.

A more conventional design was then used. The original single reactor was replaced by three horizontal reactors, each containing two B14 sockets so that two PTFE bungs could be situated diametrically opposite each other and at right angles to the gas stream (Fig. 14). The bung design was also modified in order to place the coils directly into the gas stream (Fig. 15). The new reactors were constructed from 2cm I.D. tubing, some with and some without baffles. When baffles were incorporated, they were placed before the coils in the gas stream.

2.1.2 Position of Thermocouples

Seven iron-constantan thermocouples were sited at various points on the apparatus. Thermocouples 1, 2 and 3 were situated in "pockets" in mixing column 1 (Fig. 12). The others were placed between the glass tubing and the lagged heating tapes. Thermocouple 7 (T7) was situated immediately before tap B, while T6 was placed after the bubblers. T5 was situated on one arm of the gas splitter and T4 immediately after mixing column 2. The heating tapes surrounding T1, 2, 3 and 7 were controlled by Variac 1 and the others (T4, 5 and 6) by Variac 2.

2.1.3 Calibration of Rotameters

Rotameter 1 (N_2) and rotameter 2 (O_2) were calibrated for nitrogen and oxygen respectively using a gas burette bubble-meter. The calibration curves can be seen in Graphs 1 and 2. (Table 1 Appendix 2).

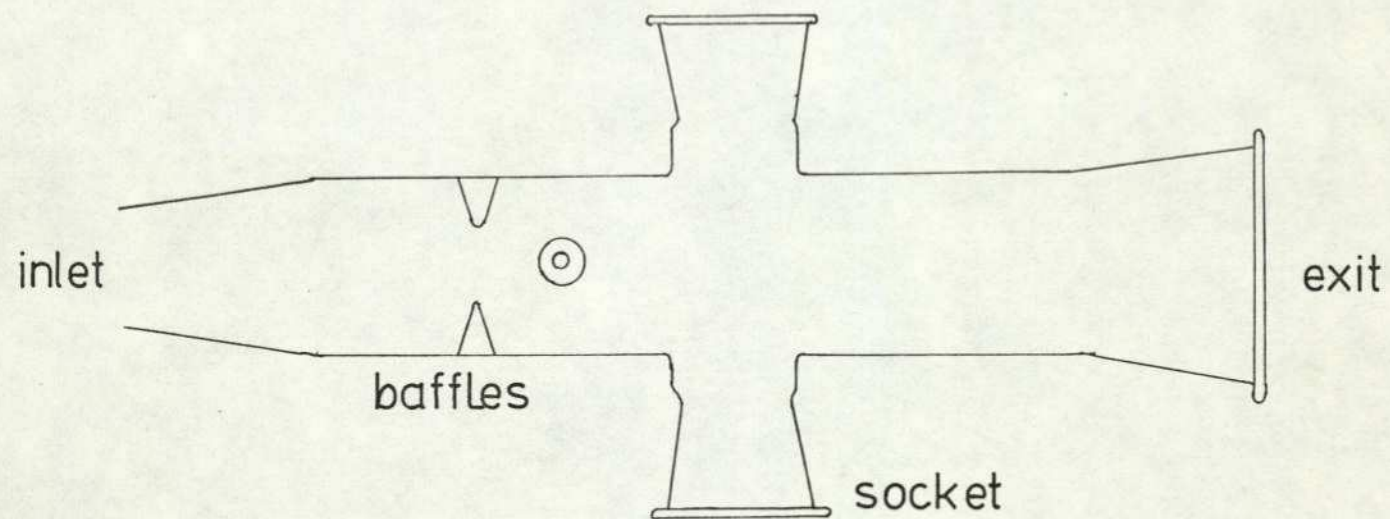


Fig 14. Modified reactor.

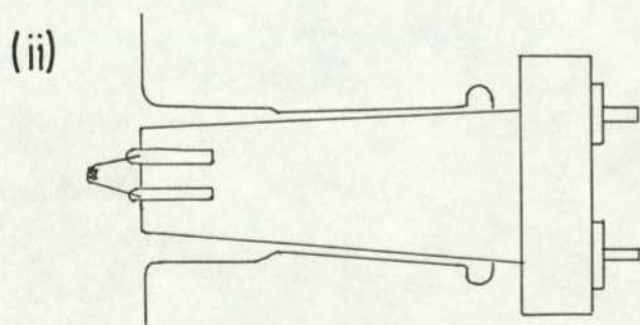
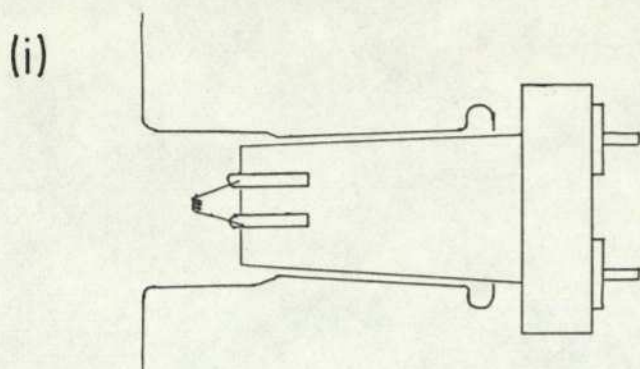
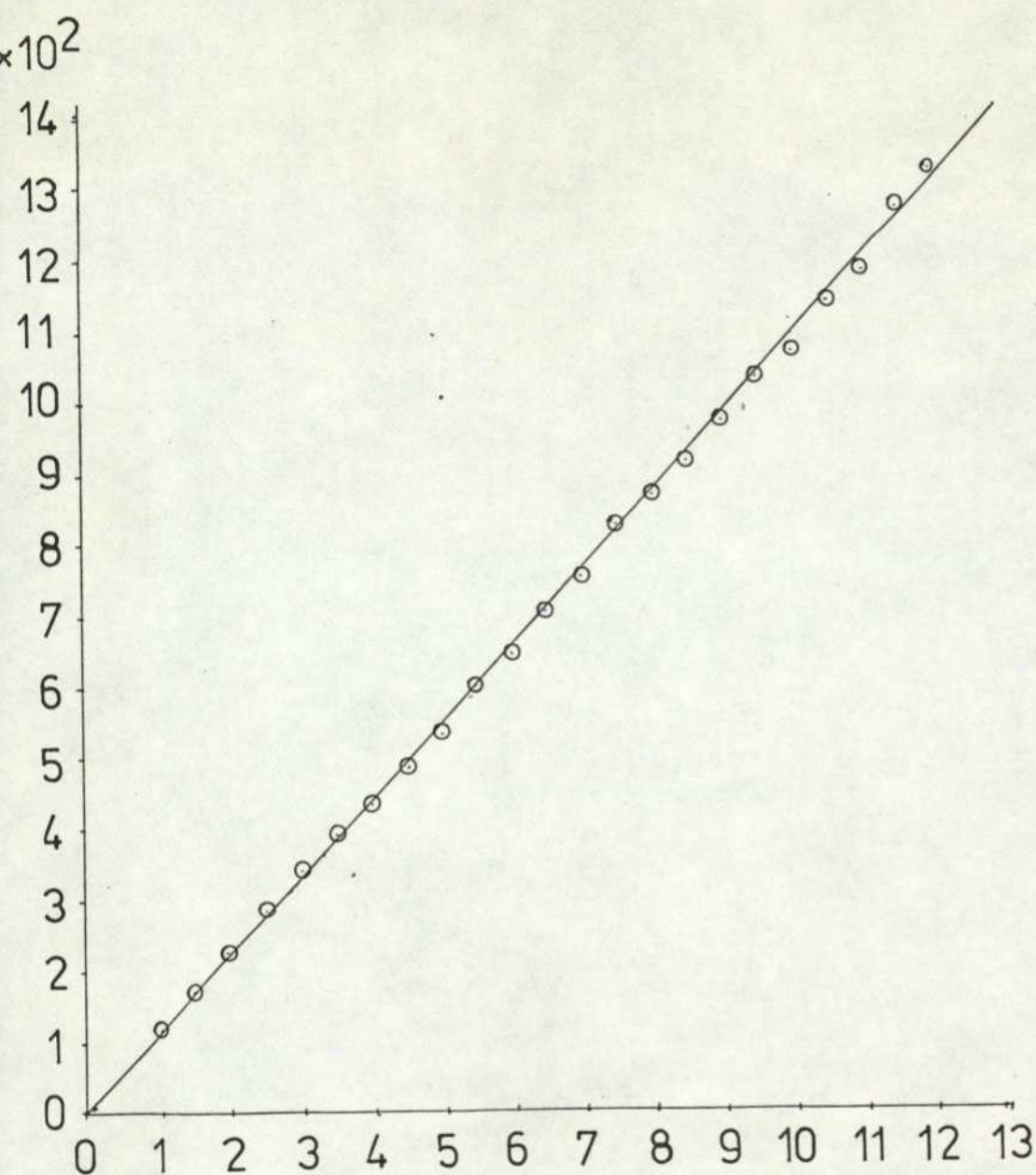


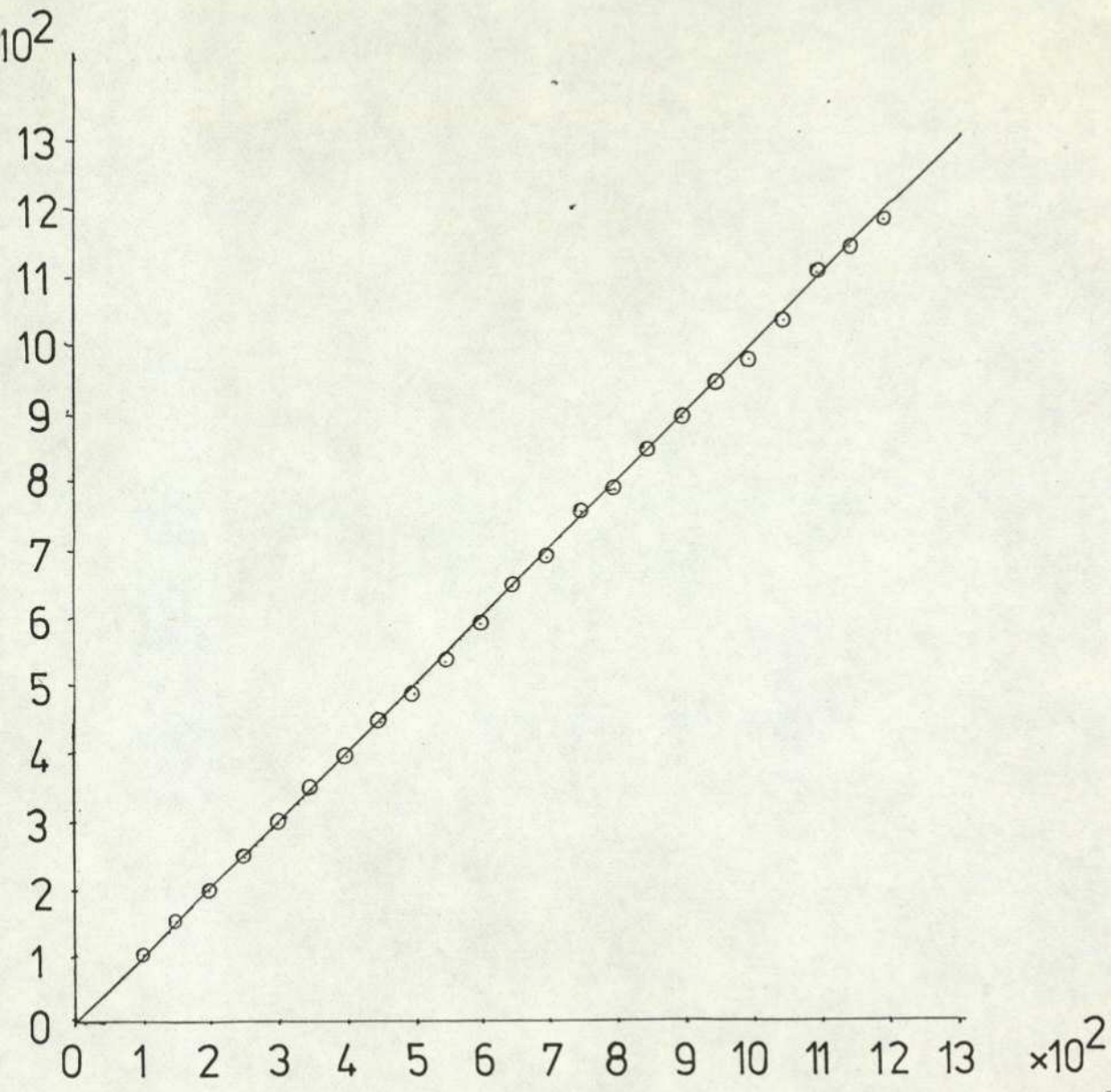
Fig 15. Detail of B14 socket with P.T.F.E. bung.
(i) original design,
(ii) modified design.

Ordinate: measured flow rate / $\text{cm}^3 \cdot \text{min}^{-1}$
Abscissa: rotameter reading / $\text{cm}^3 \cdot \text{min}^{-1}$



Graph 1. N_2 Rotameter Calibration Curve.

Ordinate: measured flow rate / $\text{cm}^3 \cdot \text{min}^{-1}$
Abscissa: rotameter reading / $\text{cm}^3 \cdot \text{min}^{-1}$



Graph 2 . O_2 Rotameter Calibration Curve.

2.1.4 Safety Aspects

All sections of the apparatus beyond the rotameters were shielded on the side away from the operator with a fine wire mesh, and on the side closest to the operator by a 12mm thick clear perspex sheet.

The following procedure was used for both alumina and titania deposition experiments. Platinum coils were spot-welded onto nickel posts set in PTFE bungs, their cold resistance was calculated before being placed into position in the purged reactor(s). By appropriate adjustment of the taps incorporated into the apparatus (Fig. 12), the gas stream was then passed through the bubblers and the reactant was thus transported to the resistance heated coils.

Six platinum coils (0.025mm wire diameter, 0.15mm pitch* and 0.45mm mandrel*) were spot-welded onto six sets of nickel posts using a Slee SM906 resistance spot welder. The cold resistance of each platinum coil was measured and their resistance at any temperature $T^{\circ}\text{C}$ could then be calculated using

$$R_t = R_o(1 + \alpha T) \quad 37$$

Where R_o is the cold resistance and α the temperature coefficient.

The coils were then placed into position in the reactors and electrically connected to a constant resistance (Wheatstone bridge) unit. As mentioned before, all sections beyond the three rotameters were heated by lagged heating tapes, controlled by two "Variacs". A temperature of approximately 130°C for $\text{Al}(\text{O}^i\text{Pr})_3$ runs was employed, but $90\text{--}100^{\circ}\text{C}$ for the TiCl_4 runs was adequate. Before a run, the apparatus was purged for one hour with dry nitrogen gas.

*Pitch can be defined as the distance between two turnings of a coil, and mandrel as the diameter of a turning.

The required amount of reactant, (approximately 15g $\text{Al}(\text{O}^i\text{Pr})_3$ or $30\text{-}35\text{cm}^3 \text{TiCl}_4$) was placed in each of two adjacent bubblers. The third bubbler was kept empty in order to trap any droplets that were carried over in the gas flow system from the two previous bubblers. The bubblers were then connected to the main apparatus via ball and socket joints and placed in a Techne SBS2 fluidized bed which was thermostatically controlled by a Skil series 9 temperature controller (model 2T) at either 125°C (for $\text{Al}(\text{O}^i\text{Pr})_3$) or 30°C (for TiCl_4).

When the reactant had reached the required temperature, the GEC-Elliott rotameters were separately adjusted so as to give a combined flow of nitrogen and oxygen of a pre-determined composition, and the coils were resistance-heated to the desired temperature. By means of tap D (Fig. 12), the gas stream was passed through the bubblers thus transporting the reactant vapour to the reactors. Before entering the reaction zone the vapour stream was split into three, as shown (Fig. 12).

For the first four alumina runs the voltage across each coil was monitored at ten-minute intervals using a Solatron 7040 multimeter. For later work a Linseis six-channel flat-bed chart recorder was used to continuously monitor each coil.

During deposition the back pressure was monitored using a mercury manometer. The rotameters required occasional adjustment in order to maintain a constant gas flow. Iron-constantan thermocouple outputs were monitored using a Solatron 7040 multimeter and the readings converted to centigrade using calibration tables.

When a sufficient deposit had been produced, the temperature of the coils was decreased by suitable adjustment of the Wheatstone bridge circuit. Tap D was then turned to divert

the gas stream from the bubblers back to the main apparatus line, which was then purged with an air mixture to remove any residual reactant.

The bubblers were removed and cleaned between each run. Hydrochloric acid was used for $\text{Al}(\text{O}^i\text{Pr})_3$ reactant, but water was quite adequate when TiCl_4 was employed.

The coils were then disconnected and examined by optical microscopy and/or a Jeol JEM 100B electron microscope.

2.2.1 Calibration of Wheatstone Bridge (Constant Resistance) System¹¹⁸

The constant resistance system consists of six identical circuits (Fig 16) designed to hold the resistance of a platinum coil constant when conditions of heat loss from the coil varies. The balance position is given when the bridge on the left of the circuit is balanced. If the ratio of the coil resistance to 1Ω is higher than the ratio of the 1K variable "set resistance" to the parallel 56Ω and 500Ω resistors, then the potential at point A will be higher than at point B and the input will fall. This reduces the voltage applied to the bridge and the power supplied to the coil. The coil resistance then decreases and balance is restored. If the ratio of the coil to 1Ω is lower than the ratio of the other bridge arm, the potential at A is lower than at B and the power to the bridge will be increased, thus causing the load resistance to increase until a balance is obtained.

The Wheatstone bridge circuits were calibrated by connecting a resistor to the load terminals and observing the voltage and current through the resistance using a Solatron 7040 multimeter. The true resistance of the load was calculated from the standard relation $R = V/I$. This was then compared

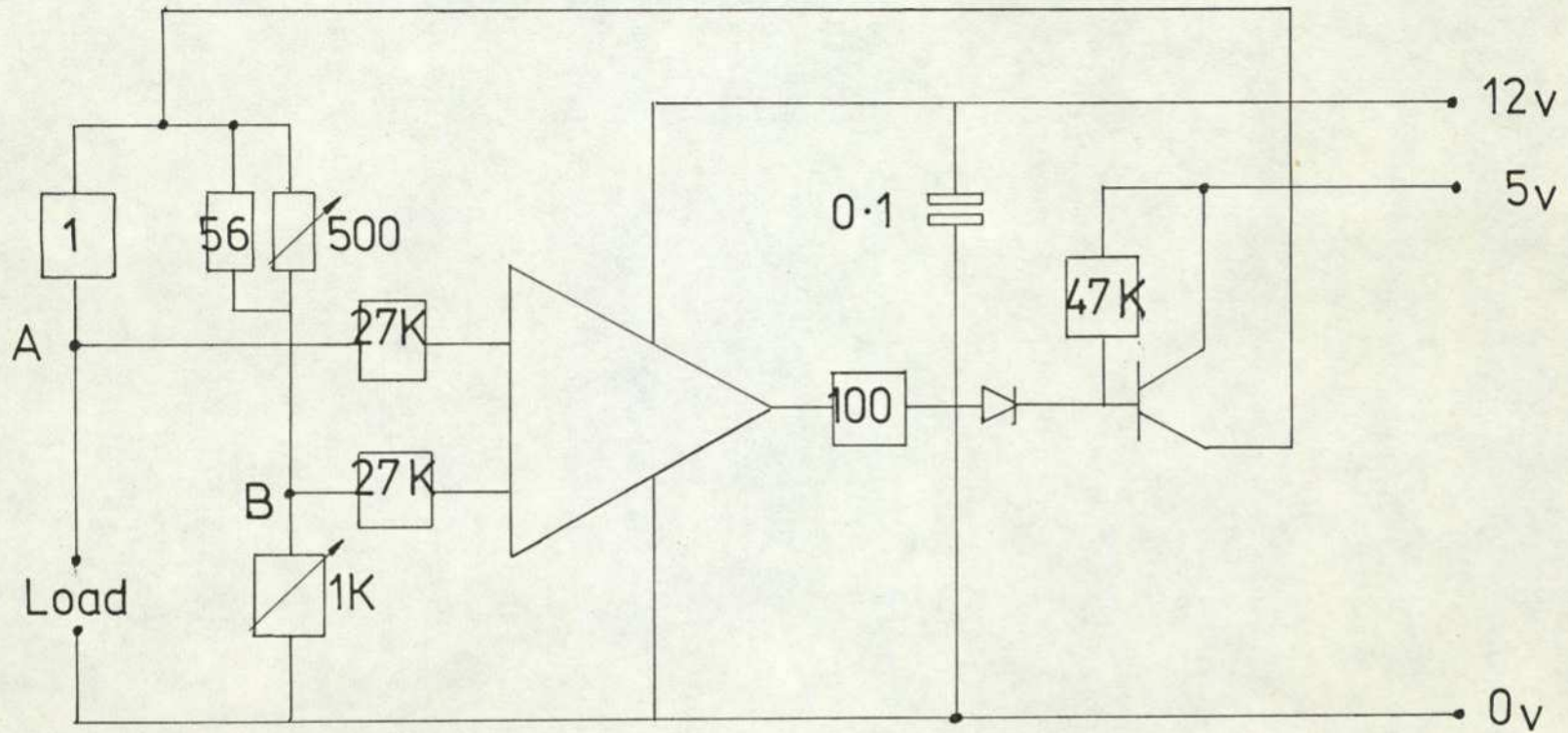


Fig 16. Wheatstone Bridge Circuit Diagram.

to the dial setting (or 1K, ten turn "set resistance"), and it was found that

$$2 \times \text{dial setting} = \text{load resistance.}$$

The results appear in Appendix 2 Table 2.

2.2.2 Determination of Cold Resistance

The cold resistance of coils used for runs A1 to DT3 (see Section 3.0 Chapter 3 Appendix 3) was determined by passing a constant current of 10mA through the coils and recording the resulting voltage using a Solatron 7040 multimeter. From an average of ten readings for each coil at room temperature the cold resistance was calculated using the equation

$$R_o = \frac{R_m}{1 + \alpha T_m} \quad 38$$

where R_o is the cold resistance, R_m the room temperature resistance, T_m the room temperature ($^{\circ}\text{C}$) and α the temperature coefficient ($0.003927/^{\circ}\text{C}$).

The resistance at temperature T was then calculated from equation 37, section 2.2.

Unfortunately the ten readings obtained for each coil frequently had a large variance, therefore the average value taken could be substantially different from the "true" value. Also the constant 10mA current had to be checked repeatedly as it tended to drift. The above procedure was therefore unsatisfactory for accurate temperature control and another method was devised for the remaining experiments.

To find the resistance of the coil at room temperature for runs DT4 to DT52 (Section 3.0 Chapter 3 Appendix 3) the coil was connected to the Wheatstone bridge circuit and the flat-bed recorder. The dial setting on the constant resistance unit (Section 2.2.1) was increased until a sudden increase in voltage was observed (ie. the room temperature balance point had been exceeded). The dial setting was then reduced, in order to imbalance the bridge, and the voltage across the coil was monitored. The dial setting was then slightly increased and a cool air stream passed over the coil. This was repeated until a response in voltage occurred. As the dial setting (and therefore the variable resistance) was set with the coil at room temperature, then when a cool air stream passes over the coil its' temperature is lowered. If the bridge was originally balanced the voltage would increase to compensate for the cooling effect, whereas if the bridge was imbalanced no response would occur. Once the balance point had been determined the dial setting and room temperature were recorded. From the calibration graphs of the Wheatstone bridge units

$$2 \times \text{dial setting} = \text{resistance of coil} \\ \text{at room temperature}$$

The cold resistance was then calculated using equation 38 and 37 (Section 2.2).

2.2.3 Calibration of Recorder

To ensure a good response when measuring the resistance of the platinum coils it was necessary to calibrate the Linseis 6-channel flat-bed recorder. Initially the recorder was allowed to "warm-up" for fifteen minutes. The input was shorted out by moving the function switch to 0, the measuring range set to 500mV and the zero line

shifted to a central position (Fig. 17). The measuring range was then adjusted to 10mV and potentiometer U adjusted until no movement of the chart pen occurred when switched through the 10 to 500mV ranges. The procedure was repeated with the 0.5 to 5mV range using potentiometer V. Finally, the function switch was then put in the "cal" position and the inputs connected. The required measuring range and chart speed could then be selected.

2.2.4 Operation of Slee SM906 Resistance Spot Welder

The following settings were found to give good results when top welding 0.025mm diameter platinum wire onto the nickel posts.

Amplitude current control:	12
Voltage control:	Medium
Time control:	5
Phase shift:	5
Variable:	Half cycle

The resistance spot welder was then operated by means of a foot lever to bring the electrodes in contact with the welding surface.

2.2.5 Operation of Jeol JEM 100B Electron Microscope

The coil was mounted onto a carbon disc using silver paint before being placed inside the microscope. A dark field image was produced so that a white image was seen against a black background. An accelerating voltage of 40kV was used with a spot size 3 and a zero angle of tilt. Heavy deposits of alumina had to be coated with gold to help prevent charging problems. Fortunately

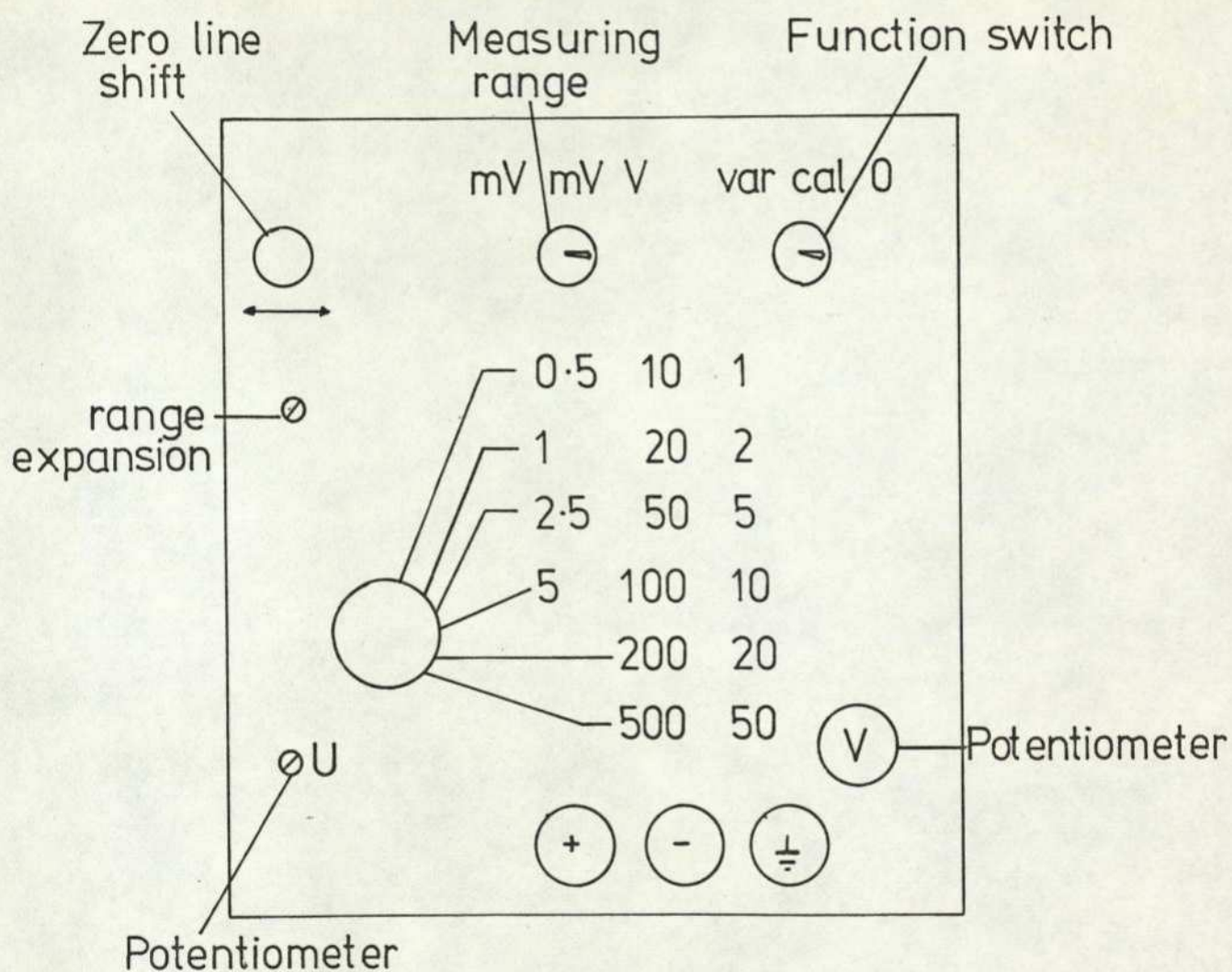


Fig 17. Linseis Chart Recorder
Measuring Module.

titania deposits did not require this treatment.

Micrographs at a magnification of 500x and 2000x were obtained, and examples can be seen in Sections 3.1 and 3.1.1. At magnifications of 500x and 2000x one centimetre on the micrograph is equivalent to 20 μ m and 5 μ m respectively.

2.2.6 Optical Photographs

All optical photographs were taken using a "Nikon Nikkormat" set-focus camera with a two second exposure time.

Magnification and focus were controlled by the "Olympus" optical microscope.

Photographs were obtained at various temperatures and gas mixtures and the build-up of deposit as a function of time could then be measured on the photographs using callipers. The results obtained are in Section 3.2.

Analysis of Aluminium

a) General Method and Observations

Approximately 15g of B.D.H. grade aluminium isopropoxide were placed in each of two adjacent bubblers. The bubblers were then placed in the fluidized bed (see Section 2.1). A measured amount of hydrochloric acid ($\text{pH} < 1$) was placed in each of the two analysis traps situated at the end of the CVD apparatus. By adjusting taps D and E (Fig. 12), the gas flow was passed through the bubblers and transported to the analysis traps. After two hours, the solutions in the traps were analysed for aluminium as follows.

Each trap was emptied and washed out with distilled water, both solutions and washings being retained. The resulting solution was made up to 250cm^3 in a volumetric flask. A 20cm^3 aliquot was then taken and analysed titrimetrically for aluminium.

A clear colourless liquid layer was observed on top of the hydrochloric acid in the analysis traps. This layer, which contained a negligible amount of aluminium, was removed for analysis before the aqueous layer plus washings were made up to 250cm^3 in the volumetric flask. Analysis on the volatile liquid layer by NMR and mass spectrometry indicated that it contained a mixture of at least two long-chain hydrocarbons. Detailed identification of the hydrocarbons was not undertaken.

b) Analysis of Aluminium

The method used followed that of Burke and Davis¹¹⁴ and involved adding an excess amount of 0.05 mol dm^{-3} CDTA disodium salt (CDTA=trans-1,2-diaminocyclohexane-N,N,N',N'-tetra acetic acid monohydrate) to an acid solution containing aluminium. The solution was then buffered with hexamine to a pH between 5.5 and 6 and then the excess CDTA was back-titrated with 0.05 mol dm^{-3} standard zinc solution,

using xylenol orange as indicator.

The order of addition was important. The excess CDTA must be added first, then buffer, then indicator. If buffer is added before CDTA, partial precipitation of aluminium occurs.

Standard Zinc

6.5437g of zinc were dissolved in dilute nitric acid and diluted to 2000cm^3 with distilled water.

Concentration of zinc = $0.050044\text{ mol dm}^{-3}$.

Disodium Salt of CDTA

8.5g of sodium hydroxide were dissolved in 500cm^3 of water. 36.4g CDTA were added and the solution diluted to 2000cm^3 .

Aliquots of the solution were titrated against the standard zinc solution.

Concentration of CDTA = $0.0499\text{ mol dm}^{-3}$.

Test Analysis

15cm^3 of CDTA were added to 10cm^3 of standard aluminium nitrate solution. The solution was buffered, and then titrated with standard zinc solution.

Theoretical Al content: 0.0100g.

Determined Al content: 0.0101g.

2.3.1 Theoretical Aluminium Isopropoxide Content

The above procedure was used to find the percentage aluminium present in the B.D.H. aluminium isopropoxide. The results obtained are shown in Table 3. Appendix 2, and it was concluded that the batch used contained ~ 15% w/w aluminium.

The theoretical amount of aluminium which should be present in the saturated gas stream can be calculated from Raoult's Law

$$X = \frac{\left[p / (760 - p) \right] V_{N_2} M}{22.4 (T_{N_2} / 273.15)} \quad 39$$

for N_2 stream only, and

$$X = \frac{\left[p / (760 - p) \right] (V_{N_2} + V_{O_2}) M}{22.4 (T_{N_2/O_2} / 273.15)} \quad 40$$

for a N_2/O_2 gas stream.

X is the quantity (g) of $Al(O^iPr)_3$ present, p the vapour pressure, V_{N_2} , V_{O_2} the volumes of nitrogen and oxygen respectively, T is the temperature of the gas stream and M the molecular weight of $Al(O^iPr)_3$.

A comparison of theoretical and experimentally determined weight can be seen in Appendix 2 (Table 4(a) and 4(b)).

Since the thermocouples were situated between the heating tapes and the glass tubing, uncertainty arose as to the actual temperature of the gas stream. The calculations were therefore performed over a range of temperatures. Generally the quantity of aluminium found experimentally was substantially less than that calculated.

Vaporization of liquids from a series of bubble-type vaporizers, each involving a porous glass sinter should virtually saturate the carrier gas with reactant vapour. However, as the alkoxide is quite volatile at the temperature of vaporization, substantial cooling of the liquid must have occurred due to the extraction of the heat of vaporization from the liquid. Therefore an appreciable temperature gradient must have existed between the bulk of the liquid and the interior of the bubblers, making determination of the actual temperature

of vaporization extremely difficult. It is probable therefore that the vapour pressure values used in the above calculations were too high, and this is the major cause of discrepancy between theory and experiment. Another problem was that condensation of the aluminium isopropoxide occurred in the apparatus lines, thus depleting the reactant concentration in the gas stream. It was not possible to increase the heating of the lines further without premature decomposition of the reactant taking place.

It was apparent from the above studies that estimations using Raoult's Law were inadequate, and frequent chemical analysis of the aluminium content in the flow were essential.

2.3.2 Theoretical Titanium Tetrachloride Concentration

Theoretical amounts of titanium tetrachloride present in the gas stream were also calculated from Raoult's Law (equations 39 and 40). Vapour pressure data was obtained from Perry and Chilton¹¹⁵. Table 5. Appendix 2. shows the results obtained using the maximum and minimum gas stream temperatures.

Unfortunately no experimental analyses could be performed as TiCl_4 could not be efficiently extracted from the gas flow.

In order to calculate the theoretical mass transport controlled growth rate of titania it was necessary to perform some initial calculations.

2.4

Calculation of Density and Viscosity

The density of each individual gas was calculated from kinetic theory⁶⁶

$$\rho = \frac{3p}{c^2} \quad 41$$

where ρ is the gas density, p the pressure and c the root mean square velocity.

$$c = \left(\frac{3kT}{m} \right)^{\frac{1}{2}} \quad 42$$

Substituting 42 into 41 one obtains for gas A under one atmosphere pressure

$$\rho_A = \frac{M_A}{RT}$$

The results obtained are present in Table 6. Appendix 2.

Viscosity values were also calculated from kinetic theory⁶⁶ when no experimental data were available.

$$\mu = \frac{1}{3} \rho c \lambda \quad 43$$

where λ is the mean free path and

$$\lambda = \frac{kT}{\sqrt{2} \cdot \pi \sigma^2 p} \quad 44$$

Substituting the above equations into equations 43 one obtains

$$\mu = \frac{(kTm)^{\frac{1}{2}}}{\sqrt{6} \cdot \pi \sigma^2}$$

where σ is the molecular diameter.

Where viscosity data were available, the viscosity at temperature T was obtained from the Sutherland equation⁴⁴, viz

$$\mu = \frac{bT^{\frac{3}{2}}}{S+T}$$

A plot of $T^{\frac{3}{2}}/\mu$ against T gives a straight line with a gradient of $1/b$ and intercept of S/b . Viscosity data for oxygen, chlorine and nitrogen was obtained from reference 116. S and b values are presented in Table 7. Appendix 2.

The gas viscosities obtained can be seen in Table 8. Appendix 2.

2.4.1 Calculation of Binary Diffusion Coefficients

Binary diffusivities were calculated using the Hirschfelder, Bird and Spotz equation. (Equation 12. Section 1.3.2. Chapter 1).

$$D_{AB} = \frac{0.0001858 T^{\frac{3}{2}} \left[(M_A + M_B) / M_A M_B \right]^{\frac{1}{2}}}{P \sigma_{AB}^2 \Omega_D} \quad 12$$

where T is the temperature (K), $M_{A,B}$ the molecular weights of components A and B, P the pressure (atm), σ_{AB} a Lennard-Jones force constant (nm) and Ω_D a dimensionless collision integral for diffusion. Ω_D is a function of kT/E_{OAB} , k being the Boltzmann constant. In order to use equation 12 it is necessary to have values of E_{OAB} and σ_{AB} for the gas pair. These are estimated from the force constants of the pure gases by use of the combining rules

$$\frac{E_{OAB}}{k} = \left(\frac{E_{OA}}{k} + \frac{E_{OB}}{k} \right)^{\frac{1}{2}}$$

$$\sigma_{AB} = \frac{1}{2} (\sigma_A + \sigma_B)$$

The collision integral was then found from Table 11-1 in Reid and Sherwood⁴⁴. In cases where the force constants were unavailable they were estimated by

$$\frac{E_O}{k} = 1.21 T_b \quad (K)$$

and

$$\sigma = 1.18 V_b^{\frac{1}{3}} \quad (nm)$$

where T_b is the boiling temperature and V_b the volume at normal boiling point ($cm^3 \text{ mole}^{-1}$). V_b for titanium tetrachloride was estimated from structural contributions¹¹⁵ where each element is assigned a numerical value and the volume calculated by addition of these values. Force constants for O_2 , N_2 and Cl_2 were obtained from reference 44 Appendix G and are listed in Table 9 Appendix 2.

Sample Calculation

$$D_{TiCl_4/N_2} = \frac{0.0001858 T^{\frac{3}{2}} [(28.0134+189.712)/(28.0134 \times 189.712)]^{\frac{1}{2}}}{1 + \frac{1}{2} (0.3798 + 0.5931)^2 \Omega_D}$$

$$\frac{E_{OTiCl_4/N_2}}{k} = (71.4 \times 495.6)^{\frac{1}{2}}$$

$$\frac{kT}{E_{OTiCl_4/N_2}} = 0.005316 \quad T$$

The binary diffusion coefficients so obtained are listed in Table 10. Appendix 2.

4.2 Mole Fractions

In order to find the density and viscosity of the gas mixture it is necessary to evaluate the mole fractions of the compounds in the gas stream. The theoretical amount of titanium tetrachloride at a sandbath temperature of 29°C and maximum gas flow temperature was used for all calculations. (Table 5. Appendix 2). All titanium tetrachloride present was assumed to cross the boundary layer which was of a thickness δ . The O_2/N_2 ratio in the boundary layer was assumed to be equal to that in the gas stream. The arithmetic mean mole fractions obtained are listed in Table 11(c). Appendix 4. Tables 11(a) and 11(b) list mole fractions assumed to be present at the limits of the boundary layer.

4.3 Fortran IV Computer Program

A computer program was devised to calculate the density and viscosity of the gas stream mixture, the effective diffusion coefficients of the components in the mixture and the deposit growth rate. The program can be seen in Appendix 4. Further details in Chapter 3.

RESULTS

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The results presented in this chapter are detailed under three basic headings: observations on chemical vapour deposition experiments, some experimental data on deposition rates, and theoretical mass-transport controlled rates.

3.0 General Experimental Trends

A list of the experiments undertaken is presented in Appendix 3, together with the detailed conditions used in each run. The experiments can be divided into four sections; initial runs for alumina deposition using the original reactor (Section 2.1.1. Fig. 13), (Runs A1-A4), alumina deposition using modified reactors (Runs NA1-NA13), feasibility tests on titania deposition (Runs T1-T6) and growth rate determinations (Runs DT1-DT52).

Initial alumina depositions were performed at various temperatures and times with a constant flow rate of $657\text{cm}^3\text{min}^{-1}$ and $\sim 19\%$ O_2 concentration. Similar conditions were used when the modified reactor design was introduced; it was not possible to use higher oxygen concentrations because of the danger of explosion (see Section 3.1). Therefore experiments with long deposition times at a $\sim 19\%$ O_2 level were undertaken in order to build up a thick alumina deposit. This was unsuccessful and attention was then turned to titania deposition.

Feasibility experiments on titania deposition were performed at various oxygen concentrations (18 to 60%) at a flow rate of $\sim 900\text{cm}^3\text{min}^{-1}$. Only one experiment (T6) used an 80% O_2 concentration. This was not repeated because of the possibility of explosions occurring when the gas stream came into contact with the glowing platinum coils. For the rate determination runs, the

flow rate was kept constant (linear flow $\sim 1.6 \text{ cm.s}^{-1}$) and only the oxygen concentration and temperature were varied.

In both alumina and titania experiments the voltage traces indicated the "state" of the coil(s). If the coil was too hot, the voltage decreased and vice versa. If the voltage was extremely erratic this indicated that the coil had broken. With titania beads, however, it was found by experience that if the voltage/time trace was initially smooth and then became erratic an extremely heavy coating had been produced.

3.1 Observations on Alumina Deposition Experiments, Appearance of Aluminium Isopropoxide

Approximately 15g of white $\text{Al}(\text{O}^i\text{Pr})_3$ were placed in bubblers 1 and 2 at the start of a run. On heating to 124°C two phases were seen to separate, one a viscous yellow liquid and the other a white solid consisting of hydrolysis products. Viscous liquid was also present in bubbler 3 and in the base of the reactor (original model; see Section 2.1.1. Fig. 13). During the experiments the alkoxide had a frothy appearance.

Runs Al-A4

Six platinum coils welded to nickel posts set in unmodified (see Section 2.1.1. Fig. 15) PTFE bungs were placed in the reactor and resistance-heated to the desired temperature. All the coils glowed yellow initially. Only sparse coatings were deposited on the platinum, but substantial amounts of white powder were found to deposit on the nickel support posts. As the rate of deposition is a function of the gas flow rate through the alkoxide, it was decided to increase the gas flow from 657 to $925\text{cm}^3\text{min}^{-1}$ (Run A3) maintaining all other parameters constant. Unfortunately, at approximately 15 minutes into the run, the reactor exploded, probably due to a build-up of isopropyl alcohol in the vicinity of the heated coils. The resulting free radical chain reaction extended back into the main body of the reactor, and chain branching reactions involving oxygen and aluminium isopropoxide caused an explosion which destroyed the main body of the apparatus.

Runs NA1-NA13

The general approach was identical to runs Al-A4, but modified reactors and continuous voltage measurement were used. Typical voltage/time traces can be seen in Figs. 18 and 19.

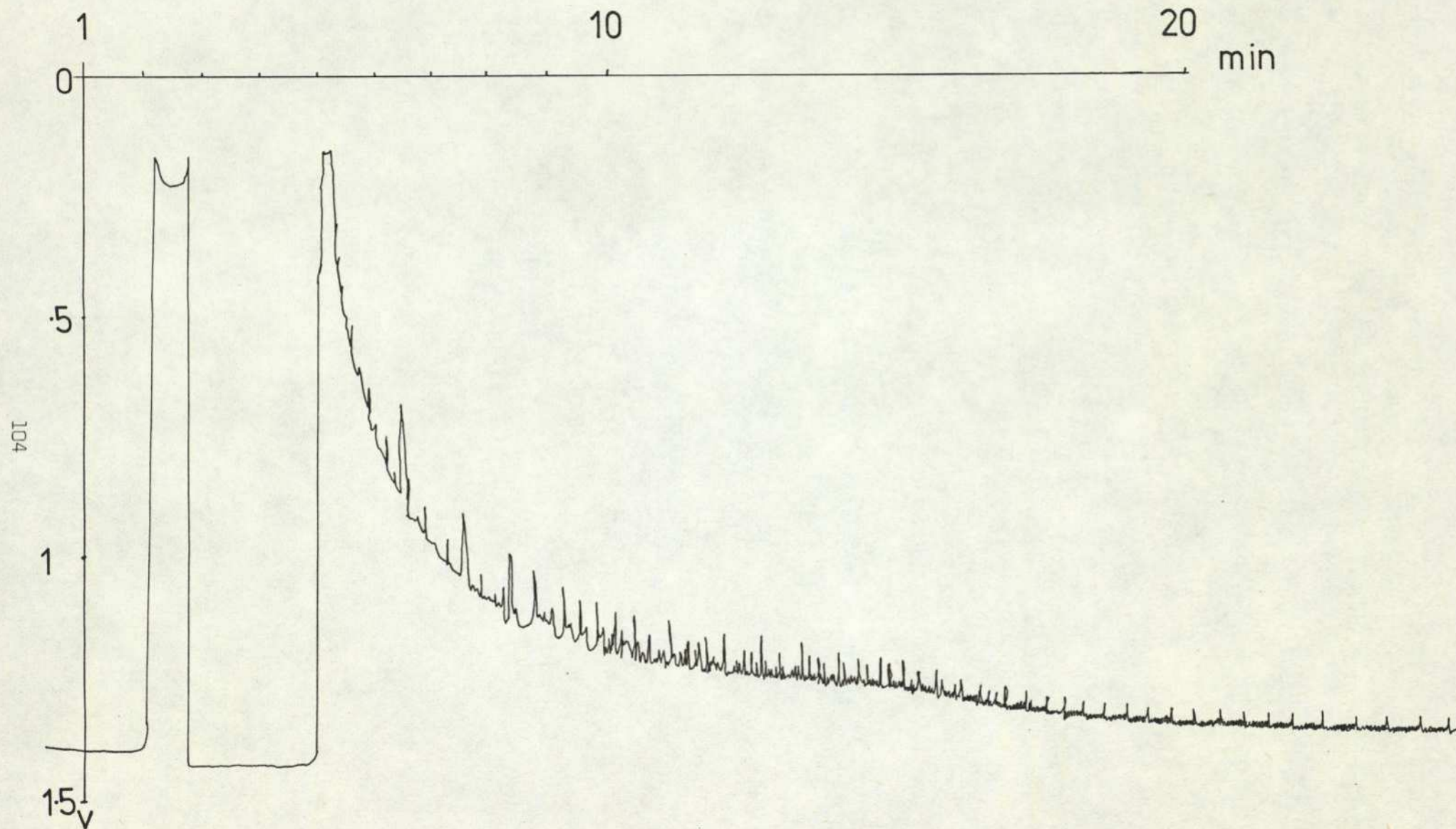
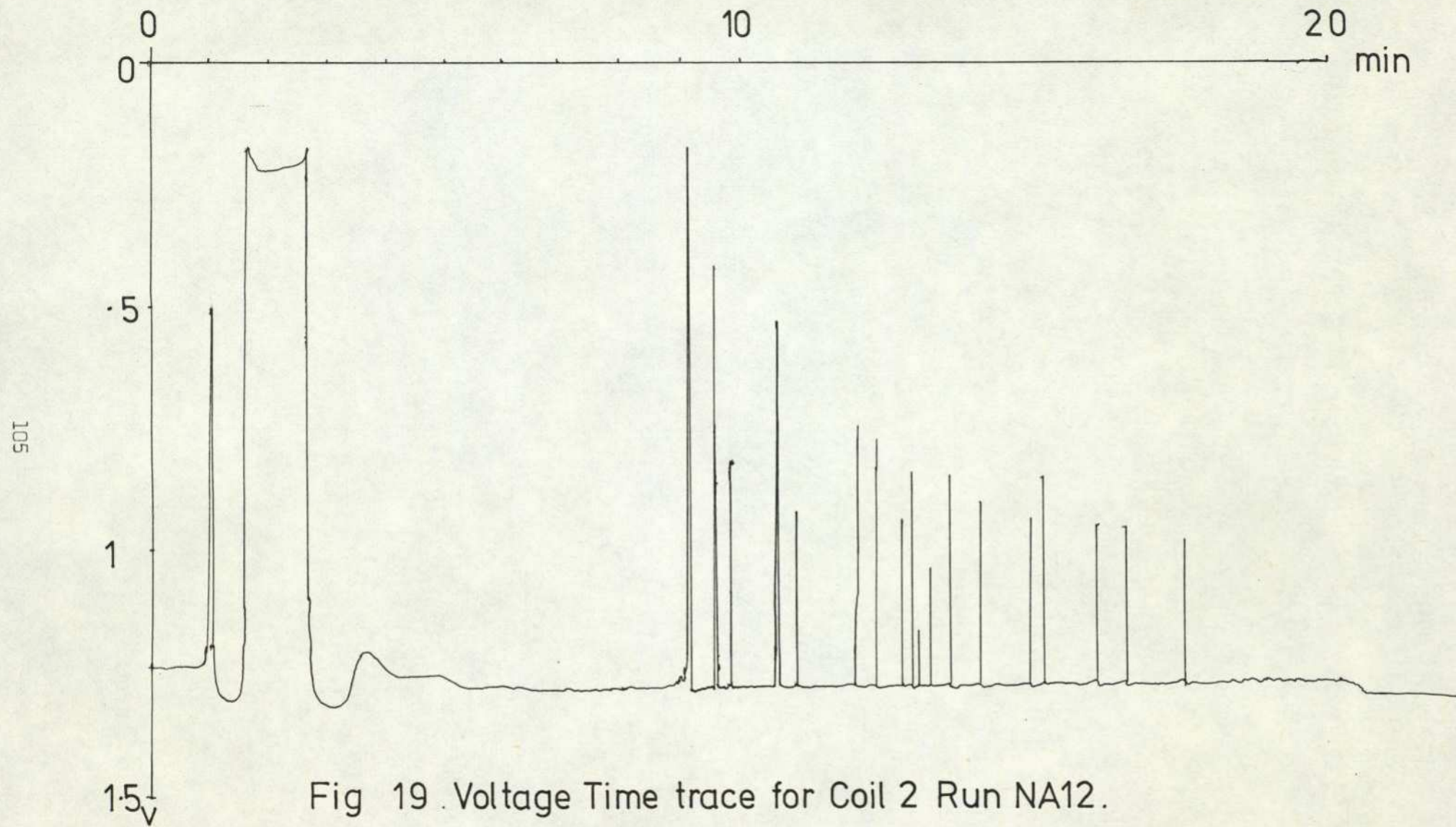


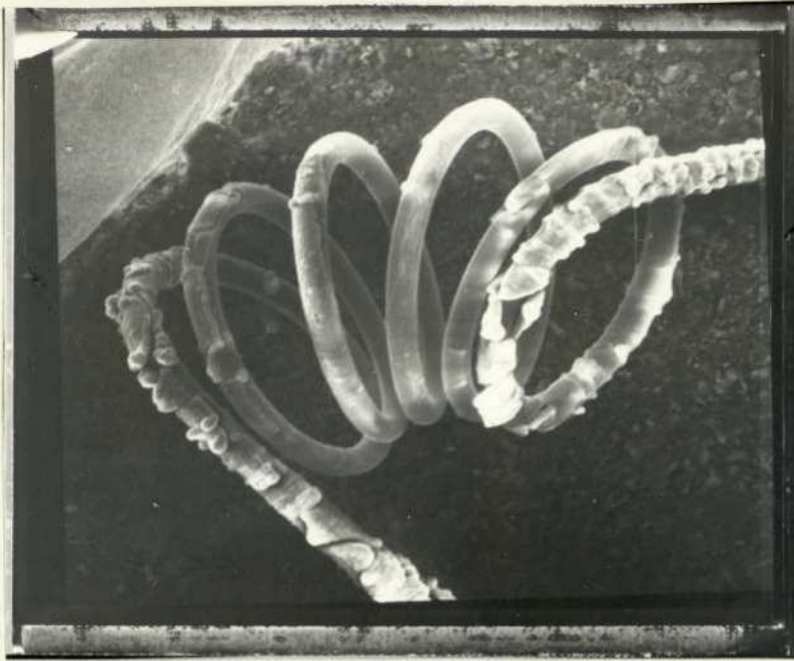
Fig 18. Voltage Time trace for Coil 5 Run NA10.



The low deposition temperatures used in NA1 and NA2 were selected in order to gain experience in using the modified apparatus.

The nature of the deposit obtained varied in character according to the position at which deposition took place. Thus on the platinum posts (the section between the nickel posts and the coil itself) a silvery-white coating at the base became a heavier brown coating further up and then finally developed into a heavier brown-black coating close to the coils. The coils themselves showed a silvery-white deposit in the middle which became darker towards each end. In addition, irregular black residues were present on the outside edges of the coils. Typical electron micrographs can be seen in Fig. 20. It was thought that the black deposits were due to "coking" of the coils, which arose from there being insufficient oxygen present in the gas stream when higher flow rates ($\sim 1300\text{cm}^3\text{min}^{-1}$) were used. The oxygen content was therefore increased from $\sim 19\%$ to $\sim 25\%$, all other parameters being kept constant.

Run NA5 progressed normally for the first five minutes. However, on diverting the gas stream through the bubblers the coils started to glow an intense colour almost immediately. This was followed by ignition of the vapour in the gas stream in the form of a series of minor explosions. Obviously the oxygen content in the gas stream was now too high, thus facilitating complete combustion of the alkoxide vapour as it came into contact with the hot platinum coils. Subsequent runs using oxygen concentrations between 20 and 30% also led to ignition and minor explosions, and it appeared that using high oxygen levels as a means of improving the nature of the alumina deposit was inadmissible.



x50



x500

Fig 20. Electron Micrographs of Alumina .

Attempts were then made to build up complete beads using long deposition times (>24 hours) and different temperatures but with lower flow rates ($\sim 900\text{cm}^3\text{min}^{-1}$) (NA8, 10, 12). Extensive white powdery deposits were formed on the nickel posts, pale brown deposits on the platinum posts and sparse, uneven coatings were obtained on the coil itself. Typical optical photographs are shown in Fig. 21.

In summary, it appears that only thin deposits of alumina can be produced by CVD using aluminium isopropoxide, and that thick, dense, coherent deposits could not be obtained. This is the conclusion of many other workers^{79,81-83,85} who have also studied aluminium alkoxides under different conditions and using substrates of different physical forms. Attention was then therefore turned to producing titania from titanium tetrachloride.

2.1.1 Observations on Titania Deposition Experiments, Appearance of Titanium Tetrachloride

For an experiment, approximately $30\text{-}35\text{cm}^3$ of clear liquid TiCl_4 were placed in bubblers 1 and 2. During the experiments the liquid thermostatted between 28 and 31°C , bubbled vigorously, and small quantities built up in bubbler 3, the lower parts of the reactors (modified model see Section 2.1.1 Fig. 14. Chapter 2) and in the exit lines.

Runs T1-T6

Initial runs were undertaken to establish the feasibility of the procedure. Excessive back-pressure tended to build up during a run and extreme care had to be taken to ensure that all lines and bubblers were dry.



x40



x20

Fig 21. Optical Photographs of Alumina.

All coils initially glowed red to orange, gradually darkening as the deposit built up. The coils obtained were evenly coated with a blue-grey crystalline deposit which did not extend significantly down the platinum posts. A typical optical photograph of a titania bead is shown in Fig. 22. A representative voltage/time trace is shown in Fig. 23.

Runs DT1-52

Having established that good beads were obtainable, a range of experiments were performed at a constant flow rate. Deposition temperature and oxygen concentration were the only variables.

Generally, the heavier the deposit the darker the colour. Crystallite size increased with increasing deposit thickness, and showed a definite pyramidal shape. Representative scanning selection micrographs are shown in Figures 24, 25 and 26, for thin, medium and heavy deposits respectively. The micrographs presented in these figures are at a magnification of x500 and are therefore directly comparable. X-ray powder crystallographic studies showed that rutile titania was formed almost exclusively under all conditions. (Fig. 27 and Table 15 Appendix 4).



x20

Fig 22. Optical Photograph of Titania.

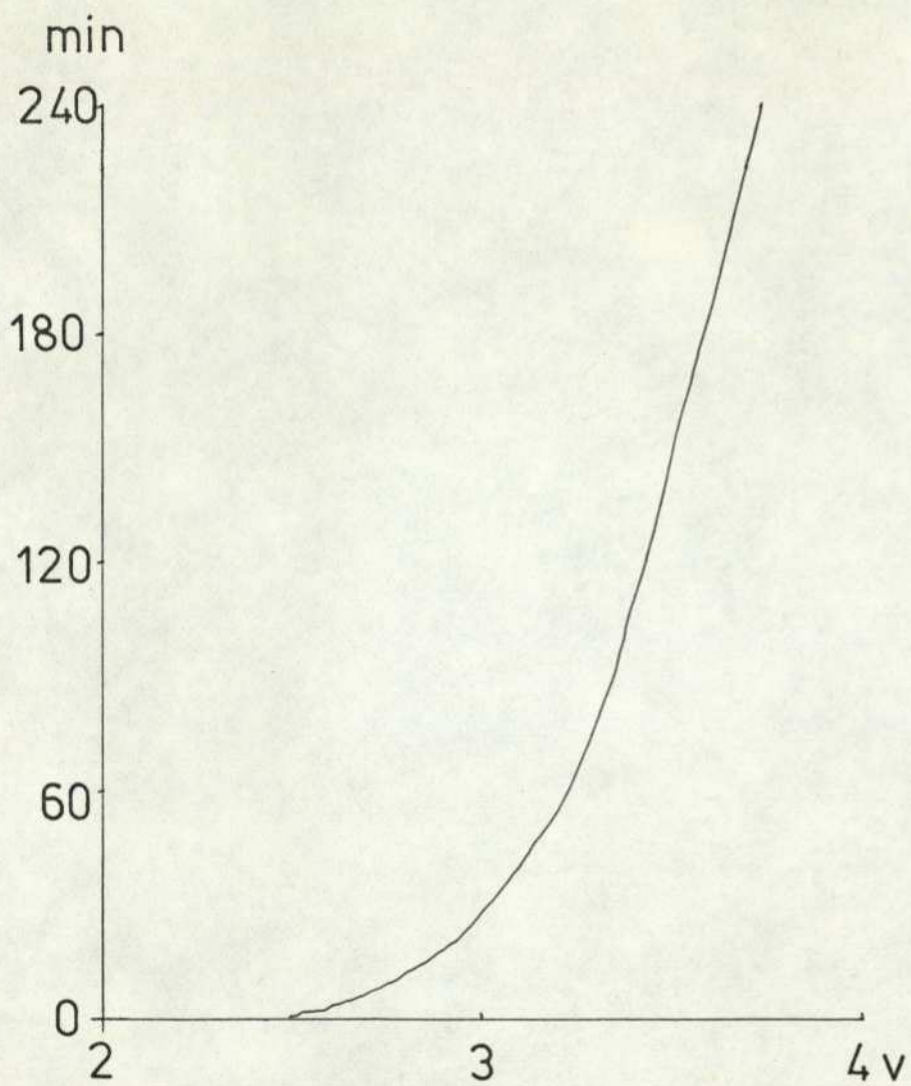
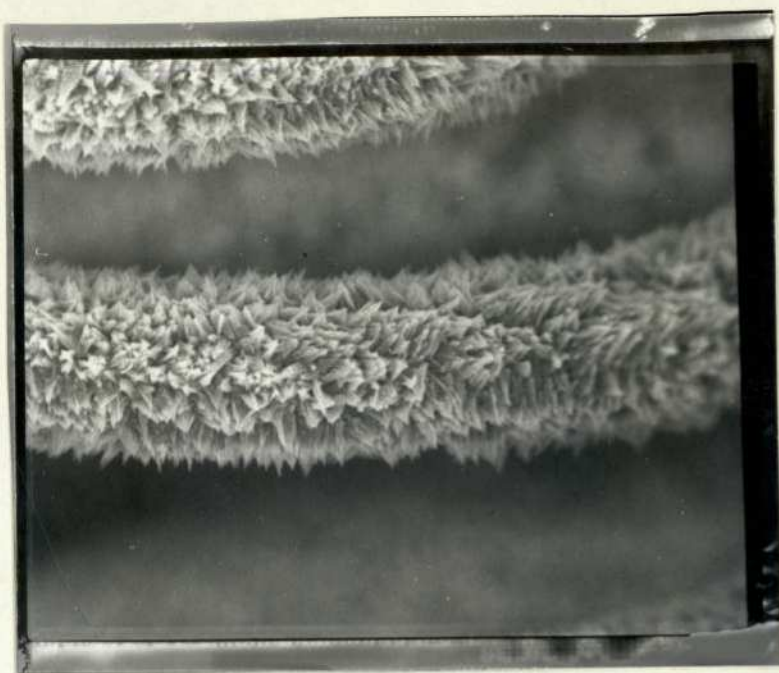


Fig 23. Voltage Time trace for Coil 3 RunDT9.

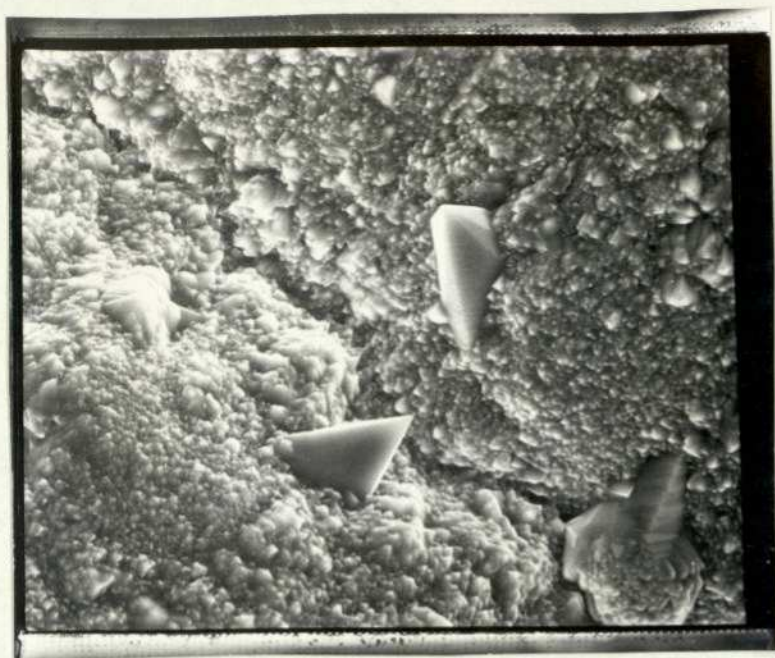


x500



x500

Fig 24. Electron Micrographs of Titania.
Thin Deposit.

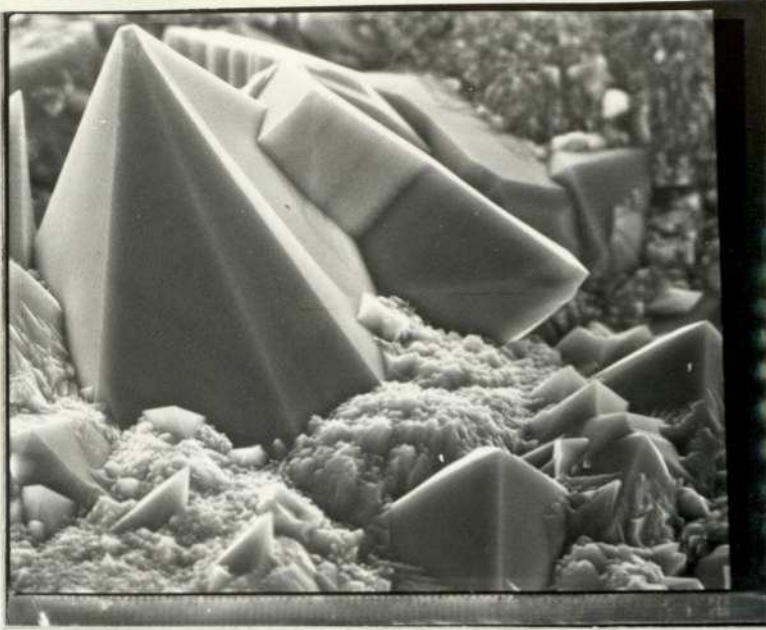


x500

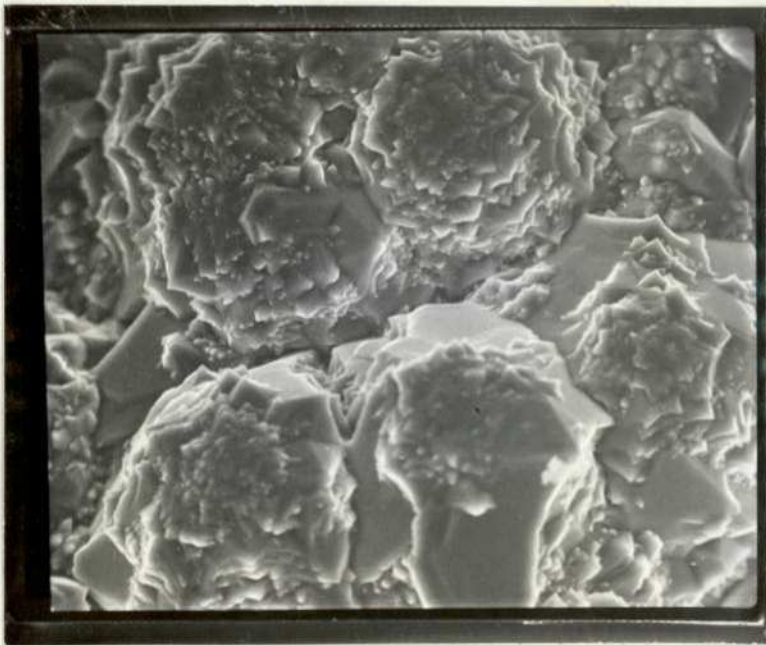


x500

Fig 25. Electron Micrographs of Titania.
Medium Deposit.



x500



x500

Fig 26. Electron Micrographs of Titania.
Thick Deposit.

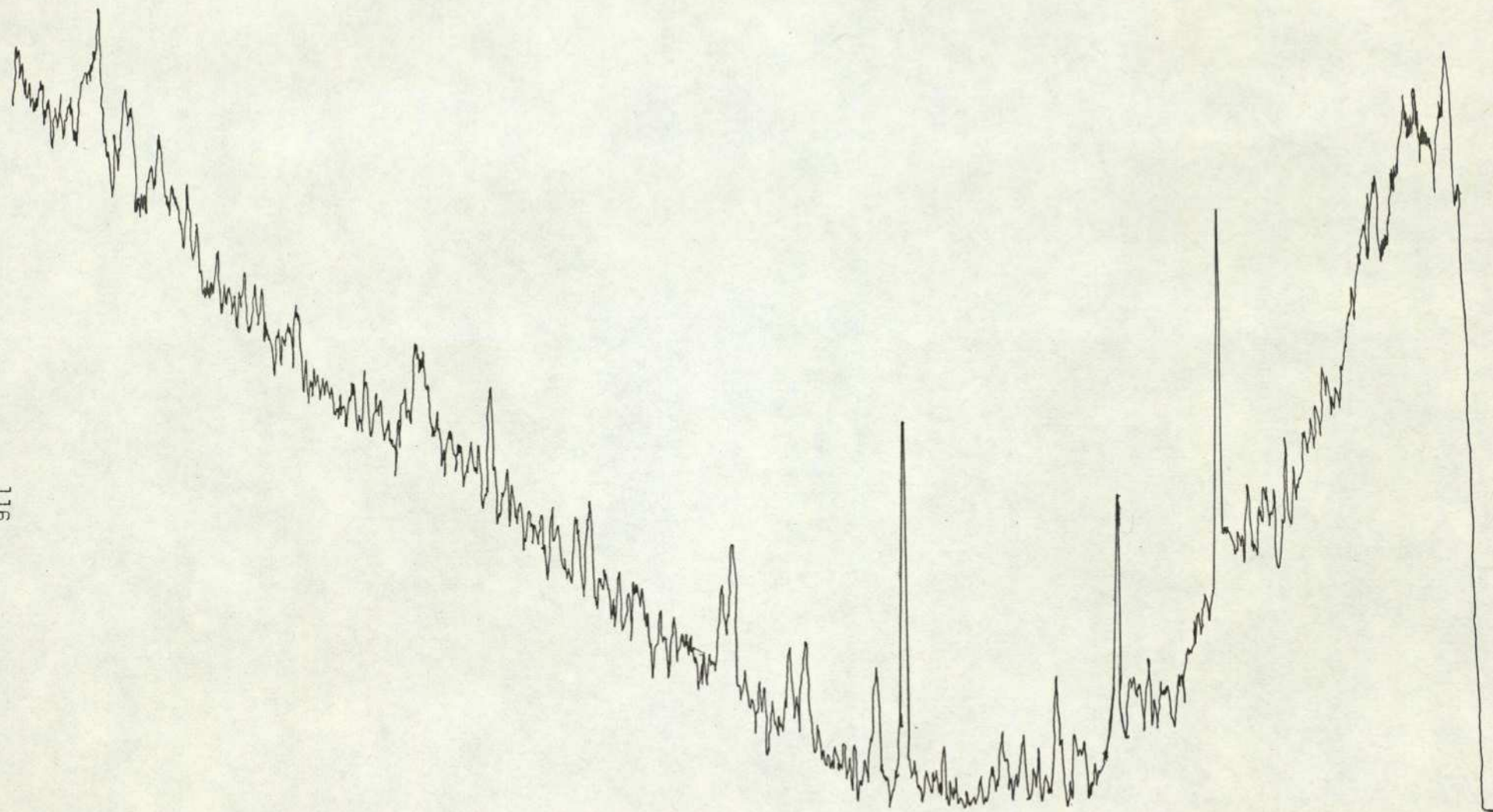


Fig 27. X-Ray Crystallograph.

Deposition Rate and Growth Profile

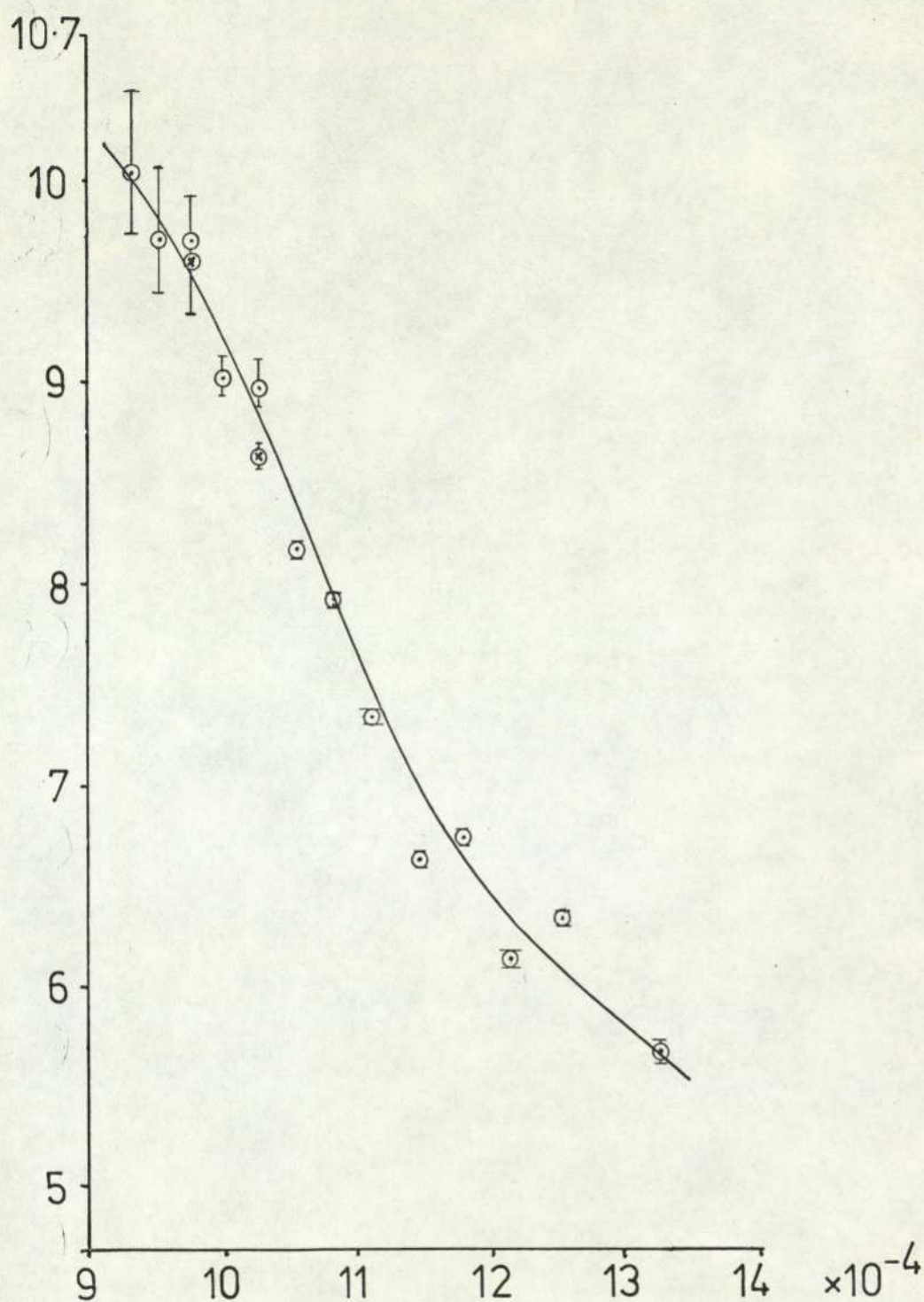
Deposition rates were obtained as described in Section 2.2.6 Chapter 2. Arrhenius curves of deposition rate versus temperature for each oxygen concentration are shown in Graphs 3-5 and Appendix 4 Tables 16-18. Deposition rate is defined as linear deposit thickness divided by duration of deposition. Estimation of errors involved in the measurements are indicated by error bars, the main error being the deposition time. This was measured from the chart recordings and was estimated to an accuracy of around $\pm 1\frac{1}{2}$ mins. Deposit thicknesses were obtained from optical photographs (examples in Fig. 28) and measurement error was estimated to be $\pm 0.0003\text{cm}$.

For each point, the average of the six coils was taken in order to minimize any individual temperature variations. Deposits were not allowed to form complete beads because of difficulty in measurement.

A growth profile was obtained with the coils being removed from the reactors at ten minute intervals, photographed and replaced. The profile obtained is shown in Graph 6 and Table 19 Appendix 4.

Ordinate: $\ln(\text{Rate})$ / nm.min^{-1}

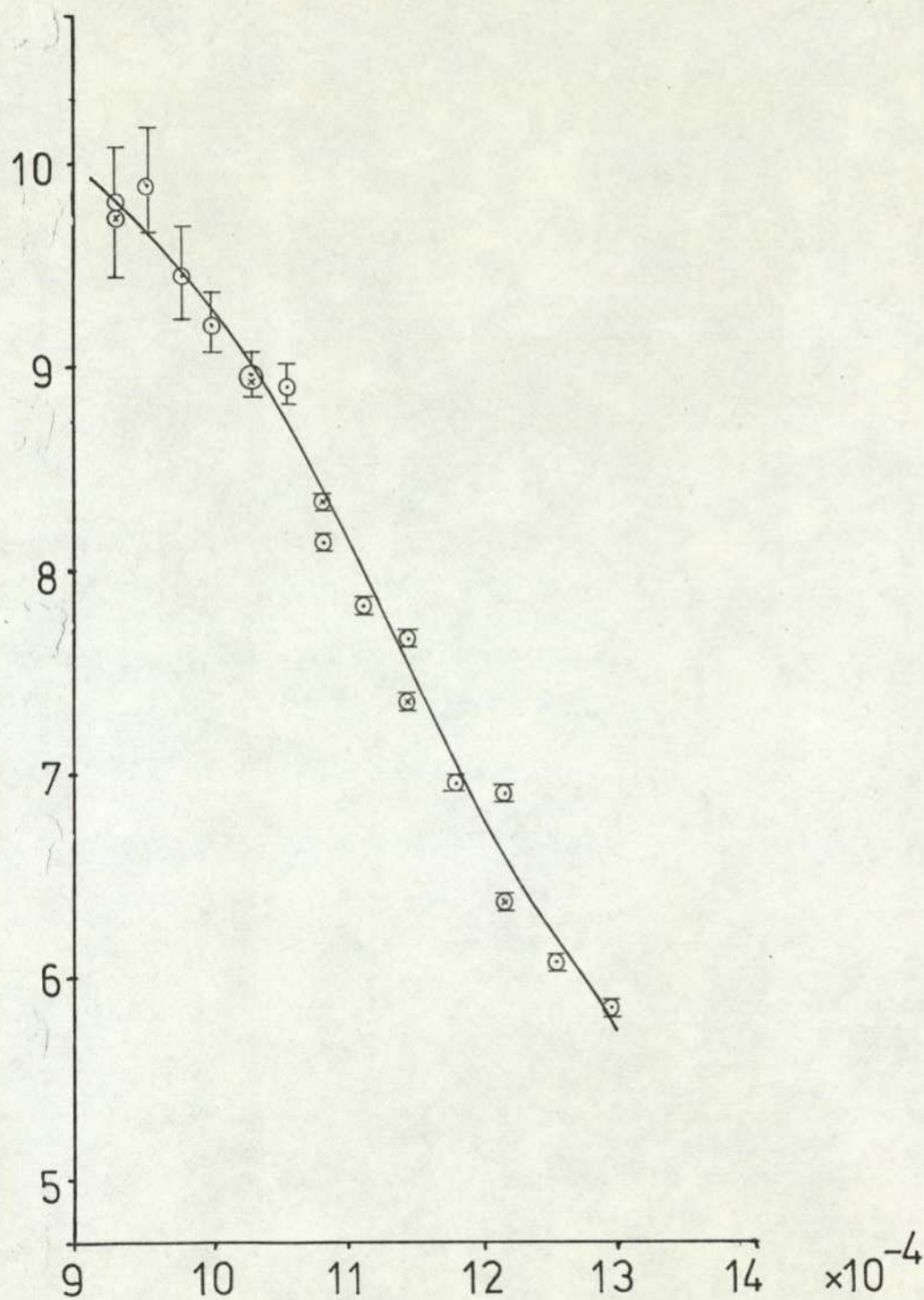
Abscissa: $1/T$ / K



Graph 3 Rate curve. ($\sim 20\% \text{O}_2$)

Ordinate: $\ln(\text{Rate}) \quad / \text{nm} \cdot \text{min}^{-1}$

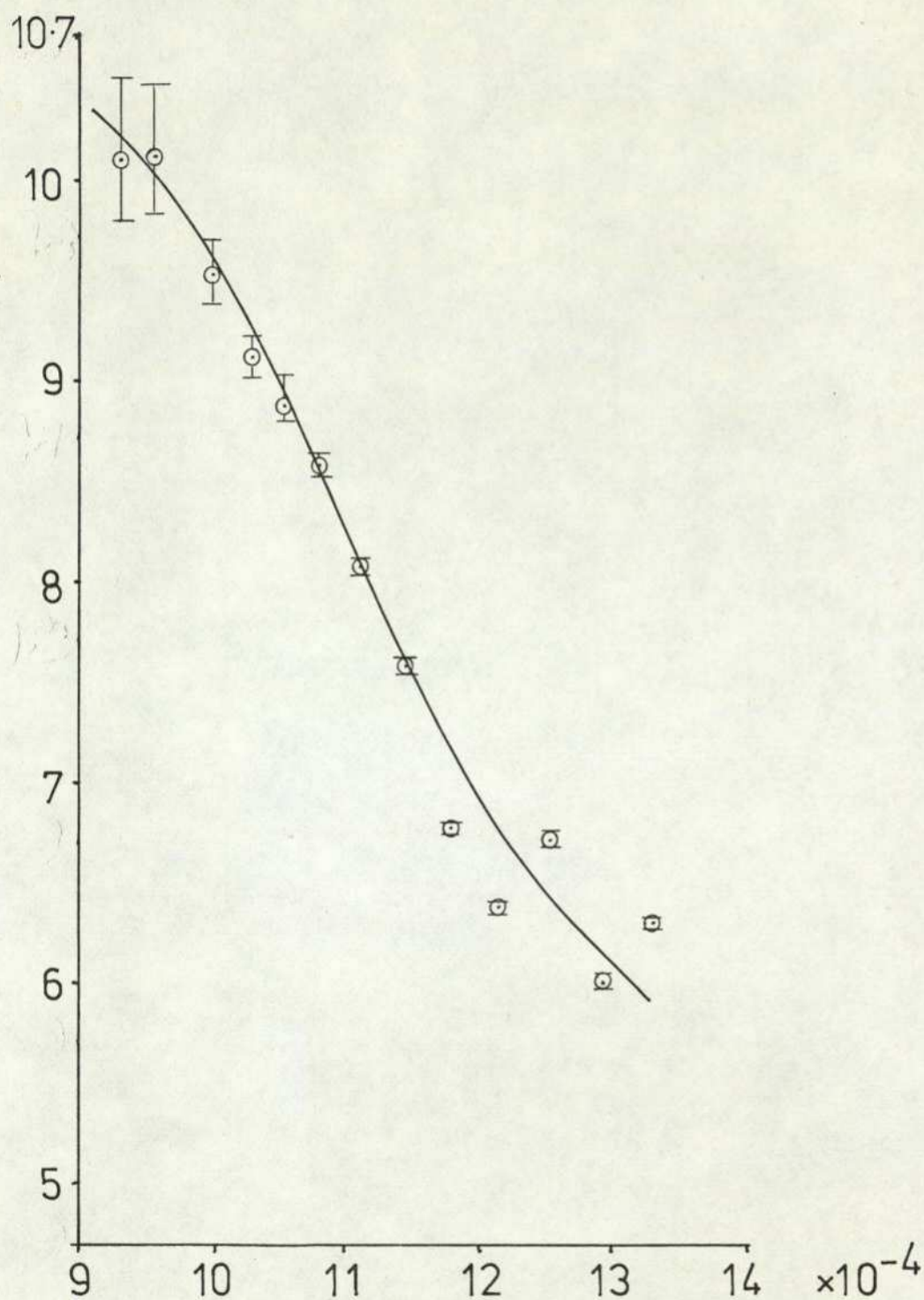
Abscissa: $1/T \quad / \text{K}$



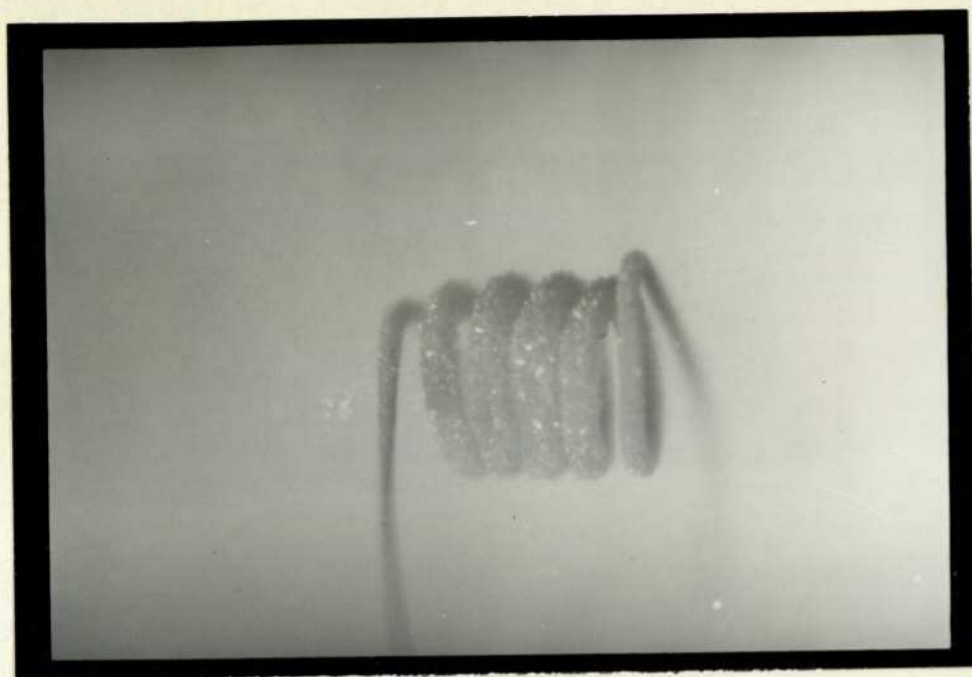
Graph 4 Rate curve. ($\sim 40\% \text{O}_2$)

Ordinate: $\ln(\text{Rate}) / \text{nm} \cdot \text{min}^{-1}$

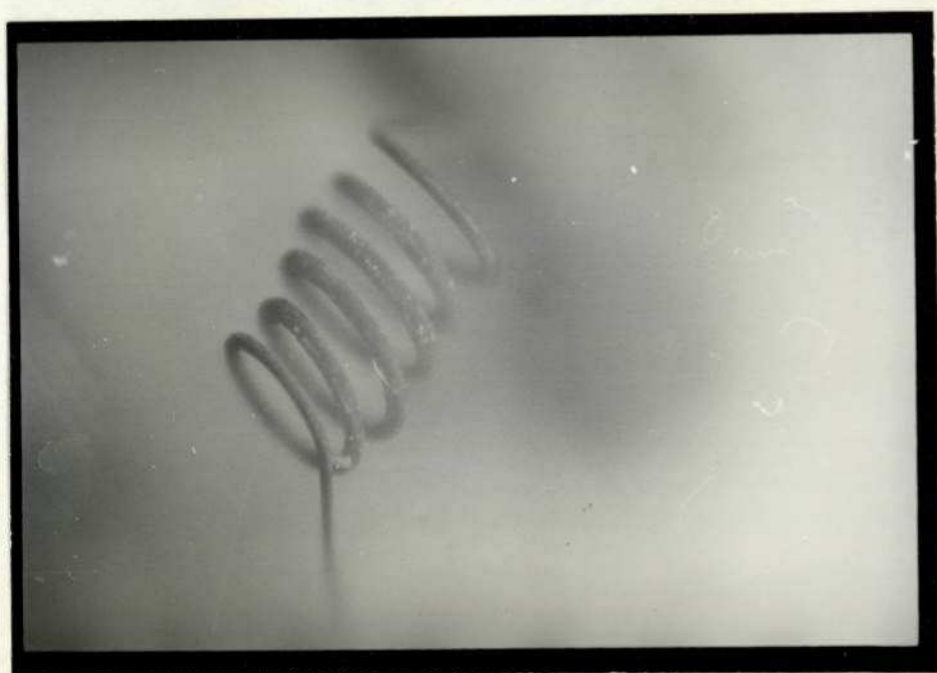
Abscissa: $1/T / \text{K}$



Graph 5 Rate curve. ($\sim 60\% \text{O}_2$)



x20

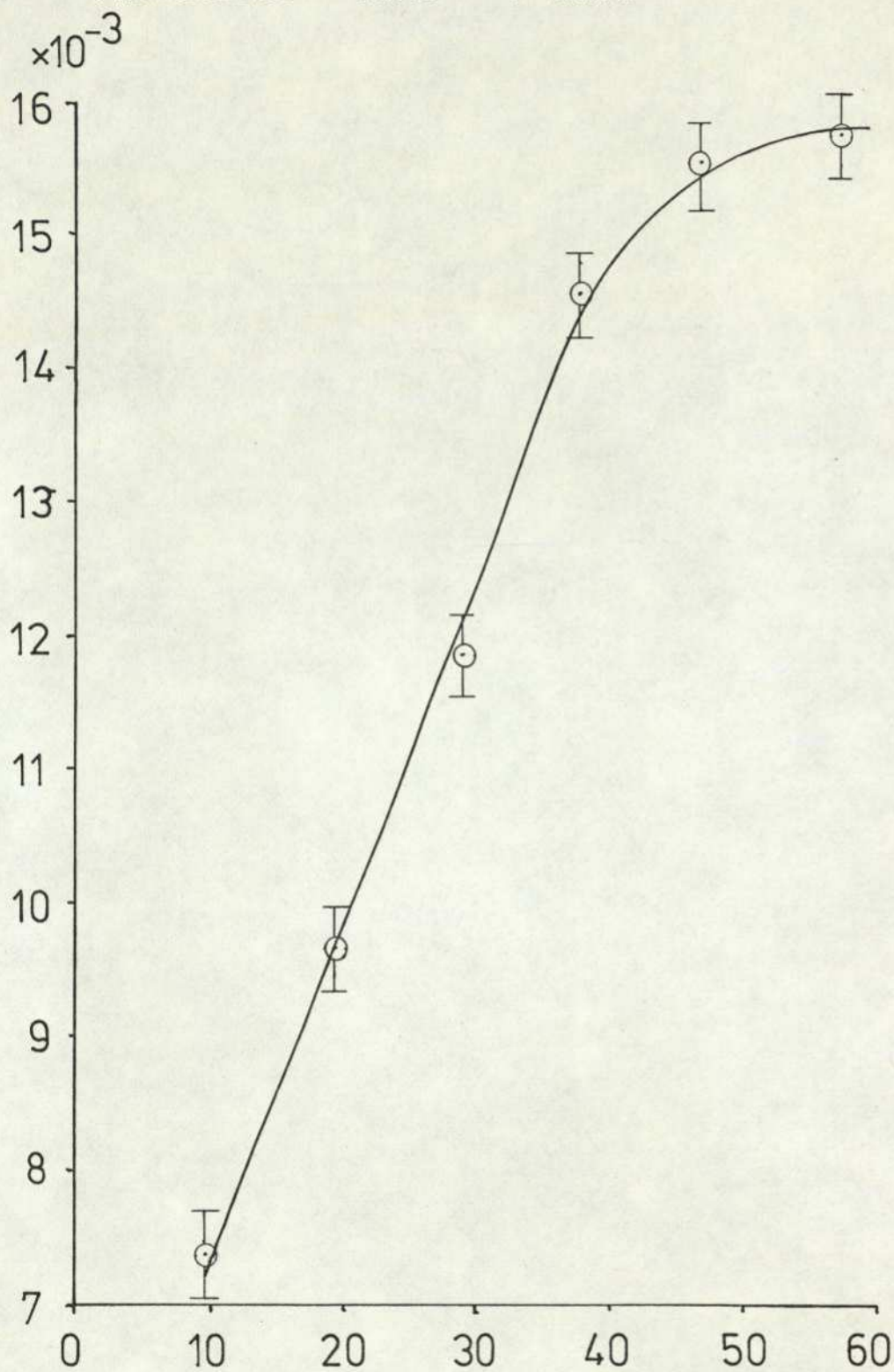


x20

Fig 28. Optical Photographs of Titania.

Ordinate: Linear growth /cm.

Abscissa: Time / min.



Graph 6 Growth Profile.

3.3 Computed Results

A Fortran IV program was constructed (Appendix 4) and results were computed on the City University Honeywell series 60 computer. From the input data the program initially calculated the density and viscosity of the gas stream mixture from

$$\rho_m = \sum_i x_i' \rho_i$$

and

$$\mu_m = \frac{\mu_i}{1 + \frac{1}{x_i'} \sum_{\substack{j=1 \\ j \neq i}}^n x_j' E_{ij}} \quad (\text{Section 1.3.3b})$$

To obtain the effective diffusion coefficients for each component initial guesses had to be made for the flux

$$\phi_{Ai} = \frac{N_A}{N_A + N_i} \quad 30$$

"Weighted" arithmetic mean mole fractions of the components was determined by

$$x_{Ai}' = \frac{x_A'}{x_A' + x_i'} \quad 29$$

where x_i' = input mean mole fraction of i across boundary layer.

The partial film pressure factors and effective mole fractions could then be determined from equations 27 and 28 respectively.

$$(pf)_{Ai} = \frac{p}{\phi_{Ai}} (x_A' + x_B') (\phi_{Ai} - x_{Ai}') \quad 28$$

$$x'_i = \frac{(pf)_{Ai}}{\sum_{i \neq A} (pf)_{Ai}} \quad 27$$

The effective diffusion coefficient could then be calculated from the effective mole fractions and inputted binary diffusion coefficients

$$D'_{A} = \frac{1}{\sum_{i \neq A} \frac{x'_i}{D_{Ai}}} \quad 25$$

where D_{Ai} is the binary diffusion coefficient evaluated from the Hirschfelder, Bird and Spotz equation (Section 1.3.2 equation 12).

In order to obtain the boundary layer thickness, δ , where $\delta = d/\text{Nu}_{AB}$ and $\text{Nu}_{AB} = f(\text{Re}^{\frac{1}{2}} \text{Sc}^{\frac{1}{3}})$, the Reynolds and Schmidt numbers were calculated from

$$\text{Re} = \frac{dV\rho}{\mu}$$

and

$$\text{Sc} = \frac{\mu}{\rho D'_{A}}$$

where d is the characteristic dimension.

For the cylinder model⁶⁴

$$\text{Nu}_{AB} = 0.35 + 0.47 \text{Re}^{\frac{1}{2}} \text{Sc}^{\frac{1}{3}} \quad 17$$

and for the sphere

$$\text{Nu}_{AB} = 2.0 + 0.60 \text{Re}^{\frac{1}{2}} \text{Sc}^{\frac{1}{3}} \quad 18$$

The flux through the boundary layer, or effective film thickness, to a surface is defined by

$$N_A = (kg)_A P (x_A - x_{AS}) \quad 20$$

where $(kg)_A$ = average mass transfer coefficient.

$$= \frac{D'_A P}{RT \delta (pf)_A} \quad 19$$

Substituting equation 19 in equation 20 gives

$$N_A = \frac{D'_A P^2 (x_A - x_{AS})}{RT \delta (pf)_A} \quad 45$$

where x_A = mole fraction of A in the main stream (input)

x_{AS} = mole fraction of A at the surface (input)

$(pf)_A$ = "partial film factor" for diffusion of A.

For equi-molar steady-state counter diffusion (Section 1.3.3b)

$$\lim_{(\delta_A \rightarrow \infty)} (pf)_A = P$$

and equation 45 under atmospheric pressure reduces to

$$N_A = \frac{D'_A (x_A - x_{AS})}{RT \delta} \quad 46$$

Equation 46 was then used to calculate the flux through the boundary layer. This calculated flux was then compared to the initial guess, and if substantially different the values were exchanged and the whole process iteratively repeated for each component in the gas stream. The growth rate was finally obtained from

$$G = \frac{m_d N_A}{\rho_d} \quad 21$$

where m_d = molecular weight of the deposit

N_A = flux of A in moles $\text{cm}^{-2}\text{s}^{-1}$

and ρ_d = density of deposit

The time required to grow through half the boundary layer thickness was taken to be

$$\text{time} = \frac{\delta}{2G} \text{ seconds}$$

where thickness of deposit = $\frac{\delta}{2}$ cm.

Therefore the rate can be defined by

$$\text{Rate} = \frac{\text{thickness}}{\text{time}}$$

The characteristic dimension was then incremented by the boundary layer thickness and the process repeated until it exceeded 1mm. The program was then repeated for each subsequent temperature.

To summarise, the program procedure calculated data as follows:

- (i) The density and viscosity of the gas mixture in the boundary layer,
- (ii) Reynolds and Schmidt numbers,
- (iii) The boundary layer thickness,
- (iv) Growth rate,
- (v) Deposit thickness,
- (vi) Deposition time,
- (vii) Deposition rate,
- (viii) Effective diffusion coefficients, and
- (ix) Flux of TiCl_4 , O_2 and Cl_2 at fourteen mean temperatures using Wilke's⁵⁷ approximation methods.

Various conversion values were inserted into the program. A value of 100% conversion assumed in effect that all the TiCl_4 present at the boundary layer/bulk stream interface reacted at the surface (ie. surface mole fraction equalled zero). Thus 100% conversion corresponded to a maximal concentration gradient across the boundary layer. 50, 10

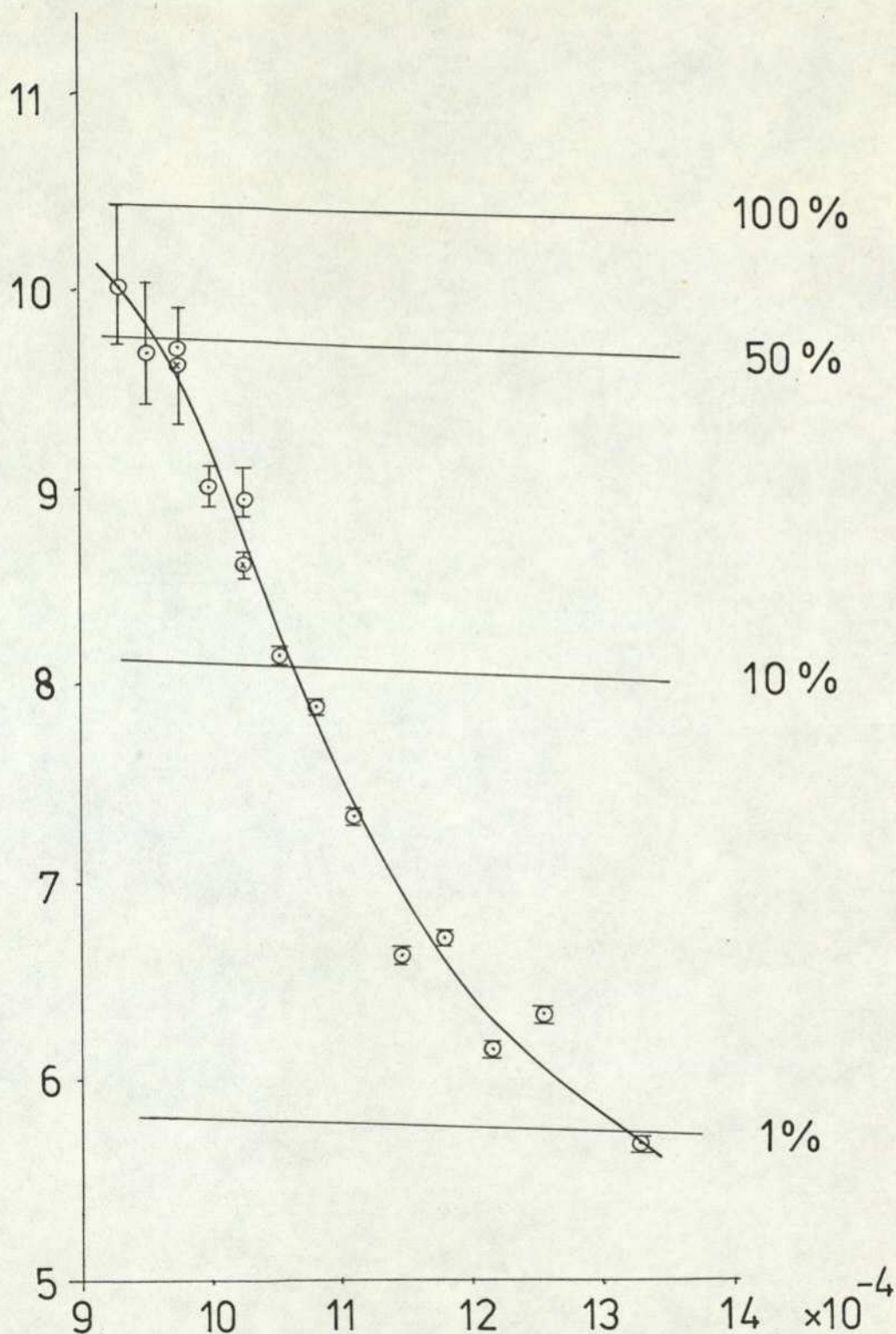
and 1% conversions were also computed for 18.92% oxygen concentration only, as there is a negligible difference in TiCl_4 mole fractions and hence the overall deposition rate between the three gas stream oxygen concentrations used in the experiments (Table 11 Appendix 4). A comparison of experimental and computed rate curves is shown in Graph 7 Table 22 Appendix 4. Similarly, a growth profile for 10% conversion compared to an experimental growth profile are shown in Graph 8 Table 23.

Equi-molar counter-diffusion was assumed when computing the flux (Table 24 and 25 Appendix 4) through the boundary layer, with nitrogen and the excess oxygen being present as diluents. The net flux of nitrogen was assumed to be zero and the nitrogen/oxygen ratio in the boundary layer was taken to be sensibly the same as in the bulk stream.

Initially the characteristic dimension, d , was incremented by the boundary layer thickness from the cylinder model (Section 1.3.3a, equation 17 Table 27 Appendix 4). When d was greater than 0.015cm (ie. the distance between each turning of the coil), the boundary layer thickness was calculated from the spherical model (Section 1.3.3a, equation 18).

In computing Schmidt numbers, (Table 29. Appendix 4) the value of diffusion coefficient of the mixture recommended by Carlton and Oxley^{50,51} was not used, but rather the individual effective diffusion coefficients (D'_A) for each separate gas. Thus three boundary layer thicknesses were obtained which only differed by a maximum of 5%. In all cases the titanium tetrachloride boundary layer thickness alone was used in incrementing the characteristic dimension.

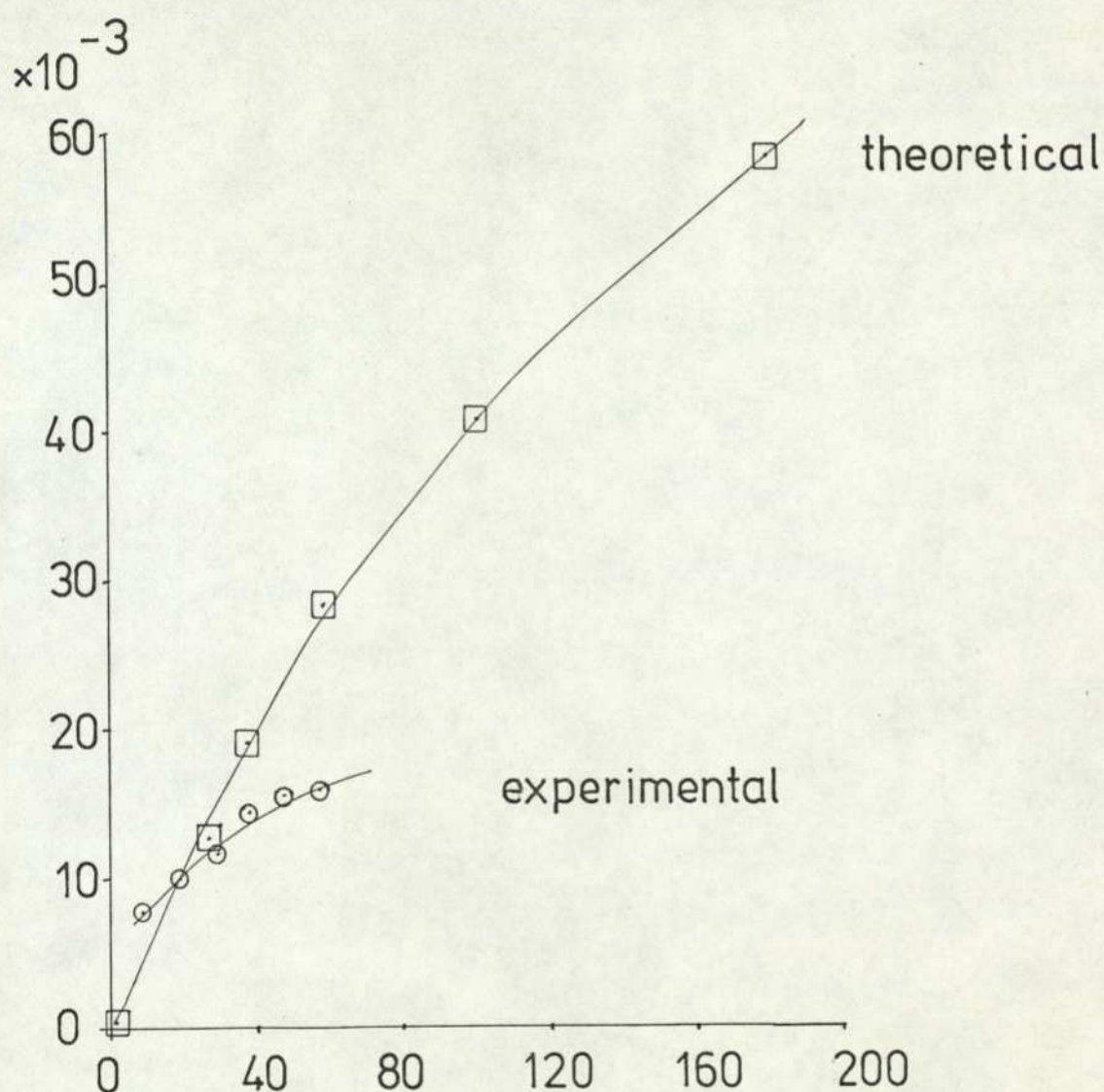
Ordinate: $\ln(\text{Rate}) / \text{nm} \cdot \text{min}^{-1}$
 Abscissa: $1/T \quad / \text{K}$



Graph 7. Comparison of experimental and computed Rate curves. ($\sim 20\% \text{O}_2$)

Ordinate: Linear growth /cm.

Abscissa: Time / min.



Graph 8. Comparison of experimental and computed Growth Profiles. (10% conversion. $\sim 20\% \text{ O}_2$)

The density of titania in the growth rate equation (Section 1.3.3a, equation 21) was assumed to be constant in the temperature range used. Although somewhat unsatisfactory, this assumption was necessary due to a lack of literature information.

DISCUSSION

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Thermodynamic Considerations

Equilibrium thermodynamics enables the prediction of the feasibility of a reaction (ie. whether the equilibrium position of a defined reaction favours products). Use of thermodynamic data (viz. $\Delta H^\ominus$, $\Delta S^\ominus$, $\Delta G^\ominus$ and $\Delta V^\ominus$) thus establishes the conditions (temperature, pressure, amounts of reactants) under which formation of the desired product will be maximised. The extensive properties $\Delta G^\ominus$, $\Delta H^\ominus$, $\Delta S^\ominus$ and $\Delta V^\ominus$ do not however give any information per se on the rate of reaction. Thus some reactions which are found to be thermodynamically feasible may proceed at such slow rates as to make a process impractical.³⁰

Using published thermodynamic data¹²⁷ the reaction between TiCl_4 and O_2 is found to be exothermic:

Temperature/K	$\Delta G^\ominus_f/\text{kJmol}^{-1}$	$\Delta H^\ominus_f/\text{kJmol}^{-1}$	K_p
100	-174.50209	-179.552176	1.4104×10^{91}
1000	-118.95112	-179.09612	1.6341×10^6

Under reversible conditions therefore, the degree of product formation at equilibrium should be seen to decrease as the temperature is increased, following van't Hoff.⁶⁶

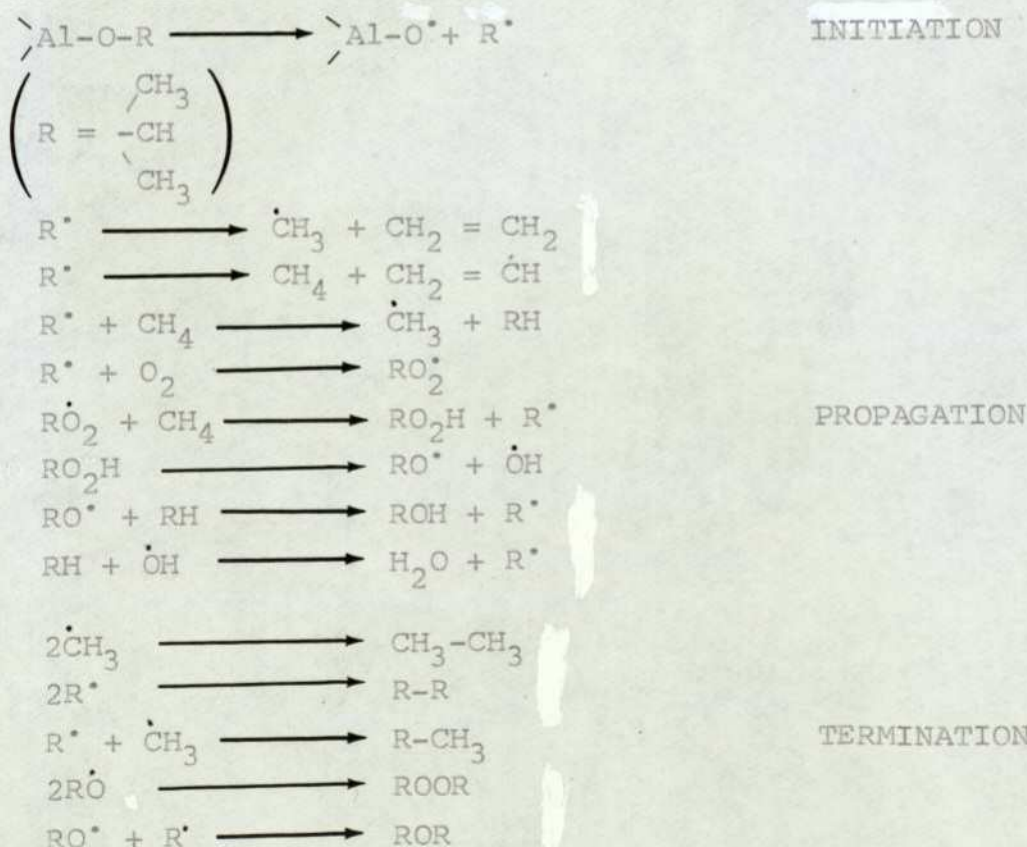
Experimentally, however, it was observed that efficiency of product formation increased as temperature was increased. This is undoubtedly due to the fact that the rate of the process (whether this be determined under particular conditions by a chemical reaction, mass transport, or combined mass transport and a chemical process) is the predominant factor that must be considered in CVD.

However, transition state theory may be formulated in terms of thermodynamics in order to provide information on rates of reactions. The thermodynamic parameters of activation $\Delta G^\ddagger$, $\Delta H^\ddagger$ and $\Delta S^\ddagger$ may be estimated from reaction data where

it is certain that the free energy of activation for the reverse reaction is negligible. This would apply, for example, in the case of the dissociation of the first halogen from titanium tetrachloride.

Although various sets of conditions were used to deposit aluminium (Section 3.1 Chapter 3), thick, dense, hard coatings, necessary for bead formation on platinum wire, were not obtained. Only thin films could be deposited. Thicker coatings tended to "craze" and then peel away (Fig. 20 Section 3.1) indicating that a major problem was poor adhesion of aluminium on the platinum substrate. Thus some parts of the deposit projected further than other parts into the surrounding gas phase boundary layer, to where the reactant concentration was relatively higher, and this resulted in preferential growth behaviour, resulting finally in a dendritic-type structure (Fig. 21 Section 3.1). The alumina so produced was, in addition, extremely brittle and non-uniform in coverage.

The pyrolytic decomposition of $\text{Al}(\text{O}^i\text{Pr})_3$ is thought to proceed via a free radical chain mechanism,⁸¹ viz:



Initially alkyl radicals are formed which can react with the oxygen present in the gas stream producing highly flammable products, such as methane, ethane, acetylene, propane, isopropanol, etc. These built up in the original reactor, (Section 2.1.1 Fig. 13) and were explosively ignited by the hot platinum coils.

Reactant depletion due to premature decomposition was a major problem. Decomposition products probably formed small particulates which could be transported to the coil. Thus the deposits formed in this work were most probably made up of a mixture of prematurely decomposed reactant and products formed by reactions in or around the boundary layer. After initial film formation, the organic free radical products (above) will build up in the boundary layer and then react with fresh $\text{Al}(\text{O}^i\text{Pr})_3$ in the gas phase producing impure deposits. This probably explains why the tips of the growths on the coil were darker in colour than at the base nearest to the platinum. (See Fig. 21 Section 3.1 Chapter 3).

R L Hough⁸⁷ produced hard, transparent, 0.0033cm thick alumina coatings on 0.0025cm diameter tungsten wires. However, in his system pressure was below 10.0 torr, which increased the mean free path of reactant molecules, and so virtually eliminated gas phase reactions. A higher growth rate ($25,000\text{nm}\cdot\text{min}^{-1}$) than that obtained by Aboaf⁸¹ ($3,300\text{nm}\cdot\text{min}^{-1}$) was produced, mainly due to the high purity of $\text{Al}(\text{O}^i\text{Pr})_3$. In this work extreme high purity of starting reagent and low pressure conditions were not used as this would increase the manufacturing cost of pellistors substantially, thus making them uncompetitive in the open market.

From the studies described in this thesis one is forced therefore to agree with the findings of McCandless and Withers,⁸⁵ that thick, dense, coherent alumina deposits cannot be

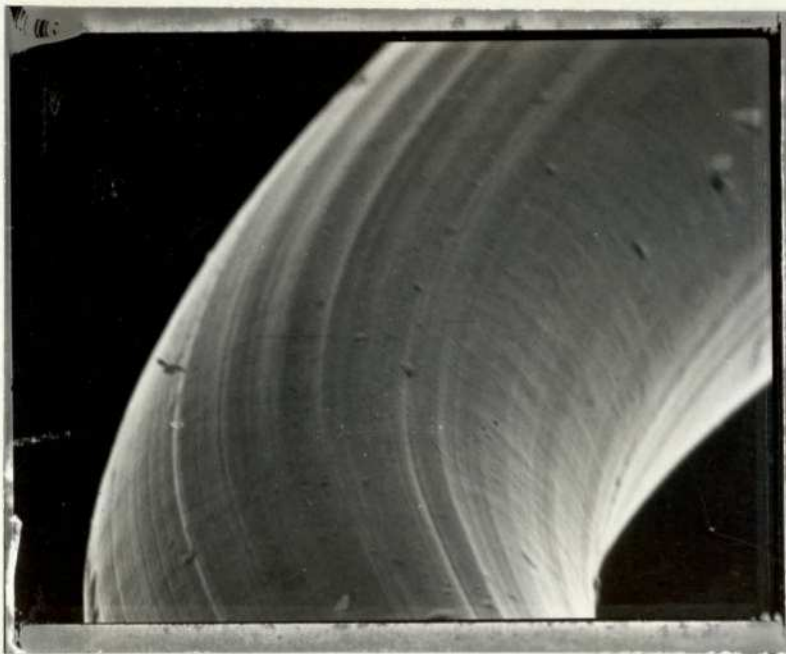
obtained in a single CVD process under atmospheric pressure from the pyrolysis of $\text{Al}(\text{O}^i\text{Pr})_3$.

Aluminium trichloride, although successfully used for the production of single crystal alumina,⁷³⁻⁷⁵ was not considered as a starting reagent due to the high deposition temperatures required ($\geq 1000^\circ\text{C}$). A platinum coil substrate at this temperature would not survive but quickly deform and "burn out". Much lower deposition temperatures are obtained using an organometallic compound, and $\text{Al}(\text{O}^i\text{Pr})_3$ was chosen in particular as it has an appreciable volatility at low temperatures.

4.1.1 Studies on Titania Growth

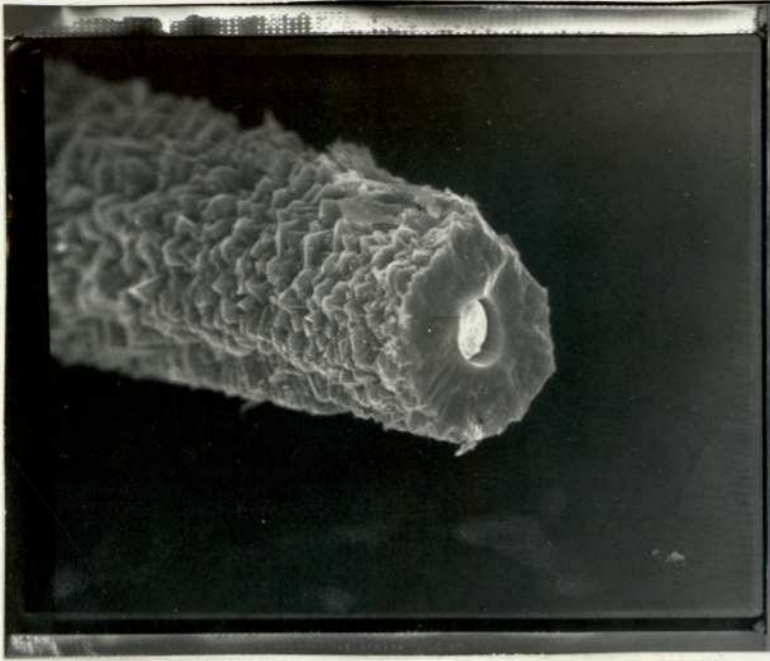
Various morphologies can be obtained when depositing a substance by chemical vapour deposition (Section 1.2.7. Fig. 6. Chapter 1). The rutile titania beads formed in this work were obviously polycrystalline (Section 3.1.1. Figs. 24,25,26). This observation is consistent with the known experimental conditions, for polycrystalline growth occurs when there is a high feed-rate of reactant to the surface, yet the mobility of the adsorbed atoms is low.²³ Many differently orientated nuclei are therefore initially obtained which upon coalescence produce a polycrystalline deposit.

It is also known that surface imperfections may exert an influence on the energetics of nuclei formation.^{32,120} Nucleation is more likely to occur on a step or ledge rather than on a smooth surface. An electron micrograph of a typical bare platinum coil is shown in Fig. 29, and grooves are plainly visible on its surface. Fig. 30 illustrates a fractured deposit, showing the internal structure of the titania. It is obvious that the titania deposit is very dense. Initial growth most likely takes



x2000

Fig 29. Electron Micrograph of a bare Pt coil.



x500



x2000

Fig 30. Electron Micrographs of a fractured
Titania Deposit.

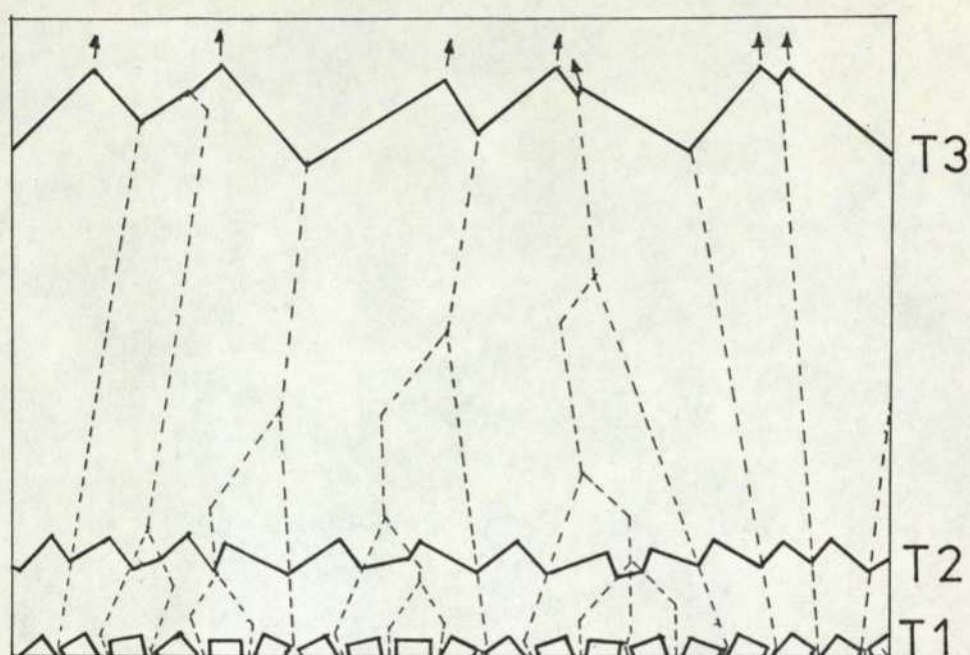
place in the grooves on the platinum surface, finally producing crystallites in definite ridges (see for example Fig. 24. Section 3.1.1).

In addition, it is apparent that the average crystallite size increases and crystallite density decreases with increasing deposit thickness, in accordance with the evolutionary selection concept of A van der Drift.³¹ This is illustrated in Fig. 31. With evolutionary selection only a few orientations survive, namely those with the fastest growth rates. As two crystallites of different orientations meet, the one with the faster growth rate will "win". In the case of three-dimensional crystals (two and one dimensional crystals being platelet and whisker growth respectively) this results in the formation of dense deposits.

The surface morphology obtained in this work agrees with that obtained by Hirashi and Hirai.¹⁰⁹ Thus, generally, crystallites formed in the central region of the coil are larger than those found on the outer turnings (Fig. 32). This phenomenon must arise from the temperature being lower at each end of the coil, thus favouring an increased nucleation density, which in turn leads to a finer-grained deposit. Numerous papers supporting this hypothesis are found in the literature dealing with nucleation, growth and structure of deposits.¹²¹⁻¹²⁶

4.1.2 The TiO_2 Growth-Rate

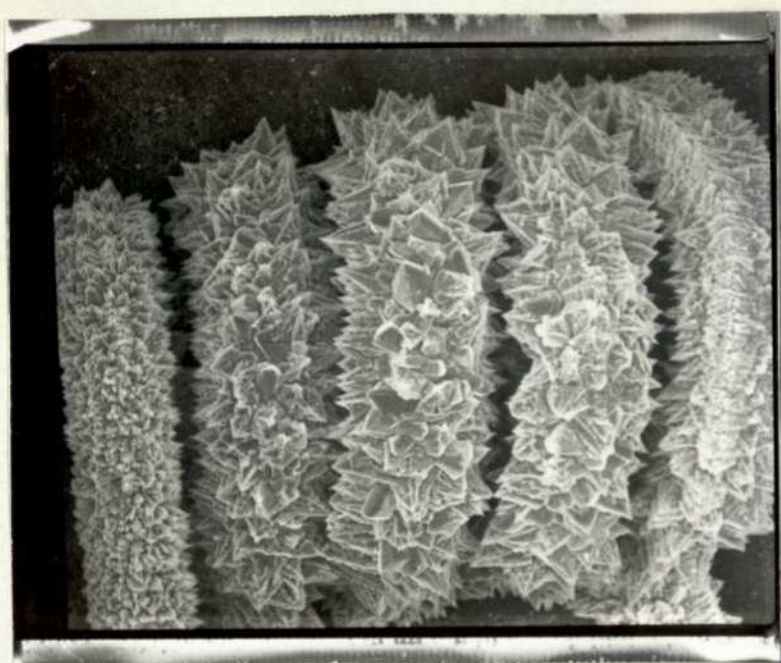
A comparison of various TiO_2 growth-rates obtained in the literature is shown in Table B. Growth-rate depends on the gas velocity and also on the concentration of reactant present. Unfortunately the majority of workers omit any information which would enable the linear gas velocity to be estimated.



— crystal front at time T.
 ----- inter-crystalline boundary.

Fig 31. Evolutionary Selection,
 Growth Orientation.

Taken from reference 31.



x50

Fig 32. Electron Micrograph of a Titania coated Pt coil.

Table B

Comparison of Maximum TiO_2 Growth-Rates

Temperature / $^{\circ}\text{C}$	Substrate /film	Reaction	Linear velocity / cm.s^{-1}	Growth rate/ nm.s^{-1}	Reference
150	Quartz covered by Pt or Si	$\text{Ti}(\text{O}^i\text{Pr})_4$ + H_2O	-	1200	104
150	Ti	"	-	29	105
150	Ge, Si, Pt, steel	TiCl_4 + H_2O	-	2.0	102
775	Pt wire	TiCl_4+O_2	1.577	411.4	This work
827	Si	"	$\sim 15^*$	1.0^*	110
900	Quartz, Si crystal	TiCl_4 + H_2O	$\sim 2^*$	24600	109
900-950	Si	$\text{Ti}(\text{O}^i\text{Pr})_4$ + H_2+CO_2	-	600	103

*Estimated from paper

The extremely high rate obtained by Hirashi and Hirai¹⁰⁹ is probably due to the very high reactant concentration (~60% TiCl_4). Conversely, Ghoshtagore¹¹⁰ used an estimated 0.03% TiCl_4 reactant concentration and obtained a growth-rate of only 1nm.s^{-1} . Generally it has been concluded¹⁰⁹ that the growth-rate does not change significantly when deposition takes place on different substances.

4.1.1.3 The TiO_2 Growth-Profile

A comparison of experimentally determined and theoretically calculated growth-profiles is shown in Graph 8 (Section 3.3, Chapter 3). The theoretical 10% conversion profile is depicted, as it is closest to the experimental conditions.

As expected, the theoretical curve predicts a faster growth-rate than that obtained, as surface kinetic effects were not incorporated into the calculations (Section 3.3). The transition point between the use of a cylindrical or spherical geometry for the model is not visible in this curve, but it becomes progressively more apparent at higher conversion percentages. However, from preliminary computations, there is little difference between the final estimated growth-rates when the combined cylindrical/spherical model is used as compared to utilising a cylindrical geometry model alone.

Knowledge of transport rates are fundamental to obtaining a quantitative picture of a chemical vapour deposition process. Mass and molecular transport in the vapour phase only is common to all systems, and it is important as it puts an upper limit on the deposition rate and also determines the flux and concentration of reactants and products in the system.

The rate of a heterogeneous chemical reaction is determined not only by the rate of reaction at the surface itself, but also by the rate of reactant supply to that surface. If transport to the surface occurs by diffusion, then at low temperature, when the heterogeneous reaction rate is small with respect to the diffusion rate, the overall rate will be determined by the surface kinetics and therefore is likely to increase exponentially with temperature and be independent of the gas flow velocity. At higher temperatures diffusion is rate-controlling and under laminar flow conditions the overall rate is indirectly dependent on flow velocity (since the flow rate affects the boundary layer thickness close to the surface). In addition, under diffusion control, the rate increases slowly with temperature (proportional to $T^{3/2}$). Thus a curved Arrhenius plot is obtained as shown in Section 1.2.2. Fig. 5. Chapter 1.

Uniformly Accessible Surface: Isothermal, Isobaric System

As a basic principle, it may be assumed that the rate of the heterogeneous reaction depends on the concentration of reactant at the surface. Thus under steady-state conditions with boundary layer diffusion control, the reaction rate should equal the amount of reactant supplied by diffusion:

$$\begin{aligned} R &= N_A \\ &= (kg)_A P (x_A - x_{Ao}) \end{aligned} \quad 20$$

where R is the rate of reaction, N_A the flux of A to the surface, $(kg)_A$ the mass transfer coefficient, and x_A , x_{Ao} the mole fractions of A in the bulk stream and on the surface respectively.

For the simplest case, where the surface reaction is of first order⁶²

$$\beta (x_A - x_{Ao}) = k' x_{Ao} \quad 47$$

where $\beta = (kg)_A P$, $k' = kP$ and k is the reaction rate constant.

Rearranging

$$x_{Ao} = \frac{\beta x_A}{k' + \beta} \quad 48$$

The overall reaction rate is therefore^{47,58}

$$R = \frac{k' \beta}{k' + \beta} x_A \quad 49$$

There are two limiting cases. If $k' \ll \beta$ (surface control) then

$$\lim_{k' \rightarrow 0} \left(\frac{k' \beta}{k' + \beta} \right) = k' \quad 50$$

and $x_{Ao} \approx x_A$, ie. the concentration at the surface is approximately the same as in the bulk stream and the overall rate is then determined by chemical kinetics on the surface.

If $k' \gg \beta$

$$\lim_{\beta \rightarrow 0} \left(\frac{k' \beta}{k' + \beta} \right) = \beta \quad 51$$

$$x_{AO} = \frac{\beta}{k'} x_A$$

and now $x_{AO} \ll x_A$, ie. the concentration at the surface is very much smaller than in the bulk stream and the overall process is determined by the diffusion rate. In this case the observed rate of reaction has nothing in common with the kinetics of the surface reaction.

In between the two limiting ranges is an intermediate one, where the process can be described, for a first order reaction, by

$$R = \frac{k'\beta}{k' + \beta} x_A \quad 49$$

4.2.2 Multi-Component Diffusion⁶²

Considering the reaction across the boundary layer



initially all the reactants should diffuse to the surface in stoichiometric amounts.

ie.
$$\frac{R_A}{a} = \frac{R_B}{b} = \dots = \frac{R_I}{i}$$

However, the concentrations of all the reactants at the surface cannot decrease to the same degree in a given time, as they diffuse at different rates. Therefore for the above equation to be satisfied a non-stoichiometric mixture results, regardless of the rate of reaction at the surface.

Assuming that the concentration of reactant I is small at the surface compared to that in the bulk, then $R_I = \beta_I x_I$ and the above equation can be fulfilled only in one special case, at such a composition of the mixture that

$$\frac{\beta_A x_A}{a} = \frac{\beta_B x_B}{b} = \dots = \frac{\beta_I x_I}{i} \quad 52$$

Now

$$\begin{aligned} \beta_I &= (kg)_I P \\ &= \frac{Nu \cdot P^2 D''_I}{d \cdot RT (pf)_I} \end{aligned} \quad 53$$

but

$$Nu = f(Re^{\frac{1}{2}} Sc^{\frac{1}{3}})$$

The Reynolds number can be considered as constant as it is a characteristic property of the system, but the Schmidt number depends on the diffusion coefficient ($Sc \propto 1/D$) and is therefore different for different substances. Hence $Nu \propto 1/D^{\frac{1}{3}}$ and equation 52 reduces to

$$\frac{D_A^{\frac{2}{3}} x_A}{a} = \frac{D_B^{\frac{2}{3}} x_B}{b} = \dots = \frac{D_I^{\frac{2}{3}} x_I}{i}$$

Therefore only where all diffusion coefficients of all reactants are equal can one have a stoichiometric mixture in the boundary layer. If the diffusion coefficients are not proportional to their stoichiometric coefficients then the rate of reaction is determined by the reactant for which $D_I^{\frac{2}{3}} x_I / i$ is a minimum. If one reactant arrives at the surface in a greater amount than that required by stoichiometry it would accumulate, x_{I0} would increase and the concentration at the surface will not be small with respect to the concentration in the gas stream. The whole process must therefore be governed by the reactant with the minimum $D_I^{\frac{2}{3}} x_I / i$ and does not depend on the concentrations of the other reactants, nor on their respective diffusion coefficients.

4.2.3 First Order Reactions

The rate of reaction in the diffusional range can be expressed in terms of concentration by

$$R = (kg)_A C_A$$
$$= \frac{Nu D_A C_A}{d}$$

where C_A is the concentration of A in the bulk stream. By definition, all reactions in the diffusional range are of first order with respect to reactant concentration under constant total pressure.

In a gas stream the Nusselt number is a function of the Reynolds number, where $Re = Vd\rho/\mu$. Also, in an ideal gas, viscosity is independent of pressure, so if the total pressure is varied at constant mass velocity ($V\rho$), the Reynolds number remains constant and therefore so does Nu and the observed rate of reaction. Therefore all reactions in the diffusional range are of first order with respect to concentration under constant total pressure.

The rate of reaction does not depend on the specific chemical mechanism and rates of various reactions will only differ as the reactant diffusion coefficients differ. For reversible reactions the rate also depends on the equilibrium position. Under no circumstances can the observed rate be greater than that calculated from the rate of diffusion.

4.2.4 Experimental and Theoretical Rate Curves

From the comparison of the experimental and computed rate curves, (Graph 7, Section 3.3) observation shows that the conversion percentage (amount of $TiCl_4$ reacted) increases

as temperature increases. At low temperatures, the conversion is ~1% (ie. only 1% difference in x_A and x_{Ao}). This increases to ~100% at higher temperatures. The difference in the upper two experimental points and the 100% calculated conversion is only 4.7%, which is within experimental and computational error. Therefore at high temperatures the process is diffusion controlled, but at lower temperatures the experimental results can be explained by considering both transport and surface kinetic effects.

In Section 4.2.2 it was stated that the rate limiting reactant is the one with the minimum value for $D''^{2/3} x_I / i$. From Tables 11(a) and 26 (Appendix 4), it is seen that at all temperatures

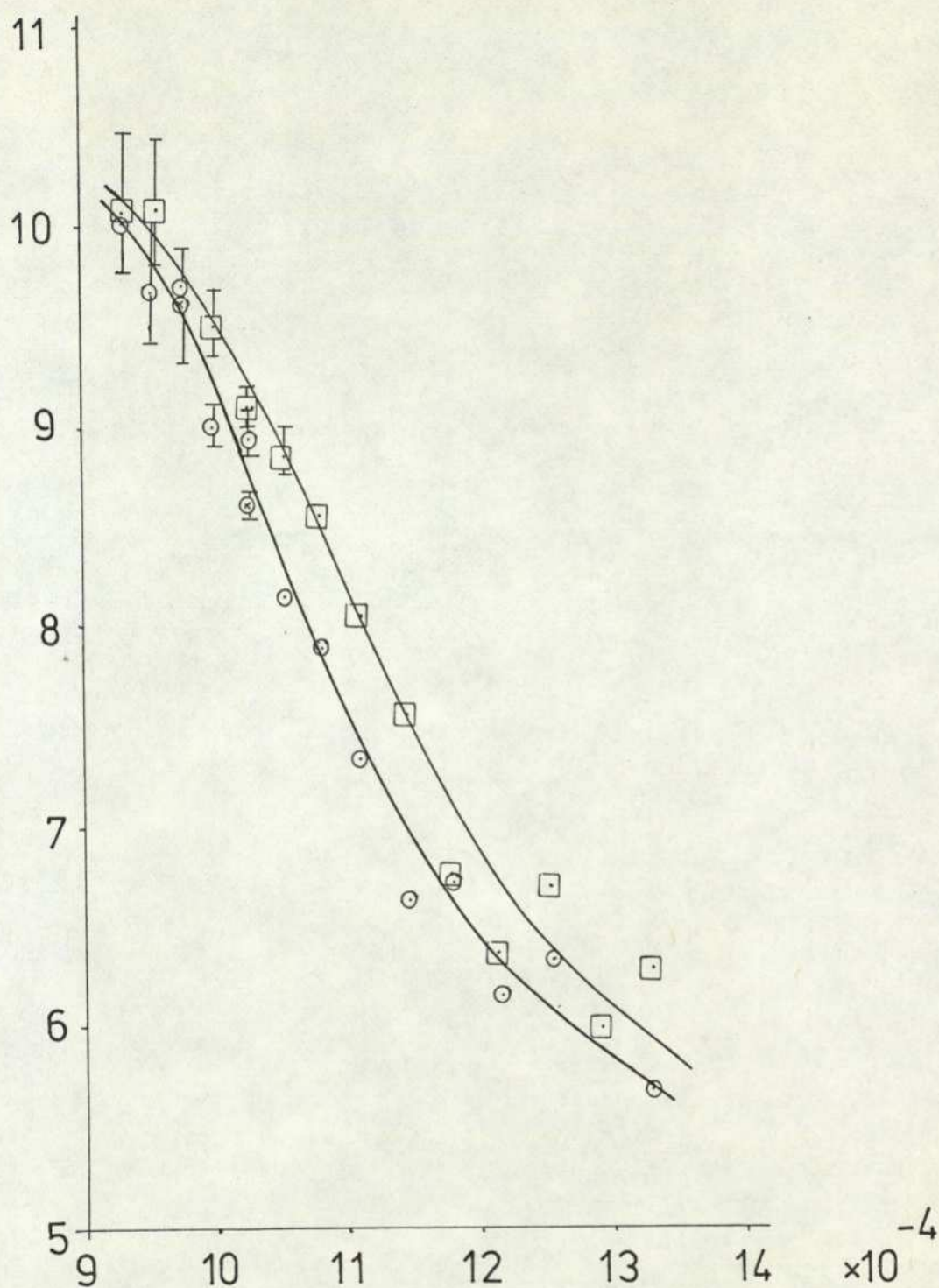
$$D''^{2/3}_{TiCl_4} x_{TiCl_4} < D''^{2/3}_{O_2} x_{O_2}$$

Therefore $TiCl_4$ may be regarded as the rate-limiting reactant and under diffusion control the reaction should be independent of oxygen concentration. This agrees with experiment, as it can be seen from Graph 9 that there is a negligible difference in the 20% and 60% O_2 concentration growth-rate curves at high temperatures.

In contrast, at lower temperatures a difference occurs between the two growth-rates, and this must therefore be due to surface kinetic effects.

Ordinate : $\ln(\text{Rate}) / \text{nm} \cdot \text{min}^{-1}$

Abscissa: $1/T / \text{K}$



Graph 9 . Comparison of experimental Rate curves.

($\circ$ ~ 20% . $\square$ ~ 60% O₂)

There are two basic mechanisms which describe the kinetics of a surface reaction.⁶⁶ One is the Langmuir-Hinshelwood mechanism, where reaction occurs between two different types of adsorbed molecules on adjacent sites on the surface. The other is the Rideal-Eley mechanism, where the reaction is again bimolecular, but only one reactant is adsorbed while the other remains in the gaseous phase (Section 1.4. Chapter 1).

If the reaction between TiCl_4 and O_2 occurs by the Langmuir-Hinshelwood mechanism then

$$v = k \cdot \theta_{\text{TiCl}_4} \theta_{\text{O}_2}$$

where v is the rate of reaction, k the chemical reaction rate constant and θ_{TiCl_4} , θ_{O_2} are the fractional coverages of TiCl_4 and O_2 respectively.

$$\text{Then } \theta_{\text{TiCl}_4} = \frac{b_{\text{TiCl}_4} p_{\text{TiCl}_4}}{1 + b_{\text{TiCl}_4} p_{\text{TiCl}_4} + (b_{\text{O}_2} p_{\text{O}_2})^{\frac{1}{2}}}$$

$$\text{and } \theta_{\text{O}_2} = \frac{(b_{\text{O}_2} p_{\text{O}_2})^{\frac{1}{2}}}{1 + (b_{\text{O}_2} p_{\text{O}_2})^{\frac{1}{2}} + b_{\text{TiCl}_4} p_{\text{TiCl}_4}}$$

where $b_{\text{TiCl}_4}, b_{\text{O}_2}$ are the respective Langmuir constants and $p_{\text{TiCl}_4}, p_{\text{O}_2}$ the partial pressures of TiCl_4 and O_2 . (The oxygen term is raised to the root power as O_2 is assumed to dissociate on adsorption).

If TiCl_4 is weakly adsorbed then

$$\lim_{b_{\text{TiCl}_4} p_{\text{TiCl}_4} \rightarrow 0} (v) = \frac{k \cdot b_{\text{TiCl}_4} p_{\text{TiCl}_4} (b_{\text{O}_2} p_{\text{O}_2})^{\frac{1}{2}}}{(1 + (b_{\text{O}_2} p_{\text{O}_2})^{\frac{1}{2}})^2} \quad 54$$

Thus the rate is proportional to the partial pressure of TiCl_4 , and as the partial pressure of O_2 increases the rate increases to a maximum and then decreases.

When O_2 is very strongly adsorbed

$$\lim_{(b_{\text{O}_2} p_{\text{O}_2})^{\frac{1}{2}} \rightarrow \infty} (v) = \frac{k \cdot b_{\text{TiCl}_4} p_{\text{TiCl}_4}}{(b_{\text{O}_2} p_{\text{O}_2})^{\frac{1}{2}}} \quad 55$$

and the order in oxygen approaches -0.5; the oxygen is acting as a poison.

In the Rideal-Eley mechanism reaction occurs between a gaseous species and an adsorbed one. Assuming oxygen is the adsorbed species,

$$v = \frac{k \cdot p_{\text{TiCl}_4} (b_{\text{O}_2} p_{\text{O}_2})^{\frac{1}{2}}}{1 + (b_{\text{O}_2} p_{\text{O}_2})^{\frac{1}{2}}} \quad 56$$

With a high O_2 partial pressure $(b_{\text{O}_2} p_{\text{O}_2})^{\frac{1}{2}} > 1$ and the rate is directly proportional to the partial pressure of TiCl_4 .

$$\lim_{(b_{\text{O}_2} p_{\text{O}_2})^{\frac{1}{2}} \rightarrow \infty} (v) = k \cdot p_{\text{TiCl}_4} \quad 57$$

For low O_2 partial pressures

$$\lim_{(b_{\text{O}_2} p_{\text{O}_2})^{\frac{1}{2}} \rightarrow 0} (v) = k \cdot p_{\text{TiCl}_4} (b_{\text{O}_2} p_{\text{O}_2})^{\frac{1}{2}} \quad 58$$

For the Rideal-Eley mechanism, no maximum occurs when increasing the partial pressure of either constituent.

It is apparent on examining the experimental rate curves (Graph 9. Section 4.2.4) that the growth rate increases as O_2 concentration increases. There is no evidence^{110,111,128,129} to suggest that any intermediate species such as TiCl_3 , TiCl_2

and TiOCl_2 are formed to any significant extent and it is considered unlikely that TiCl_4 is adsorbed. Therefore it is most likely that the mechanism is Rideal-Eley, with adsorbed monatomic oxygen reacting with gaseous TiCl_4 .

4.4 Energy of Activation

The observed growth rate (R_{OBS}) is a function of deposition rate, which in turn may be controlled by diffusion (R_D) and/or surface kinetics (R_S).

For a first order reaction Besmann and Spear⁵⁸ have shown that

$$R_{OBS} = \frac{R_S R_D}{R_S + R_D} \quad 59$$

Rearranging gives

$$\frac{1}{R_{OBS}} = \frac{1}{R_S} + \frac{1}{R_D} \quad 60$$

Therefore the deposition rate controlled by surface kinetics can be found using the experimental and computed diffusion controlled deposition rates. (See Table 30. Appendix 4). From the linear portion on Graph 10 the "true" activation energies were determined, and found to be 278.6, 333.2 and 204.4 kJ.mol⁻¹ for the 20, 40 and 60% O₂ concentrations respectively.

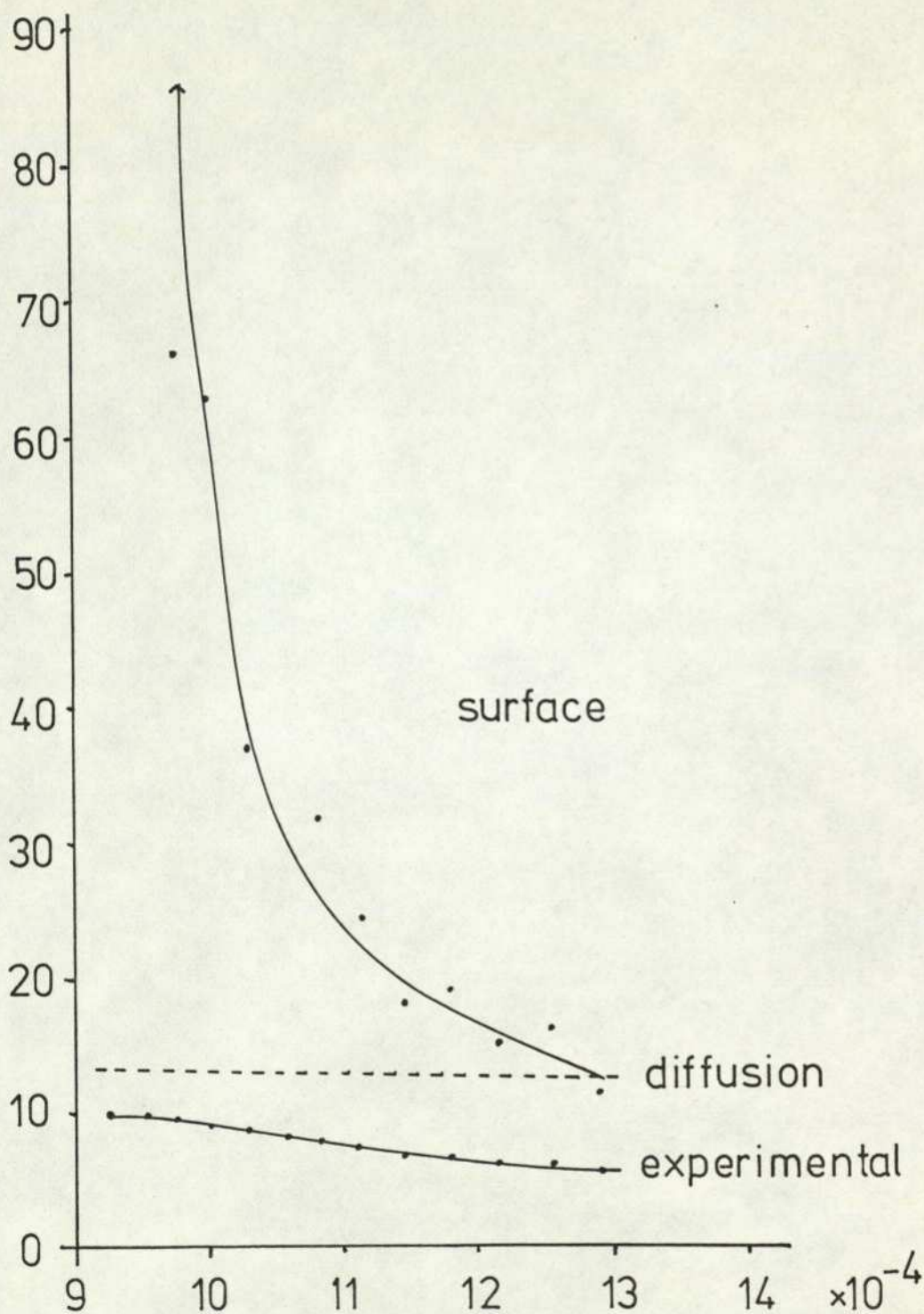
As the differential heat of adsorption is likely to decrease with increasing surface coverage,¹³⁰ the energy of activation should increase as O₂ concentration increases, since

$$E_a = E_H + \sum_i \Delta H_{i,ads} \quad 61$$

E_a is the observed activation energy, E_H the activation energy for formation of TiO₂ homogeneously, in the gas phase, and $\Delta H_{i,ads}$ is the heat of adsorption of the i th species on the surface. For the 60% O₂ concentration a very low correlation coefficient was obtained (see Table 31 Appendix 4) due to high scatter in the limited data points used for the determination of E_a , thus producing in this case an unsatisfactory value for the energy of activation.

Ordinate: $\ln(\text{Rate}) / \text{nm} \cdot \text{min}^{-1}$

Abscissa: $1/T / \text{K}$

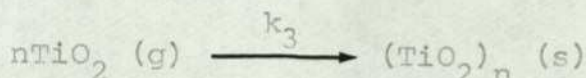
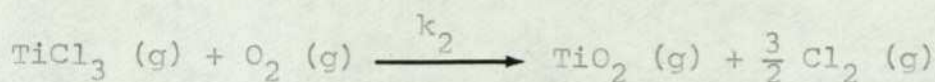
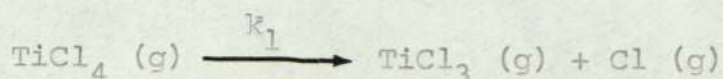


Graph 10 . Experimental, Diffusion and
Surface controlled Growth Rates .
($\sim 20\% \text{O}_2$)

It was emphasised previously (Section 4.1.2) that there seems to be little difference between growth-rates when these were obtained on different substrates. This is supported by the close agreement in activation energies when TiO_2 is deposited on a substrate ($74.80 \text{ kJ.mol}^{-1}$)^{110,111} or in powder form ($76.80 \text{ kJ.mol}^{-1}$;¹³¹ $71.128 \text{ kJ.mol}^{-1}$ ¹⁰¹). This implies that the energetics of the reaction are therefore governed by the adsorption of O_2 on the (already formed) TiO_2 surface. Although Ghoshtagore^{110,111} endeavoured to obtain his results when flow-rate was not rate-controlling his value for E_a is too low for it to be purely rate-control by a surface process alone. (Typical values for surface processes are in the range of $100\text{--}400 \text{ kJ.mol}^{-1}$).³⁰ In support of this criticism, and in agreement with this work, Suyama and Kato¹⁰¹ show a plot of TiCl_4 conversion versus reciprocal temperature which clearly shows that both surface and mass transport effects were present in their system, and that the value of $71.128 \text{ kJ.mol}^{-1}$ so obtained is an apparent and not the "true" activation energy.

Once the "true" activation energy has been found, this may be compared with the energy of activation for reaction without a substrate, ie. E_H for powder formation.

Powders may form in the gas phase by two processes, viz., homogeneous nucleation and heterogeneous growth. Homogeneous nucleation involves the accumulation of gaseous molecules into clusters of critical size.¹³² Once a cluster has attained the critical size, it can then grow by repeated reactions on its surface (heterogeneous growth). From comparison with other metal halides it has been concluded¹⁰¹ that the rate-limiting step for TiO_2 powder formation from the tetrachloride is the dissociation of the first halogen from the halide. The gas phase mechanism may be considered as



where k_1 , k_2 are rate constants, k_3 is the nucleation rate constant, and it is expected that $k_1 \ll k_2, k_3$. Therefore the E_H value which should be compared with the surface activation energy is that for the dissociation of TiCl_4 to TiCl_3 .

The homogeneous activation energy of $+120 \text{ kJ.mol}^{-1}$ quoted by Ghoshtagore¹¹¹ is much too low when one considers the temperatures required for a reasonable rate to occur in the gas phase (typically $\geq 900^\circ\text{C}$). It is not clear from the paper¹¹¹ how this value was obtained, nor exactly what it represents; indeed activation thermodynamic parameters seem to have been equated with data for the overall reaction under conditions where such a procedure is quite unjustified¹¹¹ (see Section 4.0).

From the theory of homogeneous nucleation of droplets from saturated vapours, the free energy of formation of a critical sized cluster "which is apparently the free energy of activation of this process"¹³³ can be determined from

$$\Delta G^* = N(\mu'_s - \mu'_g) + 4\pi r^2 \gamma \quad 62$$

where ΔG^* is the free energy of formation of a cluster of radius r , N the number of molecules in a cluster, μ'_s , μ'_g the chemical potentials of a molecule in the solid and gas phase respectively and γ the surface free energy.

The first term in equation 62 represents the free energy change for the transfer of N molecules from the vapour to the condensed state, while the second term represents the

free energy necessary to form the surface of the spherical cluster.¹³²

Thus
$$N = \frac{4\pi r^2 L}{3V_{\text{TiO}_2}}$$

$$\mu'_g = \mu_g^{\theta'} + kT \ln p$$

and, after condensation, the vapour pressure must be the equilibrium pressure for that temperature, ie

$$\mu'_s = \mu'_g(\text{equil}) = \mu_g^{\theta'} + kT \ln p_s$$

where L is the Avogadro constant, V_{TiO_2} the molar volume of TiO_2 and p, p_s the vapour pressure in the gas phase and solid phase respectively.

Substituting the values for N, μ'_g and μ'_s into equation 62 gives

$$\Delta G^* = - \frac{4\pi r^3 L}{3V_{\text{TiO}_2}} kT \ln (p/p_s) + 4\pi r^2 \gamma \quad 63$$

where p/p_s is the supersaturation ratio.

The first term in equation 62 can be positive or negative depending on the state of the vapour. If it is superheated, $\mu'_s > \mu'_g$ and the term is positive. If the vapour is supersaturated, $\mu'_s < \mu'_g$ and the term is negative. Consequently ΔG^* shows a maximum at a critical cluster size. Clusters smaller than this critical size are unstable and tend to evaporate whilst clusters larger than the critical size tend to grow. It follows that ΔG^* will be a maximum at the critical radius r_{crit} ,

ie.
$$\left(\frac{\partial \Delta G^*}{\partial r} \right) = 0$$

Now

$$\frac{\partial \Delta G^*}{\partial r} = 0 = \frac{-4\pi r_{\text{crit}}^2 \text{LkT}}{V_{\text{TiO}_2}} \ln(p/p_s) + 8\pi r_{\text{crit}} \gamma$$

and rearranging,

$$r_{\text{crit}} = \frac{2\gamma V_{\text{TiO}_2}}{\text{LkT} \ln(p/p_s)} \quad 64$$

Substituting equation 64 into 62 and simplifying, it follows that when $r = r_{\text{crit}}$

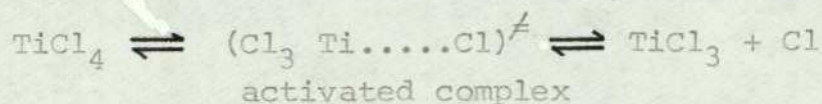
$$\begin{aligned} \Delta G^* &= \frac{16\pi\gamma^3 V_{\text{TiO}_2}^2}{3(\text{LkT} \ln(p/p_s))^2} \\ &= \frac{16\pi\gamma^3}{3\Delta G_v^2} \end{aligned} \quad 65$$

where $\Delta G_v = \frac{-RT}{V_{\text{TiO}_2}} \ln(p/p_s)$, the change in free energy per unit volume of TiO_2 formed in the vapour phase.

The free energy of formation of a critical sized cluster (ΔG^*) can be estimated using data from Suyama et al^{100,101} (see Table C). The nucleation rate constant may then be estimated using transition state theory (Section 4.0) by using reference 66

$$k_3 = \frac{kT}{h} \exp\left(-\frac{\Delta G^*}{RT}\right) \quad 66$$

A comparison of the nucleation rate constant with the dissociation rate constant can then indicate which is likely to be the rate-limiting step in the gas phase. Again using transition state theory, the free energy of formation of the activated complex roughly approximates to the free energy of formation of TiCl_3 .



ie. for this case (since $\Delta G^\ddagger$ for the association reaction is likely to tend to zero)

$$\Delta G_f^\ominus \approx \Delta G^\ddagger (\text{forward})$$

Therefore the rate constant for dissociation of TiCl_4 can be estimated by substituting the value of $\Delta G_f^\ominus$ (Table D) into equation 66.

Comparison of the rate constants for nucleation and dissociation (Table C) obtained in the above manner, shows that the rate-limiting step in the homogeneous reaction of TiCl_4 and O_2 is indeed predicted to be the dissociation of the first halogen from TiCl_4 for TiCl_4 conversions up to $\sim 40\%$. At higher conversion percentages, nucleation becomes rate-limiting.

It is emphasised that it is the gas stream temperatures that must be $\geq 900^\circ\text{C}$ for homogeneous powder formation, and not the temperature of the substrate. As TiCl_4 conversion in the gas phase decreases as gas temperature decreases, the homogeneous activation energy to be compared with the "true" surface energy of activation determined in this work must be that of the dissociation of TiCl_4 to TiCl_3 .

Using equation 61 the heat of adsorption of O_2 on titania can then be estimated using the experimentally determined "true" surface energy of activation.

$$E_a = E_H + \sum_i \Delta H_{i,\text{ads}} \quad 61$$

E_H can also be estimated using activated complex theory,

which shows that¹³⁴

$$E_H = \Delta H^\ddagger + RT - \Delta n^\ddagger RT$$

For the TiCl_4 dissociation,

$$\Delta n^\ddagger \approx 1$$

and therefore

$$\begin{aligned} E_H &\approx \Delta H^\ddagger \\ &\approx \Delta G^\ddagger + T\Delta S^\ddagger \\ &\approx \Delta G_f^\ominus + T\Delta S_f^\ominus \end{aligned}$$

since $\Delta G^\ddagger$ for the association reaction is likely to be close to zero.

A value of E_H at 1000K is given in Table E together with estimates for the heats of adsorption of oxygen on titania calculated using E_a values determined in this work. As stated before, the 60% O_2 concentration values are unsatisfactory due to the low correlation coefficient obtained when calculating E_a .

Table C

Free energy of nucleation, nucleation and dissociation rate constants

% TiCl ₄ conversion	ln p/p _s (a)	$\Delta G_{1173}^{\ddagger}/$ kJ.mol ⁻¹	k ₃ ¹¹⁷³ /s ⁻¹	k ₁ ¹⁰⁰⁰ /s ⁻¹
1	20.03	93.031	1.7592x10 ⁹	
5	16.81	132.140	3.1899x10 ⁷	
10	15.19	161.65	1.5477x10 ⁶	
~40	12.06	265.58	91.722	91.722 (b)
50	11.28	293.28	2.1289	
90	8.06	574.82	6.1821x10 ⁻¹³	

$$V_{\text{TiO}_2} = 18.74 \text{ cm}^3 \text{ mol}^{-1}$$

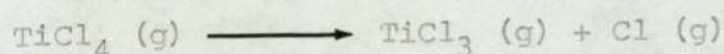
$$\gamma \text{ (a)} = 10^{-4} \text{ J.cm}^{-2}$$

(a) data obtained from reference 100

(b) obtained using transition state theory.

Table D

Dissociation of TiCl₄



T/K	$\Delta G_f^\ominus/\text{kJ.mol}^{-1}$	$\Delta H_f^\ominus/\text{kJ.mol}^{-1}$	$\Delta S_f^\ominus/\text{kJ.mol}^{-1}$	lnKp
100	332.43554	345.5733	0.131776	-399.83058
1000	217.41319	345.63606	0.1282287	-26.148962

Calculated from reference 127.

Table E

Activation energies and heats of adsorption

$E_H/\text{kJ}\cdot\text{mol}^{-1}$ Homogeneous	$E_a/\text{kJ}\cdot\text{mol}^{-1}$ Heterogeneous	% O_2 content	$\Delta H_{\text{O}_2, \text{ads}}/\text{kJ}\cdot\text{mol}^{-1}$
345.6	278.6	20	-134.0
	333.2	40	- 24.8
	204.4	60	-282.4

CONCLUSIONS AND FURTHER WORK

Chemical vapour deposition was studied as an alternative to successive thermal decompositions for the production of the refractory oxide supports which are used in catalytic gas detectors. Experiments were first undertaken to coat platinum wire coils with alumina using aluminium isopropoxide as the starting reagent. Various oxygen concentrations, flow rates and deposition times were used, but thick, dense uniform deposits could not be formed. The alumina obtained showed a dendritic type structure and was heavily contaminated with reaction products. Reaction initially occurred on the substrate surface, and thin deposits could be formed. However, these deposits then cracked and further reaction probably occurred in the gas phase, depositing particulates on the protruding surfaces.

Literature indicates that deposit cracking can be avoided if the thin coating ($\leq 0.8 \mu\text{m}$) is annealed at 800°C ^{86,87} to produce polycrystalline γ -alumina. Successive depositions and annealing treatments could therefore be undertaken in order to build up thicker deposits. Performing the reaction slowly under reduced pressure and at high temperatures would therefore aid the process as premature decomposition would then be reduced. This, however, would increase manufacturing costs and time, and makes the process commercially unattractive.

Satisfactory deposits, suitable for pellistor use, were obtained when titania was produced from titanium tetrachloride by CVD. The blue/grey polycrystalline rutile deposit evenly coated the platinum coil substrate and did not extend significantly down the platinum posts, thus permitting welding to pellistor holders. Rutile beads so produced may then be coated with various catalysts and their activity towards hydrocarbon oxidation studied. Comparisons should next be undertaken between conventional thermally decomposed "dipped" pellistors; CVD support/dipped catalysts, and CVD support/CVD thermally decomposed

catalysts in order to determine the most reliable overall manufacturing process.

Deposit growth rates for titania were determined at three oxygen concentrations over a range of temperatures between 480 and 800°C. At 800°C the rate-controlling process was diffusion and reasonable agreement between experimental and computed growth rates was obtained. The computed results showed that titanium tetrachloride was the rate-limiting reactant and that oxygen built up on the surface. The majority of the experimentally determined rates, however, fell into an intermediate region where rate control is described by combined mass transport and surface kinetic effects. By use of a first order equation, the contribution to growth by surface kinetics alone was calculated and the "true" activation energy determined. The values obtained were considerably higher than those obtained elsewhere. It is considered that even though the literature results were performed under such conditions that the rate was independent of flow rate, the activation energies quoted are too low for a surface process only,^{110,111} and should therefore also be interpreted in terms of a combined mass transfer/surface kinetic rate process.

Further work is desirable at lower temperatures (<480°C), to determine the "true" energy of activation with greater accuracy. Also, sets of experiments could be performed under various oxygen concentrations and flow rates to further clarify the mechanisms involved.

This study has, however, proved that high quality titania pellistors may be prepared by CVD with speed and high reproducibility on the platinum coils which are conventionally used for catalytic gas detection. This is in contrast to the case of alumina, where CVD is not a practical alternative to the current method of manufacture.

A P P E N D I X 1

Derivation of Collision Frequency (taken from Ref. 66)

Consider a wall of area A perpendicular to the x -axis. If a molecule has a velocity v_x lying between 0 and $+\infty$ it will strike the wall in time Δt if it lies at a distance of $v_x \Delta t$ (if its velocity is between 0 and $-\infty$ the molecule is moving away from the wall). Therefore any molecule in the volume $A v_x \Delta t$ will strike the wall in Δt . The total number of collisions is therefore

$$Z = cA\Delta t \int_0^{+\infty} v_x f(v_x) dv_x \quad (1)$$

where Z is the number of collisions, c the concentration and $f(v_x)$ the velocity distribution.

To solve the above equation one must know the explicit form of the velocity distribution.

Consider the mean velocity of a particle

$$\langle v_x \rangle = \int_{-\infty}^{+\infty} v_x f(v_x) dv_x$$

The function $f(v_x)$ gives the probability of the x -component of velocity lying in the range of v_x to $v_x + dv_x$. The probability that a molecule has a velocity component v_x in the above range, a velocity component v_y in the range v_y to $v_y + dv_y$ and a component v_z in the range v_z to $v_z + dv_z$ is $f(v_x) f(v_y) f(v_z) dv_x dv_y dv_z$, since these velocities are independent of each other.

$$\text{ie. } F(v_x, v_y, v_z) dv_x dv_y dv_z = f(v_x) f(v_y) f(v_z) dv_x dv_y dv_z \quad (2)$$

Assuming that the velocity distribution is independent of orientation, but dependent only on speed v , where $v^2 = v_x^2 + v_y^2 + v_z^2$, equation (2) becomes

$$F(v_x^2 + v_y^2 + v_z^2) = f(v_x) f(v_y) f(v_z) \quad (3)$$

It is found that $f(v_x) = K \exp(-\zeta v_x^2)$ (4)
satisfies equation (3), where K and ζ are constants. Therefore

$$f(v_x) f(v_y) f(v_z) = K^3 \exp(-\zeta (v_x^2 + v_y^2 + v_z^2)) \quad (5)$$

The probability that the velocity lies between $-\infty$ and $+\infty$ must be unity.

$$\int_{-\infty}^{+\infty} f(v_x) dv_x = 1 \quad (6)$$

Substituting (4) into (6)

$$\begin{aligned} \int_{-\infty}^{+\infty} f(v_x) dv_x &= K \int_{-\infty}^{+\infty} \exp(-\zeta v_x^2) dv_x \\ &= K(\pi/\zeta)^{\frac{1}{2}} \end{aligned}$$

Therefore

$$K = (\zeta/\pi)^{\frac{1}{2}}$$

To evaluate ζ

$$\begin{aligned} \langle v_x^2 \rangle &= \int_{-\infty}^{+\infty} v_x^2 f(v_x) dv_x \\ &= (\zeta/\pi)^{\frac{1}{2}} \int_{-\infty}^{+\infty} v_x^2 \exp(-\zeta v_x^2) dv_x \quad (7) \end{aligned}$$

The integral on the right-hand side is a standard one, and has the value $\frac{1}{2}(\pi/\zeta^3)^{\frac{1}{2}}$.

Therefore

$$\langle v_x^2 \rangle = (\zeta/\pi)^{\frac{1}{2}} \frac{1}{2}(\pi/\zeta^3)^{\frac{1}{2}} = \frac{1}{2}\zeta \quad (8)$$

The mean speed $\bar{u}$ is

$$\bar{u} = \langle v^2 \rangle = \langle v_x^2 + v_y^2 + v_z^2 \rangle$$

and therefore

$$\bar{u} = \frac{3}{2} \zeta \quad (9)$$

Also, from kinetic theory,

$$pV = \frac{1}{3} Nm\bar{u} \quad (10)$$

where N is the actual number of molecules present and m is the mass of one molecule. In addition

$$pV = NkT \quad (11)$$

Equating (10) and (11) and substituting in the value for $\bar{u}$ one obtains

$$\frac{1}{2}Nm\zeta = NkT$$

Therefore

$$\zeta = \frac{1}{2}m/kT$$

Hence the velocity distribution is

$$f(v_x) = (m/2\pi kT)^{\frac{1}{2}} \exp(-mv_x^2/2kT) \quad (12)$$

One can now evaluate the integral in equation (1).

$$Z = cA\Delta t \int_0^{+\infty} f(v_x) dv_x \quad (1)$$

Therefore

$$\int_0^{\infty} f(v_x) dv_x = (m/2\pi kT)^{\frac{1}{2}} \int_0^{\infty} \exp\left(-\frac{mv_x^2}{2kT}\right) dv_x$$

The integral on the right-hand side is again a standard one, viz:

$$\int_0^{\infty} x e^{-ax^2} dx = \frac{1}{2}a$$

whence

$$\int_0^{\infty} v_x f(v_x) dv_x = \left(\frac{kT}{2\pi m}\right)^{\frac{1}{2}}$$

Therefore the number of collisions per unit time per unit area is

$$Z = \left(\frac{kT}{2\pi m}\right)^{\frac{1}{2}} c$$

but

$$\bar{u} = \left(\frac{8kT}{\pi m}\right)^{\frac{1}{2}}$$

Therefore

$$Z = \frac{\bar{u}}{4} c.$$

APPENDIX 2

Table 1
Rotameter Calibrations

Setting $\text{cm}^3 \text{min}^{-1}$	Rotameter N_2		Rotameter O_2	
	Time to pass $110 \text{cm}^3/\text{s}$	Amount passed/ $\text{cm}^3 \text{min}^{-1}$	Time to pass $50 \text{cm}^3/\text{s}$	Amount passed/ $\text{cm}^3 \text{min}^{-1}$
100	56.2	117.44	65.8	100.3
150	38.4	171.88	43.4	152.07
200	29.4	224.49	33.2	198.8
250	23.0	280.96	26.8	246.27
300	19.4	340.21	22.2	297.3
350	16.8	392.86	19.0	347.37
400	15.2	434.21	16.8	392.86
450	13.6	485.29	14.8	445.95
500	12.4	532.26	13.6	485.29
550	11.0	600.00	12.4	532.26
600	10.2	647.06	11.2	589.29
650	9.4	702.13	10.2	647.06
700	8.8	750.00	9.6	687.5
750	8.0	825.00	8.8	750.00
800	7.6	868.42	8.4	785.72
850	7.2	916.67	7.8	846.15
900	6.8	970.59	7.4	891.89
950	6.4	1031.25	7.0	942.86
1000	6.2	1064.52	6.8	970.59
1050	5.8	1137.93	6.4	1034.25
1100	5.6	1178.57	6.0	1100.00
1150	5.2	1269.23	5.8	1137.93
1200	5.0	1320.00	5.6	1178.57

Table 2

Calibration of Wheatstone Bridge (Constant Resistance) Units

Channel	Load (Ω)	Dial Setting	I/A	V/V	R/ Ω	R/Setting
1	1.0	0.62	1.20	1.386	1.155	1.863
	2.2	1.19	1.10	2.553	2.321	1.950
	4.7	2.33	0.40	1.828	4.570	1.961
	6.8	3.415	0.28	1.910	6.821	1.998
	10.0	5.075	0.20	2.006	10.030	1.976
2	1.0	0.62	1.16	1.343	1.158	1.867
	2.2	1.205	1.08	2.511	2.325	1.9295
	4.7	2.36	0.52	2.436	4.685	1.985
	6.8	3.46	0.32	2.193	6.853	1.981
	10.0	5.125	0.20	2.022	10.110	1.981
3	1.0	0.585	1.46	1.690	1.158	1.979
	2.2	1.145	0.86	1.967	2.287	1.998
	4.7	2.29	0.42	1.936	4.6095	2.013
	6.8	3.375	0.30	2.052	6.840	2.027
	10.0	5.01	0.18	1.841	10.228	2.042
4	1.0	0.59	1.45	1.680	1.159	1.964
	2.2	1.165	1.20	2.780	2.317	1.989
	4.7	2.315	0.42	1.940	4.619	1.995
	6.8	3.42	0.28	1.915	6.839	1.948
	10.0	5.055	0.18	1.829	10.161	2.010
5	1.0	0.60	1.36	1.575	1.158	1.930
	2.2	1.175	1.16	2.698	2.326	1.9795
	4.7	2.315	0.40	1.840	4.600	1.987
	6.8	3.445	0.33	2.268	6.873	1.995
	10.0	5.065	0.19	1.902	10.015	1.976
6	1.0	0.61	1.41	1.631	1.157	1.896
	2.2	1.19	1.18	2.744	2.325	1.954
	4.7	2.325	0.79	3.693	4.595	1.976
	6.8	3.425	0.25	1.703	6.812	1.989
	10.0	5.06	0.24	2.437	10.154	2.007

Table 3

Aluminium Isopropoxide Batch Analysis

Sol. No.	$\text{Al}(\text{O}^i\text{Pr})_3$ wt/g	pH	Theoretical Al/g	Determined Al/g
1	0.1772	0.10	0.0234	0.0267
2	0.1773	0.24	0.0234	0.0271
3	0.1772	0.48	0.0234	0.0272
4	2.5535	0.50	0.3375	0.3772

Table 4(a)

Comparison of Theoretical and Determined Al Pick-up

T bath °C	Total flow	T _{N₂} /K	Theoretical Al(O ⁱ Pr) ₃ /g	Theoretical Al/g 15% w/w	Determined Al/g
124	39.96	473.15	1.4494	0.2174	0.046
					0.031
		403.15	1.7011	0.2552	0.033
	76.56	397.15	1.7266	0.2589	
					0.033
p=5.2mmHg	76.56	473.15	2.7763	0.4165	0.034
					0.0562
		403.15	3.2585	0.4888	0.0569
		397.15	3.3081	0.4962	
141	76.56	473.15	7.6185	1.1428	
					0.19
		403.15	8.9410	1.3412	0.20
		397.15	9.0759	1.3614	
142	109.08	473.15	11.4825	1.7224	0.3175
					0.3196
		403.15	13.4761	2.0214	0.32
		397.15	13.6796	2.0519	
144	38.28	473.15	4.5271	0.6791	
					0.158
		403.15	5.3273	0.7991	0.157
		397.15	5.3937	0.8091	

Table 4(b)

T _{bath} (°C)	Flow N ₂ /dm ³	Flow O ₂ /dm ³	T _{N₂} /O ₂ /K	Theoret -ical Al(O ⁱ Pr) ₃ /g	Theoret -ical Al/g 15%	Deter -mined Al/g
141	58.8	15.0	473.15	3.5264	0.5289	0.137
						0.149
			403.15	4.1388	0.6208	0.146
144	86.4	21.0	473.15	6.0931	0.9139	0.395
						0.394
			403.15	7.1511	1.0727	

Table 5

Theoretical TiCl_4 Content

$T_{\text{bath}} (^{\circ}\text{C})$	Flow N_2 /dm ³	Flow O_2 /dm ³	$T_{\text{N}_2/\text{O}_2}$ /K	Theoretical TiCl_4 /g
28	7.5	1.75	338.15	1.1876
VP=14.0mmHg			393.15	1.0215
29			338.15	1.2395
VP=14.6mmHg			393.15	1.0661
30				
VP=15.5mmHg			338.15	1.3175
			393.15	1.1332
28	5.75	3.75	338.15	1.2197
			393.15	1.0491
29			338.15	1.2730
			393.15	1.0949
30			338.15	1.3531
			393.15	1.1638
28	3.60	5.32	338.15	1.1452
			393.15	0.9850
29			338.15	1.1953
			393.15	1.0281
30			338.15	1.2705
			393.15	1.0928

Table 6Gas Densities

T/K (Tb+Ts)/2	ρ_{TiCl_4} /g cm ⁻³	ρ_{O_2}	ρ_{Cl_2}	ρ_{N_2}
573.15	0.00403374	0.00068037	0.00150764	0.00059563
583.15	0.00396457	0.00066871	0.00148178	0.00058542
595.15	0.00388137	0.00065467	0.00145069	0.00057313
608.15	0.00380159	0.00064122	0.00142087	0.00056135
620.65	0.00372503	0.00062830	0.00139225	0.00055005
633.15	0.00365149	0.00061590	0.00136477	0.00053919
645.65	0.00358079	0.00060397	0.00133834	0.00052875
658.15	0.00351279	0.00059250	0.00131292	0.00051871
670.65	0.00344731	0.00058146	0.00128845	0.00050904
683.15	0.00338423	0.00057082	0.00126488	0.00049973
695.65	0.00332342	0.00056056	0.00124215	0.00049075
708.15	0.00326476	0.00055067	0.00122022	0.00048208
720.65	0.00320813	0.00054112	0.00119906	0.00047372
733.15	0.00315343	0.00053189	0.00117861	0.00046564

Table 7Sutherland Equation Constants

Compound	S/K	$b/g \text{ K}^{-\frac{1}{2}} \text{ cm}^{-1} \text{ s}^{-1}$
O ₂	124.89325	16.877460
Cl ₂	300.16949	15.59322
N ₂	107.07428	13.816036

Table 8

Gas Viscosities

$T(^{\circ}\text{K})$ (T_b+T_s)/2	TiCl_4 / 10^{-6} $\text{gcm}^{-1}\text{s}^{-1}$	η_{O_2}	η_{Cl_2}	η_{N_2}
573.15	170.199	331.76	244.999	278.70
583.15	172.38	335.67	248.59	281.88
595.65	175.66	340.51	253.05	286.63
608.15	179.60	345.30	257.46	289.71
620.65	182.83	350.03	261.84	293.55
633.15	186.63	354.71	266.17	297.36
645.65	189.81	359.34	270.47	301.12
658.15	193.58	363.92	274.73	304.85
670.65	196.85	368.46	278.96	308.53
683.15	200.55	372.95	283.15	312.28
695.65	203.72	377.39	287.30	315.79
708.15	207.38	381.79	291.42	319.37
720.65	210.46	386.15	295.51	322.91
733.15	214.05	390.47	299.57	326.42

Table 9

Lennard-Jones Parameters^{44,115}

	σ/nm	E_{OA}/k
TiCl_4	0.5931	495.6
N_2	0.3798	71.4
O_2	0.3467	106.7
Cl_2	0.4217	316.0

Table 10

Binary Diffusion Coefficients

T/K (T _b +T _s)/2	$D_{\text{TiCl}_4/\text{O}_2}$ /cm ² s ⁻¹	$D_{\text{TiCl}_4/\text{Cl}_2}$	$D_{\text{TiCl}_4/\text{N}_2}$	$D_{\text{O}_2/\text{Cl}_2}$	$D_{\text{O}_2/\text{N}_2}$	$D_{\text{Cl}_2/\text{N}_2}$
573.15	0.22048064	0.11344552	0.23081011	0.39172132	0.62538341	0.39665782
583.15	0.22761785	0.11710209	0.23793467	0.40399682	0.6438351	0.4085478
595.65	0.23637729	0.12220247	0.24707052	0.4190741	0.66732653	0.42399329
608.15	0.24549522	0.12713318	0.25612106	0.43467197	0.69140440	0.43939513
620.65	0.25450182	0.13207603	0.26548444	0.45052891	0.71527408	0.45497358
633.15	0.26355077	0.13713561	0.27500086	0.46659148	0.73943213	0.47109619
645.65	0.27305116	0.14219245	0.28445145	0.48285092	0.76416295	0.48718035
658.15	0.28242201	0.14748596	0.29422852	0.49902281	0.78898337	0.5033651
670.65	0.29217749	0.15303833	0.30408418	0.51569473	0.81428239	0.51999501
683.15	0.30174147	0.15830891	0.3139048	0.53259823	0.84018109	0.53671678
695.65	0.31173164	0.16194833	0.32406526	0.54966814	0.86614273	0.55357736
708.15	0.3215985	0.16752312	0.33428788	0.56695754	0.89225157	0.57089998
720.65	0.33155852	0.17476038	0.34444666	0.58452812	0.91884585	0.58815293
733.15	0.34193514	0.18046300	0.35495842	0.60190537	0.94544415	0.60558984

APPENDIX 3

List of Experiments Using $\text{Al}(\text{O}^i\text{Pr})_3$

Run Number	Temperature of Coil/ $^{\circ}\text{C}$	Percentage O_2	Duration /min
Ala	300	19.03	100
Alb	300	19.03	230
A2	350	19.03	180
A3	350	18.92	15
A4	420	19.03	90
NA1	~ 185	19.03	180
NA2	~ 185	19.03	180
NA3	350	19.03	210
NA4	350	18.76	140
NA5	350	29.30	10
NA6	350	24.27	10
NA7	350	18.92	180
NA8	375	18.92	1920
NA9	400	18.92	300
NA10	420	18.92	1920
NA11 Repeat of NA4	350	18.76	180
NA12 Repeat of NA7	350	18.92	1620
NA13 Repeat of NA9	400	18.92	330

List of Experiments Using TiCl_4

Run Number	Temperature of Coils/ $^{\circ}\text{C}$	Percentage O_2	Duration /min
T1	400	18.92	180
T2	500	18.92	360
T3	500	39.47	180
T4	480	39.47	360
T5	480	59.64	360
T6	480	78.35	360
DT1	500	18.92	360
DT2	500	39.47	360
DT3	480	39.47	360
DT4	480	59.64	240
DT5	500	18.92	240
DT6	500	39.47	240
DT7	500	59.64	240
DT8	525	18.92	240
DT9	525	39.47	240
DT10	525	59.64	240
DT11	550	18.92	240
DT12	550	39.47	240
DT13	550	59.64	240
DT14	575	18.92	240
DT15	575	39.47	180
DT16	575	59.64	180
DT17	600	18.92	180
DT18	600	39.47	90
DT19	600	59.64	90
DT20	625	18.92	75
DT21	625	39.47	60
DT22	625	59.64	30
DT23	650	18.92	60
DT24	650	39.47	48
DT25	650	59.64	25.5
DT26	675	18.92	40
DT27	675	39.47	15

Run Number	Temperature of Coils/°C	Percentage O ₂	Duration /min
DT28	675	59.64	10
DT29	700	18.92	15
DT30	700	39.47	15
DT31	700	59.64	15
DT32	725	18.92	15
DT33	725	39.47	10
DT34	725	59.64	10
DT35	750	18.92	6
DT36	750	39.47	6
DT37	750	59.64	6
DT38	775	18.92	5
DT39	775	39.47	6
DT40	775	59.64	5
DT41	800	18.92	4.5
DT42	800	39.47	6
DT43	800	59.64	4.5
DT44 Repeat of DT4	480	59.64	240
DT45 " " DT5	500	18.92	240
DT46 " " DT12	550	39.47	240
DT47 " " DT18	600	39.47	90
DT48 " " DT24	650	39.47	39
DT49 " " DT29	700	18.92	20
DT50 " " DT30	700	39.47	16.5
DT51 " " DT35	750	18.92	5
DT52 " " DT42	800	39.47	5

Run Al.a.

Temperature of coils, 300°C

19.03% O₂

Coil No.	R _o /Ω	R _t /Ω	Dial Setting
1	2.663	8.657	4.33
2	3.736	12.145	6.07
3	3.736	12.145	6.07
4	3.822	12.424	6.21
5	3.018	9.811	4.905
6	3.473	11.289	5.645

Bubbler 1: 15.2963g Al(OⁱPr)₃

Bubbler 2: 16.4904g Al(OⁱPr)₃

N₂ setting: 0.500 532cm³min⁻¹

O₂ setting: 0.125 125cm³min⁻¹

Back pressure: 39mm Hg

Sandbath: 124°C

Thermocouple Readings

No	mV	°C
1	6.38	138
2	5.56	124
3	6.29	138
5	5.43	123
6	4.40	103
7	4.20	98

Ambient temperature: 20°C

Variac 1 setting: 180

Variac 2 setting: 80

Voltage Across the Coils

Mins after Start	1	2	Coil No. 3	4	5	6
10	0.957	1.604	2.032	2.558	1.244	1.689
20	1.498	2.267	1.957	2.120	1.803	2.085
30	1.606	2.370	1.923	2.250	1.861	2.204
40	1.602	2.402	1.922	2.294	1.889	2.236
50	1.612	2.423	1.904	2.320	1.907	2.256
60	1.620	2.436	1.903	2.342	1.917	2.267
70	1.628	2.453	1.900	2.364	1.927	2.277
80	1.634	2.475	1.916	2.391	1.936	2.290
90	1.636	2.485	1.943	2.409	1.933	2.300
100	1.636	2.496	1.947	2.420	1.940	2.302

Run Al.b.

Temperature of coils, 300°C

19.03% O₂

Same coils used as in Run A2.a.

Bubbler 1: 16.6539g Al(OⁱPr)₃
Bubbler 2: 16.2289g Al(OⁱPr)₃
N₂ setting: 0.500 532cm³min⁻¹
O₂ setting: 0.125 125cm³min⁻¹
Back pressure: 44mm Hg
Sangbath: 124°C

Thermocouple Readings

No.	mV	°C	
1	6.28	138	
2	5.45	123	Ambient temperature: 21°C
3	6.13	136	Variac 1 setting: 180
5	6.22	139	Variac 2 setting: 90
6	5.16	118	
7	4.11	98	

Voltage Across the Coils

Mins after Start	1	2	Coil No. 3	4	5	6
10	1.724	2.634	Coil	3.447	2.074	2.367
20	1.700	2.566	broke	3.468	2.038	2.329
30	1.697	2.363	in	3.486	2.017	2.225
40	1.695	2.457	Run Ala	3.515	1.978	2.235
50	1.693	2.544		3.530	1.970	2.248
60	1.690	2.554		3.416	1.977	2.258
70	1.687	2.566		3.374	1.988	2.268
80	1.683	2.584		3.365	2.005	2.282
90	1.684	2.594		3.372	2.012	2.290
100	1.684	2.599		3.420	2.015	2.295
110	1.685	2.600		3.403	2.017	2.297
120	1.685	2.604		3.396	2.020	2.298
130	1.686	2.606		3.375	2.023	2.298
140	1.686	2.608		3.345	2.026	2.299
150	1.693	2.614		3.319	1.977	2.306
160	1.693	2.597		3.389	1.974	2.296
170	1.692	2.592		3.409	1.969	2.294
180	1.691	2.592		3.415	1.966	2.295
190	1.691	2.593		3.410	1.966	2.296
200	1.691	2.595		3.389	1.966	2.297
210	1.692	2.596		3.350	1.966	2.299
220	1.692	2.597		3.272	1.966	3.000
230	1.692	2.599		3.196	1.968	3.001

Total Run Time = 5½ hours (Al.a. and Al.b.)

Run A2

Temperature of coils, 350°C.

19.03% O₂

Coil No.	R _O /Ω	R _t /Ω	Dial Setting
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1	3.532	12.175	6.09
2	3.698	12.747	6.37
3	3.901	13.447	6.72
4	3.809	13.130	6.57
5	3.528	12.161	6.08
6	3.717	12.813	6.40

Bubbler 1: 15.3309g Al(OⁱPr)₃Bubbler 2: 14.7820g Al(OⁱPr)₃N₂ setting: 0.500 532cm³min⁻¹O₂ setting: 0.125 125cm³min⁻¹

Back pressure: 44mm Hg

Sandbath: 124°C

Thermocouple Readings

No.	mV	°C	
1	6.26	136	
2	5.38	121	Ambient temperature: 20°C
3	6.01	133	Variac 1 setting: 180
5	6.73	157	Variac 2 setting: 90
6	5.58	125	
7	4.10	97	

Voltage Across the Coils

Mins after Start	Coil No.					
	1	2	3	4	5	6
10	2.762	2.251	2.152	3.537	3.224	2.781
20	2.808	2.255	2.159	3.560	3.206	2.880
30	2.522	2.306	2.188	3.587	3.273	2.435
40	2.676	2.307	2.179	3.583	3.267	2.638
50	2.699	2.305	2.175	3.573	3.263	2.657
60	2.714	2.315	2.183	3.591	3.276	2.675
70	2.712	2.293	2.159	3.552	3.237	2.678
80	2.749	2.277	2.139	3.519	3.210	2.724
90	2.764	2.265	2.130	3.510	3.203	2.734
100	2.763	2.245	2.119	3.485	3.180	2.732
110	2.766	2.224	2.095	3.456	3.153	2.736
120	2.761	2.238	2.104	3.475	3.171	2.732
130	2.722	2.230	2.100	3.461	3.150	2.785
140	2.727	2.240	2.103	3.469	3.173	2.795
150	2.724	2.321	2.175	3.576	3.264	2.789
160	2.721	2.343	2.190	3.594	3.280	2.286
170	2.718	2.352	2.206	3.618	3.306	2.781
180	2.713	2.360	2.209	3.621	3.301	2.771

Run A3Temperature of coils, 350°C. 18.92% O₂

Coil No.	R_o/Ω	R_t/Ω	Dial Setting
1	3.336	11.499	5.75
2	3.214	11.079	5.54
3	3.564	12.286	6.14
4	3.398	11.713	5.85
5	3.670	12.651	6.325
6	3.758	12.952	6.48

Bubbler 1: 13.4788g Al(OⁱPr)₃
Bubbler 2: 13.9554g Al(OⁱPr)₃
N₂ setting: 0.700 750cm³min⁻¹
O₂ setting: 0.175 175cm³min⁻¹
Back pressure: 46mm Hg.
Sandbath: 124°C

Voltage Across the Coils

Mins after Start	Coil No.					
	1	2	3	4	5	6
10	1.881	1.737	2.059	3.447	3.234	2.049
20	Reactor exploded at t = 15 mins.					

Run A4

Temperature of coils, 420°C

19.03% O₂

Coil No.	R _O /Ω	R _T /Ω	Dial Setting
1	4.123	15.35	7.67
2	3.230	12.02	5.97
3	2.999	11.16	5.58
4	3.498	13.02	6.51
5	3.609	13.43	6.72
6	3.122	11.62	5.81

Bubbler 1: 15.0001g Al(OⁱPr)₃Bubbler 2: 14.9983g Al(OⁱPr)₃N₂ setting: 0.500 532cm³min⁻¹O₂ setting: 0.125 125cm³min⁻¹

Back pressure reading: 20mm Hg

Sandbath: 128°C

Thermocouple Readings

No.	mV	°C	
1	6.01	132	
2	5.28	119	Ambient temperature: 20°C
3	6.10	134	Variac 1 setting: 180
5	4.92	103	Variac 2 setting: 80
6	6.12	136	
7	3.95	98	

Voltage Across the Coils

Mins after Start	Coil No.					
	1	2	3	4	5	6
10	2.72	2.41	2.15	3.78	3.53	2.79
20	2.795	2.485	2.21	3.89	3.63	2.875
30	2.75	2.45	2.178	3.82	3.58	2.825
40	2.75	2.445	2.180	3.835	3.585	2.830
50	2.77	2.52	2.245	3.935	3.68	2.92
60	2.88	2.575	2.29	4.000	3.75	2.98
70	2.92	2.61	2.32	4.04	3.77	2.99
80	2.97	2.665	2.365	4.115	3.850	3.050
90	2.95	2.65	2.345	4.090	3.830	3.045

Run NA1

Temperature of coil $\sim 185^{\circ}\text{C}$ 19.03% O_2 2cm ID
unbaffled reactors

Coil No.	R_m/Ω	R_o/Ω	R_t/Ω	Dial Setting
1	3.360	1.553	5.355	2.68
2	3.492	1.614	5.565	2.78
3	3.688	1.705	5.878	2.94
4	3.296	1.524	5.253	2.625
5	3.632	1.679	5.788	2.895
6	3.424	1.583	5.467	2.735

Bubbler 1: 16.2147g $\text{Al}(\text{O}^i\text{Pr})_3$

Bubbler 2: 15.5936g $\text{Al}(\text{O}^i\text{Pr})_3$

N_2 setting: 0.500 $532\text{cm}^3\text{min}^{-1}$

O_2 setting: 0.125 $125\text{cm}^3\text{min}^{-1}$

Back pressure: 50mm Hg.

Sandbath: 124°C

Run time: 3 hours.

Thermocouple Readings

No.	mV	$^{\circ}\text{C}$	
1	9.92	207	
2	7.94	173	Ambient temperature: 25°C
3	8.85	189	Variac 1 setting: 160
4	2.74	80	Variac 2 setting: 140
5	4.57	112	
6	2.51	73	
7	6.82	152	

Voltage Across Coils

Coil No.	Initial Value	Increases To	Decreases To	Final Value
1	1.69	-	0.30	0.30
2	0.55	0.600	-	0.600
3	0.06	0.644	0.63	0.63
4	0.75	0.766	-	0.766
5	0.67	0.72	-	0.72
6	0.103	-	0.095	0.095

All coils exhibited usual erratic behaviour at the start of the experiment.

Run NA2

Temperature of coils $\sim 185^{\circ}\text{C}$ 19.03% O_2 2cm ID
unbaffled reactors

Coil No.	R_m / Ω	R_o / Ω	R_t / Ω	Dial Setting
1	3.330	1.538	5.302	2.65
2	3.788	1.75	6.032	3.015
3	3.978	1.838	6.334	3.165
4	3.862	1.784	6.15	3.075
5	3.319	1.533	5.285	2.64
6	2.918	1.348	4.646	2.32

Bubbler 1: 15.2708g $\text{Al}(\text{O}^i\text{Pr})_3$
 Bubbler 2: 15.4882g $\text{Al}(\text{O}^i\text{Pr})_3$
 N_2 setting: 0.500 $532\text{cm}^3\text{min}^{-1}$
 O_2 setting: 0.125 $125\text{cm}^3\text{min}^{-1}$
 Back pressure: 40mm Hg
 Sandbath: 125°C
 Run time: 3 hours

Thermocouple Readings

No.	mV	$^{\circ}\text{C}$	
1	10.05	209	
2	8.01	173	Ambient temperature: 24°C
3	8.88	189	Variac 1 setting: 160
4	3.23	88	Variac 2 setting: 150
5	5.17	112	
6	2.77	77	
7	6.99	154	

Voltage Across Coils

Coil No.	Initial Value	Increases To	Decreases To	Final Value
1	0.580	0.640	-	0.640
2	0.694	0.720	-	0.720
3	0.700	0.730	-	0.730
4	0.690	0.715	-	0.715
5	0.565	0.585	-	0.585
6	0.500	0.505	-	0.505

All coils exhibited usual erratic behaviour at the start of the experiment (see Fig. 18 & 19).

Run NA5

Temperature of coils 350°C 29.3% O_2 2mm ID
unbaffled reactors

Coil No.	R_{m}/Ω	R_{o}/Ω	R_{t}/Ω	Dial Setting
1	2.635	2.412	5.728	2.865
2	2.613	2.392	5.680	2.840
3	4.158	3.807	9.039	4.520
4	2.646	2.423	5.752	2.875
5	2.892	2.648	6.287	3.145
6	2.844	2.604	6.182	3.090

Bubbler 1: 15.1685g $\text{Al}(\text{O}^{\text{i}}\text{Pr})_3$
Bubbler 2: 15.1606g $\text{Al}(\text{O}^{\text{i}}\text{Pr})_3$
 N_2 setting: 0.825 $905\text{cm}^3\text{min}^{-1}$
 O_2 setting: 0.375 $375\text{cm}^3\text{min}^{-1}$
Back pressure: Not obtained
Sandbath: 124°C
Run time: ~10 minutes

Thermocouple Readings

Not obtained. Experiment terminated prematurely due to near explosion.

Voltage Across the Coils

Behaviour highly erratic immediately prior to shut down.

Run NA8

Temperature of coils 375°C 18.92% O₂ 2mm ID
unbaffled reactors

Coil No.	R _m /Ω	R _o /Ω	R _t /Ω	Dial Setting
1	4.681	4.356	10.771	5.385
2	3.715	3.457	8.548	4.275
3	3.407	3.170	7.839	3.920
4	3.417	3.179	7.862	3.930
5	4.186	3.895	9.632	4.815
6	3.747	3.487	8.622	4.310

Bubbler 1: 16.0089g, 14.8154g, 17.2775g, 14.7033g, 16.6429g,
15.7370g, 17.1726g, 16.7507g Al(OⁱPr)₃

Bubbler 2: 15.3383g, 15.1583g, 15.0336g, 16.4191g, 16.4711g,
15.4859g, 16.8432g, 16.1212g Al(OⁱPr)₃

N₂ setting: 0.700 750cm³min⁻¹

O₂ setting: 0.175 175cm³min⁻¹

Back pressure: 56, 43, 43, 47, 47, 76, 49, 55mm Hg

Sandbath: 124°C throughout

Run time: 3½hrs+3hrs+4hrs+5hrs+4hrs+4½hrs+4hrs+4hrs

Total 32hrs.

Thermocouple ReadingsNo.mV°C

1	8.19	8.16	8.30	8.07	8.16	8.19	8.40	8.47	173	172	175	173	174	174	177	180
2	6.80	6.80	6.92	6.74	6.80	6.79	6.92	7.02	148	148	151	149	150	149	151	153
3	7.74	7.77	7.96	7.75	7.92	7.74	7.88	7.99	165	166	170	168	171	166	169	171
4	3.63	3.75	3.70	3.56	3.70	3.69	3.75	3.85	93	95	95	93	96	95	96	98
5	5.86	6.75	6.84	6.66	6.70	6.49	6.77	6.98	132	148	151	149	149	144	149	153
6	2.86	3.00	3.21	3.02	3.10	3.06	3.20	3.29	75	78	83	80	82	80	83	84
7	6.09	6.09	6.22	6.15	6.14	6.09	6.18	6.26	134	134	138	137	137	135	137	138

Ambient temperature: 21.5, 21, 22, 23, 23, 22, 22, 22°C

Variac 1 setting: 140

Variac 2 setting: 160

Voltage Across the Coils

Coil 1: Initially 1.560V, usual erratic behaviour, smooths to 1.525V, fluctuates twice first decreases to 0.625V, second to 1.105V. Increases to 1.605V at the end.

The rest of the experimental voltages for coil 1 are tabulated below:

Run	Initial Value	Increases To	Decreases To	Final Value
2	1.615	1.645	1.625	1.625
3	1.640	1.690	1.643	1.650
4	1.643	1.695	1.645	1.715
5	1.760	1.800	1.750	1.750
6	1.750	1.815	1.750	1.790
7	1.810	1.865	1.800	1.810
8	1.810	1.870	1.810	1.830

Coil 2: Initially 1.415V, usual erratic behaviour observed, fluctuates twice first decreasing to 0.870V, second to 0.205V. Increases to 1.510V at the end.

The rest of the voltages are tabulated below:

Run	Initial Value	Increases To	Decreases To	Final Value
2	1.515	1.550	1.515	1.525
3	1.535	1.580	1.535	1.535
4	1.515	1.563	1.515	1.613
5	1.630	1.660	1.625	1.615
6	1.620	1.665	1.620	1.663
7	1.620	1.675	1.620	1.640
8	1.730	1.775	1.720	1.753

Coil 3: Initially 1.155V follows the customary erratic behaviour, fluctuates twice both decreasing to 0.070V, settling to 1.160V increasing to 1.250V at the end.

The rest of the voltages are tabulated below:

Run	Initial Value	Increases To	Decreases To	Final Value
2	1.180	1.180	1.180	1.185
3	1.210	1.230	1.205	1.210
4	1.205	1.223	1.205	1.255
5	1.265	1.285	1.260	1.260
6	1.265	1.280	1.265	1.290
7	1.300	1.325	1.300	1.310
8	1.310	1.330	1.310	1.330

Coil 4: Initially 1.210V, follows usual erratic behaviour, fluctuates once to 1.010V, increases to 1.315V at the end.

The rest of the voltages for coil 4 are tabulated below:

Run	Initial Value	Increases To	Decreases To	Final Value
2	1.340	1.350	1.340	1.340
3	1.350	1.365	1.350	1.350
4	1.350	1.370	1.350	1.405
5	1.420	1.450	1.420	1.420
6	1.430	1.445	1.430	1.460
7	1.455	1.478	1.460	1.465
8	1.450	1.465	1.450	1.435

Coil 5: Initially 1.550V, follows usual erratic behaviour, fluctuates three times, first to 0.970V, the second and third to 1.080V, settling to 1.570V increasing to 1.650V at the end.

The rest of the voltages for coil 4 are tabulated below:

Run	Initial Value	Increases To	Decreases To	Final Value
2	1.650	1.680	1.660	1.660
3	1.650	1.690	1.660	1.660
4	1.650	1.690	1.660	1.740
5	1.770	1.800	1.770	1.770
6	1.770	1.800	1.770	1.810
7	1.830	1.850	1.820	1.830
8	1.840	1.870	1.840	1.850

Coil 6: Initially 1.30V, usual erratic behaviour, fluctuates twice, first to 0.19V second to 0.595V, smooths to 1.300V increasing to 1.370V at the end.

The rest of the volates obtained for coil 6 are tabulated below:

Run	Initial Value	Increases To	Decreases To	Final Value
2	1.370	1.390	1.370	1.370
3	1.370	1.390	1.370	1.370
4	1.365	1.390	1.365	1.435
5	1.485	1.500	1.475	1.470
6	1.470	1.485	1.470	1.510
7	1.510	1.530	1.510	1.510
8	1.505	1.550	1.505	1.550

Run NA10

Temperature of coils 420°C 18.92% O₂ 2mm ID unbaffled
reactors

Coil No.	R_m/Ω	R_o/Ω	R_t/Ω	Dial Setting
1	3.628	3.358	8.896	4.450
2	3.971	3.682	9.755	4.875
3	3.771	3.441	9.116	4.560
4	3.729	3.458	9.159	4.580
5	3.057	2.829	7.496	3.750
6	4.170	3.859	10.225	5.115

Bubbler 1: 16.3261g, 15.4555g, 15.2355g, 15.5852g, 16.6826g,
16.866g, 15.8581g Al(OⁱPr)₃

Bubbler 2: 19.4850g, 16.2646g, 16.6780g, 17.1268g, 17.1615g,
16.9896g, 16.4430g Al(OⁱPr)₃

N₂ setting: 0.700 750cm³min⁻¹

O₂ setting: 0.175 175cm³min⁻¹

Back pressure: 62,50,45,47,55,70,62mm Hg

Sandbath: 124°C throughout

Run time: 5hrs+4hrs+5hrs+4hrs+6hrs+4hrs+4hrs

Total 32 hours

Thermocouple Readings

<u>No.</u>	<u>mV</u>							<u>°C</u>						
1	8.21	8.33	8.49	8.62	8.26	8.27	8.39	175	178	179	180	175	182	177
2	6.77	6.87	6.98	7.12	6.82	6.96	6.92	150	152	152	155	150	151	151
3	7.78	7.96	8.05	8.30	7.97	8.04	7.99	168	172	172	176	170	171	171
4	3.58	3.55	3.81	3.79	3.76	3.70	3.76	94	94	97	96	96	94	96
5	6.44	6.86	6.78	6.93	6.62	6.50	6.64	144	153	150	153	147	144	147
6	2.90	3.05	3.13	3.21	3.16	2.86	3.18	78	82	81	83	82	77	82
7	6.11	6.08	6.27	6.41	6.13	6.20	6.14	138	138	139	141	136	136	136

Ambient temperature: 23, 24, 22, 22, 22, 21, 22 °C

Variac 1 setting: 140

Variac 2 setting: 160

Voltage Across the Coils

Coil 1: Initially 1.390V, follows usual erratic pattern then periodic fluctuations occur which decrease exponentially finally settling to 1.401V, increasing to 1.462V at the end.

The remaining voltages are tabulated below:

Run	Initial Value	Increases To	Decreases To	Final Value
2	1.462	1.520	1.460	1.492
3	1.500	1.582	1.495	1.555
4	1.570	1.643	1.575	1.581
5	1.575	1.660	1.580	1.638
6	1.658	1.710	1.650	1.630
7	1.624	1.695	1.635	1.628

Coil 2: Initially 1.698V follows usual erratic pattern then periodic fluctuations occur which decrease exponentially finally settling to 1.684V increasing to 1.765V at the end.

The remaining voltages are tabulated below:

Run	Initial Value	Increases To	Decreases To	Final Value
2	1.765	1.834	1.765	1.808
3	1.810	1.899	1.810	1.884
4	1.911	1.990	1.920	1.910
5	1.900	2.000	1.910	2.000
6	2.040	2.080	2.020	2.000
7	2.000	2.080	2.010	2.010

Coil 3: Initially 1.520V follows same general pattern as coils 1 and 2, settles to 1.505V increasing to 1.540V at the end.

The remaining voltages are tabulated below:

Run	Initial Value	Increases To	Decreases To	Final Value
2	1.540	1.599	1.540	1.565
3	1.563	1.635	1.560	1.698
4	1.720	1.778	1.710	1.710
5	1.710	1.799	1.710	1.830
6	1.830	1.900	1.820	1.810
7	1.810	1.900	1.820	1.820

Coil 4: Initially 1.64V, follows same general pattern as previous coils, settles to 1.63V increasing to 1.66V at the end.

The remaining voltages are tabulated below:

Run	Initial Value	Increases To	Decreases To	Final Value
2	1.73	1.80	1.72	1.74
3	1.75	1.85	1.75	1.81
4	Not obtained - loose connection		1.90	1.91
5	1.90	2.00	1.91	2.01
6	2.04	2.12	2.03	2.02
7	2.03	2.13	2.04	2.03

Coil 5: Initially 1.350V follows same general pattern as previous coils, settles to 1.372V, increasing to 1.410V at the end.

The remaining voltages are tabulated below:

Run	Initial Value	Increases To	Decreases To	Final Value
2	1.428	1.465	1.430	1.435
3	1.443	1.510	1.440	1.495
4	1.512	1.560	1.505	1.505
5	1.500	1.560	1.505	1.550
6	1.630	1.630	1.580	1.580
7	1.560	1.630	1.580	1.580

Coil 6: Initially 1.86V follows same general pattern as previous coils, settles to 1.83V increasing to 1.87V at the end.

The remaining voltages are tabulated below:

Run	Initial Value	Increases To	Decreases To	Final Value
2	1.85	1.91	1.86	1.88
3	1.88	1.97	1.88	2.01
4	2.02	2.08	2.02	2.02
5	2.02	2.11	2.03	2.20
6	2.25	2.30	2.23	2.21
7	2.23	2.31	2.23	2.23

Run NA12 Repeat of NA7

Temperature of coils 350°C 18.92% O₂ 2mm ID unbaffled
reactors

Coil No.	R_m/Ω	R_o/Ω	R_t/Ω	Dial Setting
1	3.751	3.484	8.273	4.140
2	3.705	3.442	8.172	4.085
3	3.765	3.497	8.304	4.150
4	3.660	3.399	8.072	4.035
5	4.037	3.750	8.904	4.450
6	3.303	3.068	7.285	3.645

Bubbler 1: 15.1722g, 15.4615g, 16.5148g, 17.4495g,
18.6095g Al(OⁱPr)₃

Bubbler 2: 15.1101g, 17.1531g, 16.7845g, 16.4481g,
15.8076g Al(OⁱPr)₃

N₂ setting: 0.700 750cm³min⁻¹

O₂ setting: 0.175 175cm³min⁻¹

Back pressure: 46, 50, 46, 56, 52mm Hg

Sandbath: 124°C throughout each run

Run time: 5hrs+4hrs+3½hrs+5hrs+5hrs Total 22½ hours

<u>No.</u>	<u>Thermocouple Readings</u>					<u>°C</u>				
	<u>mV</u>									
1	8.43	8.51	8.38	8.30	8.22	178	181	178	177	174
2	6.95	7.04	6.92	6.93	6.84	152	155	152	151	150
3	7.85	8.01	7.86	7.84	7.75	168	173	169	168	166
4	3.68	3.61	3.72	3.76	3.48	94	95	96	96	89
5	6.12	6.17	5.99	6.02	6.02	138	140	118	136	136
6	2.75	2.77	2.86	2.71	2.73	74	73	77	73	74
7	6.31	6.35	6.15	6.21	6.15	139	142	137	138	136

Ambient temperature: 22, 24, 23, 22.5, 22°C

Variac 1 setting: 140

Variac 2 setting: 160

Voltage Across Coils

Coil 1: Initially 1.180V, follows usual erratic pattern, six fluctuations occur the first to 0.79V, the other fluctuations increasing to 0.910V (for the sixth), assumes a smooth value of 1.195, increasing to 1.505V at the end.

The remaining voltages are tabulated below:

Run	Initial Value	Increases To	Decreases To	Final Value
2	1.515	1.550	1.525	1.555
3	1.570	1.598	1.560	1.555
4	1.540	1.583	1.545	1.605
5	1.540	1.578	1.545	1.568

Coil 2: Initially 1.125V, follows usual erratic pattern, four fluctuations occur, the first to 0.815V, increasing to 0.908V for the fourth, smooths to 1.258V increasing to 1.515V at the end.

The remaining voltages are tabulated below:

Run	Initial Value	Increases To	Decreases To	Final Value
2	1.515	1.550	1.525	1.545
3	1.555	1.575	1.545	1.540
4	1.550	1.590	1.560	1.583
5	1.590	1.615	1.590	1.590

Coil 3: Initially 1.160V, follows the usual erratic behaviour, eighteen fluctuations occur, the lowest (first) to 0.70, other fluctuations do not evenly decrease in size, assumes a smooth value of 1.190V increasing to 1.515V at the end.

The remaining voltages are tabulated below:

Run	Initial Value	Increases To	Decreases To	Final Value
2	1.515	1.560	1.520	1.555
3	1.570	1.600	1.570	1.560
4	1.555	1.600	1.560	1.585
5	1.590	1.630	1.595	1.598

Coil 4: Initially 1.290V, follows usual erratic pattern, two fluctuations occur, the first to 0.220V, the second to 0.970V, assumes a smooth value of 1.315V increasing to 1.850V at the end.

The remaining voltages are tabulated below:

Run	Initial Value	Increases To	Decreases To	Final Value
2	1.950	2.020	1.950	1.975
3	2.000	2.040	1.980	1.970
4	1.970	2.025	1.975	2.000
5	2.000	2.050	2.020	2.020

Coil 5: Initially 1.320V, follows usual erratic behaviour, three fluctuations occur, first to 0.335, the third to 0.945V, assumes a smooth value of 1.360V, increases to 1.720V at the end.

The remaining voltages are tabulated below:

Run	Initial Value	Increases To	Decreases To	Final Value
2	1.720	1.760	-	1.760
3	1.770	1.780	1.740	1.730
4	1.730	1.770	1.710	1.740
5	1.760	1.780	1.710	1.710

Coil 6: Initially 1.115V, follows usual erratic behaviour, three fluctuations occur, the first to 0.215V, the third to 0.890V, assumes a smooth value 1.160V increasing to 1.625V at the end.

The remaining voltages are tabulated below:

Run	Initial Value	Increases To	Decreases To	Final Value
2	1.640	1.680	-	1.680
3	1.770	1.780	1.740	1.730
4	1.730	1.775	1.690	1.760
5	1.740	1.775	1.750	1.750

Run T1

Temperature of coils 400°C, 18.92% O₂, 2mm ID unbaffled reactors

Coil No.	R_m/Ω	R_o/Ω	R_t/Ω	Dial Setting
1	3.436	3.186	8.190	4.095
2	3.731	3.459	8.893	4.445
3	4.014	3.722	9.568	4.785
4	4.117	3.817	9.813	4.905
5	4.723	4.379	11.258	5.625
6	3.478	3.225	8.290	4.145

Bubbler 1: Approximately 30-35cm³ TiCl₄ in each

Bubbler 2:

N₂ setting: 0.700 750cm³min⁻¹

O₂ setting: 0.175 175cm³min⁻¹

Back pressure: 116mm Hg and 83mm Hg

Sandbath: 34°C, 26°C

Run time: 1hr+2hrs

Thermocouple Readings

No.	mV	°C	
1	5.19	117	Ambient temperature: 21°C
2	4.45	105	Variac 1 setting: 100
3	5.11	117	Variac 2 setting: 90
4	1.63	55	Thermocouple readings not
5	2.19	63	obtained for first (1 hour)
6	1.78	54	run.
7	4.16	98	

Voltage Across the Coils

Coil No.	Run	Initial Value	Final Value
1	1	1.438	1.490
	2	1.502	1.520
2	1	1.460	1.462
	2	1.490	1.482
3	1	1.628	1.670
	2	1.670	1.678
4	1	0.238 loose	0.300
	2	0.420 connection	1.470
5	1	2.25	2.75
	2	2.70	3.13
6	1	1.78	1.84
	2	1.84	1.82

Run T2

Temperature of coils 500°C , 18.92% O_2 , 2mm ID unbaffled reactors

Coil No.	R_m/Ω	R_o/Ω	R_t/Ω	Dial Setting
1	4.185	3.880	11.499	5.750
2	4.691	4.349	12.889	6.445
3	4.015	3.723	11.032	5.515
4	3.752	3.479	10.309	5.155
5	3.676	3.408	10.101	5.050
6	4.573	4.240	12.565	6.280

Bubbler 1: Approximately $30\text{--}35\text{cm}^3$ TiCl_4 in each

Bubbler 2:

N_2 setting: 0.700 $750\text{cm}^3\text{min}^{-1}$

O_2 setting: 0.175 $175\text{cm}^3\text{min}^{-1}$

Back pressure: 157mm increasing to 202mm Hg,
89mm increasing to 222mm Hg

Sandbath: 25°C

Run time: 3hrs+3hrs

Thermocouple Readings

No.	mV	$^{\circ}\text{C}$	
1	3.44	85	
2	3.43	86	Ambient temperature: 21.5°C
3	3.96	98	Variac 1 setting: 80
4	1.92	60	Variac 2 setting: 100
5	2.70	73	Thermocouple readings not
6	1.91	57	obtained for first (3 hour)
7	3.30	83	run.

Voltage Across the Coils

Coil No.	Run	Initial Value	Final Value
1	1	2.04	2.41
	2	2.40	2.46
2	1	2.42	2.77
	2	2.81	2.88
3	1	2.04	2.30
	2	2.38	2.45
4	1	2.02	2.32
	2	2.33	2.42
5	1	2.12	2.74
	2	2.83	3.07
6	1	2.52	2.75
	2	2.69	2.77

Run T3

Temperature of coils 500°C, 39.47% O₂, 2mm ID unbaffled reactors

Coil No.	R_m/Ω	R_o/Ω	R_t/Ω	Dial Setting
1	4.516	4.180	12.386	6.195
2	4.202	3.889	11.525	5.760
3	4.114	3.808	11.284	5.640
4	4.384	4.057	12.024	6.010
5	3.551	3.286	9.739	4.870
6	3.572	3.306	9.797	4.900

Bubbler 1: Approximately 30-35cm³ TiCl₄ in each

Bubbler 2:

N₂ setting: 0.525 575cm³min⁻¹

O₂ setting: 0.375 375cm³min⁻¹

Back pressure: 78mm rising to 275mm Hg

Sandbath: 30-31°C

Run time: 3 hours

Thermocouple Readings

No.	mV	°C	
1	3.82	93	
2	3.35	85	Ambient temperature: 22°C
3	3.88	95	Variac 1 setting: 80
4	1.90	61	Variac 2 setting: 100
5	2.65	73	
6	1.89	58	
7	3.26	84	

Voltage Across Coils

Coil No.	Initial Value		Final Value
1	2.13	Erratic	3.75 (average)
2	2.13		2.41
3	2.03		2.14 (average)
4	2.99	Erratic	3.85 (average)
5	1.76		1.93
6	3.56	Erratic	3.66 (average)

Run T4

Temperature of coils 480°C , 39.47% O_2 , 2mm ID unbaffled reactors

Coil No.	R_m/Ω	R_o/Ω	R_t/Ω	Dial Setting
1	4.072	3.776	10.892	5.445
2	3.099	2.873	8.289	4.145
3	3.727	3.456	9.969	4.985
4	3.569	3.309	9.547	4.770
5	3.126	2.898	8.362	4.180
6	3.430	3.180	9.175	4.585

Bubbler 1: Approximately $30\text{--}35\text{cm}^3$ TiCl_4 in each

Bubbler 2:

N_2 setting: 0.525 $575\text{cm}^3\text{min}^{-1}$

O_2 setting: 0.375 $375\text{cm}^3\text{min}^{-1}$

Back pressure: 78mm rising to 260mm Hg, 83mm rising to 249mm Hg

Sandbath: 31°C

Run time: 3hrs+3hrs

Thermocouple Readings

No.	mV		$^{\circ}\text{C}$	
1	3.79	3.88	93	94
2	3.34	3.42	85	87
3	3.90	3.97	96	97
4	2.00	1.93	63	62
5	2.66	2.68	74	74
6	1.99	1.91	60	58
7	3.23	3.29	82	83

Ambient temperature: 22°C
 Variac 1 setting: 80
 Variac 2 setting: 100

Voltage Across Coils

Coil No.	Run	Initial Value	Final Value
1	1	1.94	2.16
	2	2.18	2.25
2	1	1.485	1.482
	2	1.521	1.585
3	1	1.80	1.97
	2	2.03	2.09
4	1	3.16 Erratic	3.84 (average)
	2	3.86 Erratic	3.75 (average)
5	1	1.56	1.67
	2	1.70	1.75
6	1	2.13	2.95
	2	2.95	3.30

Run T5

Temperature of coils 480°C , 59.64% O_2 , 2mm ID unbaffled reactors

Coil No.	R_m/Ω	R_o/Ω	R_t/Ω	Dial Setting
1	3.988	3.711	10.706	5.355
2	3.604	3.354	9.676	4.835
3	4.329	4.028	11.622	5.810
4	3.291	3.063	8.835	4.420
5	4.659	4.336	12.508	6.255
6	3.779	3.517	10.145	5.070

Bubbler 1: Approximately $30\text{--}35\text{cm}^3$ TiCl_4 in each

Bubbler 2:

N_2 setting: $0.325 \quad 360\text{cm}^3\text{min}^{-1}$

O_2 setting: $0.550 \quad 532\text{cm}^3\text{min}^{-1}$

Back pressure: 72mm increasing to 144mm Hg, 83mm increasing to 260mm Hg

Sandbath: 31°C

Run time: 4hrs+2hrs

Thermocouple Readings

No.	mV	$^{\circ}\text{C}$	
1	3.85	94	
2	3.35	85	Ambient temperature: 22°C
3	3.86	95	Variac 1 setting: 80
4	1.87	60	Variac 2 setting: 100
5	2.53	71	Thermocouple readings not
6	2.06	61	obtained for first (4hr) run
7	3.15	82	

Voltage Across Coils

Coil No.	Run	Initial Value	Final Value
1	1	1.80	2.05
	2	2.05	2.12
2	1	2.31	3.31
	2	3.43	3.82
3	1	1.98	2.23
	2	2.28	2.29
4	1	2.72erratic T=12min	3.75 (average)
	2	3.82erratic	3.74
5	1	2.49	2.82
	2	2.87	2.92
6	1	1.74	1.94
	2	2.00	2.03

Run T6

Temperature of coils 480°C , 78.35% O_2 , 2mm ID unbaffled reactors

Coil No.	R_m/Ω	R_o/Ω	R_t/Ω	Dial Setting
1	4.121	3.807	10.983	5.490
2	3.769	3.482	10.045	5.020
3	3.652	3.374	9.733	4.865
4	4.336	4.006	11.556	5.780
5	4.204	3.884	11.204	5.600
6	4.243	3.920	11.308	5.650

Bubbler 1: Approximately $30\text{--}35\text{cm}^3$ TiCl_4 in each

Bubbler 2:

N_2 setting: 0.175 $199\text{cm}^3\text{min}^{-1}$

O_2 setting: 0.725 $720\text{cm}^3\text{min}^{-1}$

Back pressure: 79mm increasing to 220mm Hg, 82mm increasing to 297mm Hg

Sandbath: 31°C , 32°C

Run time: 4hrs+2hrs

Thermocouple Readings

No.	mV		$^{\circ}\text{C}$		
1	3.86	3.85	94	94	
2	3.39	3.35	86	85	Ambient temperature: 22°C
3	3.95	3.87	97	95	Variac 1 setting: 80
4	1.94	1.86	62	60	Variac 2 setting: 100
5	2.63	2.66	73	73	
6	1.98	2.05	60	61	
7	3.25	3.25	82	82	

Voltage Across Coils

Coil No.	Run	Initial Value		Final Value
1	1	3.04	erratic	3.82 (average)
	2	3.75	erratic	3.82 (average)
2	1	2.47		3.67
	2	3.70	erratic	3.87 (average)
3	1	1.86		2.12
	2	2.12		2.17
4	1	2.17		2.51
	2	2.15		2.57
5	1	2.04		2.32
	2	2.32		2.39
6	1	3.38	erratic	3.88 (average)
	2	3.82	erratic	3.92 (average)

Run DT1

Temperature of coils 500°C, 18.92% O₂, 2mm ID baffled reactors

Coil No.	R_m/Ω	R_o/Ω	R_t/Ω	Dial Setting
1	4.432	4.079	12.090	6.045
2	4.004	3.686	10.922	5.460
3	3.861	3.554	10.532	5.265
4	4.352	4.007	11.875	5.935
5	4.484	4.127	12.231	6.115
6	3.629	3.341	9.901	4.950

Bubbler 1: Approximately 30-35cm³ TiCl₄ in each

Bubbler 2:

N₂ setting: 0.700 750cm³min⁻¹

O₂ setting: 0.175 175cm³min⁻¹

Back pressure: 80mm increasing to 308mm Hg,
decreasing finally to 296mm Hg

Sandbath: 30°C

Run time: 6 hours

Thermocouple Readings

No.	mV	°C	
1	4.01	97	
2	3.53	89	Ambient temperature: 22°C
3	4.13	100	Variac 1 setting: 80
4	2.07	64	Variac 2 setting: 100
5	2.82	76	
6	1.81	56	
7	3.37	85	

Voltage Across Coils

Coil No.	Initial Value	Final Value
1	2.25 erratic T=5hr50min	4.10 (average)
2	2.05	2.16
3	2.18	2.85
4	2.36	2.74
5	2.28	2.72
6	1.94	2.22

Run DT3

Temperature of coils 480°C , 39.47% O_2 , 2mm ID baffled reactors

Coil No.	R_m/Ω	R_o/Ω	R_t/Ω	Dial Setting
1	3.240	3.004	8.667	4.335
2	3.876	3.555	10.256	5.130
3	3.331	3.055	8.814	4.410
4	4.362	4.001	11.542	5.770
5	3.798	3.483	10.049	5.025
6	3.803	3.488	10.063	5.030

Bubbler 1: Approximately $30\text{--}35\text{cm}^3$ TiCl_4 in each

Bubbler 2:

N_2 setting: 0.525 $575\text{cm}^3\text{min}^{-1}$

O_2 setting: 0.375 $375\text{cm}^3\text{min}^{-1}$

Back pressure: 83mm rising to 135mm, 110mm rising to 174mm, 117mm rising to 208mm, 132mm decreasing to 90mm Hg

Sandbath: 31°C

Run time: 1hr+1hr+1hr+1hr+2hrs Total 6 hours

Thermocouple Readings

No.	mV	$^{\circ}\text{C}$
1	5.33	121
2	4.78	112
3	4.34	104
4	2.16	66
5	3.60	91
6	2.42	68
7	3.27	83

Ambient temperature: 22°C

Variac 1 setting: 80

Variac 2 setting: 110

Voltage Across Coils

<u>Coil No.</u>	<u>Run</u>	<u>Initial Value</u>	<u>Final Value</u>
1	1	3.10 coil broke	readings not recorded
2	1	2.45	3.15
	2	3.22	3.45
	3	3.45	3.65
	4	3.67	3.83
	5	3.75	3.90
3	1	2.31 erratic	3.88 (average)
	2	3.88(av) erratic	3.60 (average)
	3	3.73(av) erratic	3.76 (average)
	4	3.76(av) erratic	3.77 (average)
	5	coil became detached from posts	
4	1	3.50 erratic	3.97 (average)
	2	3.97(av) erratic	3.70 (average)
	3	3.82(av) erratic	3.86 (average)
	4	3.85(av) erratic	3.85 (average)
	5	4.00(av) erratic	4.07 (average)
5	1	1.82	1.93
	2	1.98	1.98
	3	1.96	2.01
	4	2.06	2.07
	5	2.10	2.10
6	1	1.92	2.12
	2	2.18	2.19
	3	2.23	2.29
	4	2.29	2.28
	5	2.31	2.34

Run DT5Temperature of coils 500°C, 18.92% O₂, 2mm ID baffled reactors

Coil No.	Dial Reading	R_m / Ω	R_t / Ω	Dial Setting
1	1.695	3.39	9.116	4.555
2	1.970	3.94	10.595	5.295
3	2.105	4.21	11.240	5.620
4	2.065	4.13	11.027	5.510
5	2.020	4.04	10.787	5.390
6	1.790	3.58	9.558	4.780

Bubbler 1: Approximately 30-35cm³ TiCl₄ in each

Bubbler 2:

N₂ setting: 0.700 750cm³min⁻¹O₂ setting: 0.175 175cm³min⁻¹

Back pressure: 76mm rising to 206mm, 128mm rising to 258mm Hg

Sandbath: 31-33°C

Run time: 2hrs+2hrs

Thermocouple Readings

No.	mV	°C
1	4.62	113
2	4.73	116
3	4.29	108
4	3.15	69
5	1.93	91
6	3.33	64
7	2.05	86

Ambient temperature: 27°C

Variac 1 setting: 80

Variac 2 setting: 110

Voltage Across Coils

Coil No.	Run	Initial Value	Final Value
1	1	1.51	1.57
	2	1.59	1.61
2	1	1.97	2.33
	2	2.37	2.47
3	1	1.89	1.99
	2	1.76	1.76
4	1	3.85 erratic	3.87 (average)
	2	3.97(av) erratic	4.03 (average)
5	1	1.97	2.06
	2	2.04	2.06
6	1	1.76	1.81
	2	1.80	1.81

Run DT7

Temperature of coils 500°C, 59.64% O₂, 2mm ID baffed reactors

Coil No.	Dial Reading	R_m/Ω	R_t/Ω	Dial Setting
1	2.170	4.34	11.712	5.855
2	1.785	3.57	9.634	4.820
3	2.195	4.39	11.847	5.925
4	2.230	4.46	12.036	6.020
5	1.740	3.48	9.391	4.695
6	1.565	3.13	8.447	4.225

Bubbler 1: Approximately 30-35cm³ TiCl₄ in each

Bubbler 2:

N₂ setting: 0.325 360cm³min⁻¹

O₂ setting: 0.550 532cm³min⁻¹

Back pressure: 82mm rising to 207mm Hg

Sandbath: 32°C

Run time: 4 hours

Thermocouple Readings

No.	mV	°C	
1	4.78	115	
2	4.92	119	Ambient temperature: 26°C
3	4.49	111	Variac 1 setting: 80
4	2.14	70	Variac 2 setting: 110
5	3.50	93	
6	2.05	64	
7	3.27	87	

Voltage Across Coils

Coil No.	Initial Value	Final Value
1	2.28	2.68
2	1.75	2.17
3	3.55 Becomes erratic	3.97 (average)
4	2.23	2.69
5	1.74	2.09
6	1.64 Becomes erratic	2.00 (average)

Run DT9

Temperature of coils 525°C, 39.47% O₂, 2mm ID baffled reactors

Coil No.	Dial Reading	$R_{m\Omega}$	R_t/Ω	Dial Setting
1	1.945	3.89	10.845	5.425
2	1.665	3.33	9.284	4.640
3	1.860	3.72	10.371	5.185
4	1.915	3.83	10.678	5.340
5	1.935	3.87	10.789	5.395
6	1.670	3.34	9.312	4.655

Bubbler 1: Approximately 30-35cm³ TiCl₄ in each

Bubbler 2:

N₂ setting: 0.525 575cm³min⁻¹

O₂ setting: 0.375 375cm³min⁻¹

Back pressure: 78mm increasing to 208mm Hg

Sandbath: 31°C

Run time: 4 hours

Thermocouple Readings

No.	mV	°C
1	4.48	109
2	4.67	114
3	4.28	107
4	2.10	69
5	3.28	89
6	1.87	61
7	3.00	82

Ambient temperature: 26°C

Variac 1 setting: 80

Variac 2 setting: 110

Voltage Across Coils

Coil No.	Initial Value	Final Value
1	1.81	2.31
2	1.79	2.19
3	1.81	2.15
4	2.13	2.62
5	2.13	2.51
6	1.81	2.19

Run DT11

Temperature of coils 550°C, 18.92% O₂, 2mm ID baffled reactors

Coil No.	Dial Reading	R_m/Ω	R_t/Ω	Dial Setting
1	1.480	2.96	8.532	4.265
2	1.730	3.46	9.974	4.990
3	1.770	3.54	10.204	5.100
4	2.065	4.13	11.905	5.955
5	1.965	3.93	11.328	5.665
6	1.745	3.49	10.059	5.030

Bubbler 1: Approximately 30-35cm³ TiCl₄ in each

Bubbler 2:

N₂ setting: 0.700 750cm³min⁻¹

O₂ setting: 0.175 175cm³min⁻¹

Back pressure: 28mm rising to 257mm Hg

Sandbath: 32°C

Run time: 4 hours

Thermocouple Readings

No.	mV	°C	
1	4.70	113	
2	4.85	116	Ambient temperature: 25°C
3	4.51	110	Variac 1 setting: 80
4	2.05	67	Variac 2 setting: 110
5	3.36	90	
6	2.08	64	
7	3.19	84	

Voltage Across Coils

Coil No.	Initial Value	Final Value
1	2.40 Becomes erratic	3.60 (average)
2	2.22	3.66
3	1.88	2.31
4	2.34	2.97
5	2.13	2.57
6	2.11	2.55

Run DT13

Temperature of coils 550°C, 59.64% O₂, 2mm ID baffled reactors

Coil No.	Dial Reading	R_m/Ω	R_t/Ω	Dial Setting
1	1.320	2.64	7.596	3.800
2	1.400	2.80	8.057	4.030
3	1.915	3.83	11.020	5.510
4	1.690	3.38	9.726	4.865
5	1.625	3.25	9.351	4.675
6	1.955	3.91	11.251	5.625

Bubbler 1: Approximately 30-35cm³ TiCl₄ in each

Bubbler 2:

N₂ setting: 0.325 360cm³min⁻¹

O₂ setting: 0.550 532cm³min⁻¹

Back pressure: 80mm rising to 370mm Hg

Sandbath: 30°C

Run time: 4 hours

Thermocouple Readings

No.	mV	°C	
1	4.46	109	
2	4.58	111	Ambient temperature: 25°C
3	4.25	105	Variac 1 setting: 80
4	2.07	67	Variac 2 setting: 110
5	3.36	90	
6	1.96	62	
7	3.07	82	

Voltage Across Coils

Coil No.	Initial Value	Final Value
1	1.50	2.02
2	1.51	1.96
3	2.05	2.62
4	2.54 Becomes erratic	3.75 (average)
5	1.93	2.47
6	2.41	3.10

Run DT15

Temperature of coils 575°C , 39.47% O_2 , 2mm ID baffled reactors

Coil No.	Dial Reading	R_m/Ω	R_t/Ω	Dial Setting
1	1.730	3.46	10.283	5.140
2	1.725	3.45	10.254	5.130
3	1.660	3.32	9.867	4.935
4	1.750	3.50	10.402	5.200
5	2.025	4.05	12.037	6.020
6	1.835	3.67	10.908	5.455

Bubbler 1: Approximately $30\text{--}35\text{cm}^3$ TiCl_4 in each

Bubbler 2:

N_2 setting: 0.525 $575\text{cm}^3\text{min}^{-1}$

O_2 setting: 0.375 $375\text{cm}^3\text{min}^{-1}$

Back pressure: 78mm rising to 259mm Hg

Sandbath: 31°C

Run time: 2 hours

Thermocouple Readings

No.	mV	$^{\circ}\text{C}$
1	4.44	109
2	4.62	113
3	4.27	107
4	2.12	69
5	3.36	91
6	2.23	68
7	3.08	83

Ambient temperature: 26°C

Variac 1 setting: 80

Variac 2 setting: 110

Voltage Across Coils

Coil No.	Initial Value	Final Value
1	2.00	2.65
2	2.30	3.72
3	1.95	2.63
4	2.38 Becomes erratic	3.90 (average)
5	2.20	2.89
6	2.02	2.77

Run DT17

Temperature of coils 600°C , 18.92% O_2 , 2mm ID baffled reactors

Coil No.	Dial Reading	R_m / Ω	R_t / Ω	Dial Setting
1	1.755	3.51	10.737	5.370
2	1.610	3.22	9.850	4.925
3	1.705	3.41	10.431	5.215
4	1.815	3.63	11.104	5.550
5	1.420	2.84	8.695	4.350
6	1.875	3.75	11.481	5.740

Bubbler 1: Approximately $30\text{--}35\text{cm}^3$ TiCl_4 in each

Bubbler 2:

N_2 setting: 0.700 $750\text{cm}^3\text{min}^{-1}$

O_2 setting: 0.175 $175\text{cm}^3\text{min}^{-1}$

Back pressure: 76mm rising to 221mm Hg

Sandbath: 32°C

Run time: 2 hours

Thermocouple Readings

No.	mV	$^{\circ}\text{C}$	
1	4.62	112	
2	4.83	117	Ambient temperature: 26°C
3	4.45	110	Variac 1 setting: 80
4	2.22	71	Variac 2 setting: 110
5	3.54	94	
6	2.01	64	
7	3.21	86	

Voltage Across Coils

Coil No.	Initial Value	Final Value
1	2.12	2.77
2	2.04	2.61
3	1.99	2.76
4	2.02	2.90
5	1.73	2.36
6	2.20	3.10

Run DT19

Temperature of coils 600°C, 59.64% O₂, 2mm ID baffled reactors

Coil No.	Dial Reading	R_m/Ω	R_t/Ω	Dial Setting
1	1.685	3.37	10.309	5.155
2	1.910	3.82	11.695	5.850
3	1.635	3.27	10.003	5.000
4	1.740	3.48	10.645	5.320
5	1.760	3.53	10.798	5.400
6	1.755	3.51	10.737	5.370

Bubbler 1: Approximately 30-35cm³ TiCl₄ in each

Bubbler 2:

N₂ setting: 0.325 360cm³ min⁻¹

O₂ setting: 0.550 532cm³ min⁻¹

Back pressure: 74mm rising to 180mm Hg

Sandbath: 29°C

Run time: 1½ hours

Thermocouple Readings

No.	mV	°C	
1	4.59	111	
2	4.74	115	Ambient temperature: 26°C
3	4.39	109	Variac 1 setting: 80
4	2.24	71	Variac 2 setting: 110
5	3.62	95	
6	2.07	65	
7	3.25	88	

Voltage Across Coils

Coil No.	Initial Value	Final Value
1	1.92	2.53
2	2.42	3.03
3	1.96	2.65
4	2.04	2.99
5	2.25	3.15
6	2.21	3.02

Run DT21

Temperature of coils 625°C , 39.47% O_2 , 2mm ID baffled reactors

Coil No.	Dial Reading	R_m/Ω	R_t/Ω	Dial Setting
1	1.560	3.12	9.957	4.980
2	1.315	2.63	8.393	4.195
3	1.365	2.73	8.712	4.355
4	1.415	2.83	9.031	4.515
5	1.845	3.69	11.776	5.890
6	1.515	3.03	9.669	4.835

Bubbler 1: Approximately $30\text{--}35\text{cm}^3$ TiCl_4 in each

Bubbler 2:

N_2 setting: 0.525 $575\text{cm}^3\text{min}^{-1}$

O_2 setting: 0.375 $375\text{cm}^3\text{min}^{-1}$

Back pressure: 82mm rising to 188mm Hg

Sandbath: 31°C

Run time: 1 hour

Thermocouple Readings

No.	mV	$^{\circ}\text{C}$	
1	4.27	103	
2	4.50	108	Ambient temperature: 23°C
3	4.19	102	Variac 1 setting: 80
4	2.15	67	Variac 2 setting: 110
5	3.73	94	
6	1.97	60	
7	3.06	80	

Voltage Across Coils

Coil No.	Initial Value	Final Value
1	2.06	2.75
2	1.73	2.40
3	1.66	2.10
4	2.00	3.19
5	2.44	3.13
6	1.97	2.64

Run DT23Temperature of coils 650°C, 18.92% O₂, 2mm ID baffled reactors

Coil No.	Dial Reading	R_m/Ω	R_t/Ω	Dial Setting
1	1.610	3.22	10.454	5.230
2	1.655	3.31	10.746	5.370
3	1.760	3.52	11.428	5.715
4	1.730	3.46	11.233	5.620
5	1.310	2.62	8.506	4.250
6	1.675	3.35	10.876	5.440

Bubbler 1: Approximately 30-35cm³ TiCl₄ in each

Bubbler 2:

N₂ setting: 0.700 750cm³min⁻¹O₂ setting: 0.175 175cm³min⁻¹

Back pressure: 74mm rising to 174mm Hg

Sandbath: 31°C

Run time: 1 hour

Thermocouple Readings

No.	mV	°C	
1	4.45	107	
2	4.65	112	Ambient temperature: 24°C
3	4.25	104	Variac 1 setting: 80
4	2.18	68	Variac 2 setting: 110
5	3.23	86	
6	2.01	62	
7	2.93	78	

Voltage Across Coils

Coil No.	Initial Value	Final Value
1	2.11	2.56
2	2.31	2.94
3	2.22	3.02
4	2.36	3.23
5	1.88	2.80
6	2.29	3.16

Run DT25Temperature of coils 650°C, 59.64% O₂, 2mm ID baffled reactors

Coil No.	Dial Reading	R_m/Ω	R_t/Ω	Dial Setting
1	1.625	3.25	10.551	5.275
2	2.090	4.18	13.571	6.785
3	1.745	3.49	11.331	5.665
4	1.935	3.87	12.564	6.280
5	2.035	4.07	13.214	6.610
6	1.300	2.60	8.441	4.220

Bubbler 1: Approximately 30-35cm³ TiCl₄ in each

Bubbler 2:

N₂ setting: 0.325 360cm³min⁻¹O₂ setting: 0.550 532cm³min⁻¹

Back pressure: 98mm rising to 125mm Hg

Sandbath: 28°C

Run time: 25½ mins.

Thermocouple Readings

No.	mV	°C	
1	4.59	111	
2	4.69	112	Ambient temperature: 24°C
3	4.30	115	Variac 1 setting: 80
4	2.17	68	Variac 2 setting: 110
5	3.50	93	
6	2.08	66	
7	3.10	85	

Voltage Across Coils

Coil No.	Initial Value	Final Value
1	2.28	3.09
2	3.04 Becomes erratic	4.04 (average)
3	2.31	3.05
4	2.74	3.65
5	3.04	3.83
6	1.85	2.50

Run DT27Temperature of coils 675°C, 39.47% O₂, 2mm ID baffled reactors

Coil No.	Dial Reading	R_m/Ω	R_t/Ω	Dial Setting
1	1.465	2.93	9.991	4.995
2	1.470	2.94	10.025	5.010
3	1.740	3.48	11.866	5.930
4	1.525	3.05	10.362	5.180
5	1.640	3.28	11.143	5.570
6	1.595	3.19	10.837	5.420

Bubbler 1: Approximately 30-35cm³ TiCl₄ in each

Bubbler 2:

N₂ setting: 0.525 575cm³ min⁻¹O₂ setting: 0.375 375cm³ min⁻¹

Back pressure: 74mm Hg

Sandbath: 28°C

Run time: 15 mins.

Thermocouple Readings

No.	mV	°C	
1	4.68	108	
2	4.77	111	Ambient temperature: 21°C
3	4.37	103	Variac 1 setting: 80
4	2.32	68	Variac 2 setting: 110
5	3.99	97	
6	2.19	62	
7	3.23	81	

Voltage Across Coils

Coil No.	Initial Value	Final Value
1	2.12	2.80
2	2.19	2.92
3	2.47	3.07
4	2.65	3.92
5	2.30	2.88
6	2.86	3.72

Run DT29

Temperature of coils 700°C, 18.92% O₂, 2mm ID baffled reactors

Coil No.	Dial Reading	R_m / Ω	R_t / Ω	Dial Setting
1	1.535	3.07	10.556	5.280
2	1.665	3.33	11.450	5.725
3	1.765	3.53	12.137	6.070
4	1.785	3.57	12.275	6.140
5	1.985	3.97	13.650	6.825
6	2.080	4.16	14.303	7.150

Bubbler 1: Approximately 30-35cm³ TiCl₄ in each

Bubbler 2:

N₂ setting: 0.700 750cm³min⁻¹

O₂ setting: 0.175 175cm³min⁻¹

Back pressure: 73mm Hg

Sandbath: 29°C

Run time: 15 mins.

Thermocouple Readings

No.	mV	°C	
1	4.48	108	
2	4.52	110	Ambient temperature: 25°C
3	4.16	103	Variac 1 setting: 80
4	2.11	68	Variac 2 setting: 110
5	3.47	95	
6	2.14	66	
7	3.03	81	

Voltage Across Coils

Coil No.	Initial Value	Final Value
1	2.12	2.87
2	2.58	3.53
3	2.58	3.34
4	2.74	3.70
5	3.49	3.36
6	3.55	3.40

Run DT31

Temperature of coils 700°C, 59.64% O₂, 2mm ID baffled reactors

Coil No.	Dial Reading	R_m/Ω	R_t/Ω	Dial Setting
1	1.865	3.73	12.825	6.410
2	1.765	3.53	12.137	6.070
3	1.445	2.89	9.937	4.970
4	1.610	3.22	11.072	5.535
5	1.570	3.14	10.796	5.400
6	1.455	2.91	10.006	5.000

Bubbler 1: Approximately 30-35cm³ TiCl₄ in each

Bubbler 2:

N₂ setting: 0.325 360cm³min⁻¹

O₂ setting: 0.550 532cm³min⁻¹

Back pressure: 73mm rising to 82mm Hg

Sandbath: 29°C

Run time: 15 mins.

Thermocouple Readings

No.	mV	°C	
1	4.73	112	
2	4.69	112	Ambient temperature: 24°C
3	4.29	105	Variac 1 setting: 80
4	2.15	68	Variac 2 setting: 110
5	3.59	93	
6	2.18	65	
7	3.09	82	

Voltage Across Coils

Coil No.	Initial Value	Final Value
1	2.65	3.58
2	2.59	3.62
3	1.96	2.67
4	2.58	3.56
5	2.42	2.43
6	2.22	2.21

Run DT33

Temperature of coils 725°C , 39.47% O_2 , 2mm ID baffled reactors

Coil No.	Dial Reading	R_m / Ω	R_t / Ω	Dial Setting
1	1.585	3.17	11.266	5.630
2	1.775	3.55	12.617	6.310
3	1.730	3.46	12.297	6.150
4	1.660	3.32	11.799	5.900
5	1.685	3.37	11.977	5.990
6	1.625	3.25	11.551	5.775

Bubbler 1: Approximately $30\text{--}35\text{cm}^3$ TiCl_4 in each

Bubbler 2:

N_2 setting: 0.525 $575\text{cm}^3\text{min}^{-1}$

O_2 setting: 0.375 $375\text{cm}^3\text{min}^{-1}$

Back pressure: 73mm rising to 85mm Hg

Sandbath: 24°C

Run time: 10 mins.

Thermocouple Readings

No.	mV	$^{\circ}\text{C}$	
1	4.37	105	
2	4.53	109	Ambient temperature: 24°C
3	4.05	100	Variac 1 setting: 80
4	2.13	66	Variac 2 setting: 110
5	3.73	95	
6	2.12	64	
7	3.23	84	

Voltage Across Coils

Coil No.	Initial Value	Final Value
1	2.40	3.31
2	2.88	4.04
3	2.99 Erratic	2.95
4	2.81	3.82
5	2.73	3.37
6	2.46 Erratic	3.09

Run DT35

Temperature of coils 750°C , 18.92% O_2 , 2mm ID baffled reactors

Coil No.	Dial Reading	R_m/Ω	R_t/Ω	Dial Setting
1	1.700	3.40	12.259	6.130
2	1.885	3.77	13.593	6.795
3	1.770	3.54	12.763	6.380
4	1.555	3.11	11.213	5.610
5	1.675	3.35	12.078	6.040
6	1.795	3.59	12.944	6.470

Bubbler 1: Approximately $30\text{--}35\text{cm}^3$ TiCl_4 in each

Bubbler 2:

N_2 setting: 0.700 $750\text{cm}^3\text{min}^{-1}$

O_2 setting: 0.175 $175\text{cm}^3\text{min}^{-1}$

Back pressure: 70mm Hg

Sandbath: 30°C

Run time: 6 mins.

Thermocouple Readings

No.	mV	$^{\circ}\text{C}$	
1	3.19	83	
2	3.56	91	Ambient temperature: 24°C
3	3.91	98	Variac 1 setting: 80
4	2.18	68	Variac 2 setting: 110
5	3.46	90	
6	2.13	64	
7	3.37	87	

Voltage Across Coils

Coil No.	Initial Value	Final Value
1	2.93	3.79
2	3.12	4.02
3	2.85	3.66
4	2.72	3.69
5	2.42	2.31
6	3.13	4.60

Run DT37

Temperature of coils 750°C, 59.64% O₂, 2mm ID baffled reactors

Coil No.	Dial Reading	R_m/Ω	R_t/Ω	Dial Setting
1	1.745	3.49	12.674	6.340
2	1.635	3.27	11.875	5.940
3	1.765	3.53	12.819	6.410
4	1.755	3.51	12.747	6.370
5	1.560	3.12	11.330	5.665
6	1.455	2.19	10.568	5.285

Bubbler 1: Approximately 30-35cm³ TiCl₄ in each

Bubbler 2:

N₂ setting: 0.325 360cm³min⁻¹

O₂ setting: 0.550 532cm³min⁻¹

Back pressure: 72mm Hg

Sandbath: 29°C

Run time: 6 mins.

Thermocouple Readings

No.	mV	°C	
1	4.74	109	
2	4.68	109	Ambient temperature: 21°C
3	4.26	101	Variac 1 setting: 80
4	2.19	65	Variac 2 setting: 110
5	3.44	87	
6	2.44	67	
7	3.12	79	

Voltage Across Coils

Coil No.	Initial Value	Final Value
1	2.80	3.85
2	3.16 Becomes erratic	4.04 (average)
3	2.81	3.78
4	2.86	3.87
5	2.51	2.80
6	2.33	2.70

Run DT39

Temperature of coils 775°C , 39.47% O_2 , 2mm ID baffled reactors

Coil No.	Dial Reading	R_m/Ω	R_t/Ω	Dial Setting
1	2.030	4.06	15.111	7.555
2	1.845	3.69	13.734	6.870
3	1.770	3.54	13.176	6.590
4	1.845	3.69	13.734	6.870
5	1.945	3.89	14.531	7.265
6	1.680	3.36	12.551	6.275

Bubbler 1: Approximately $30\text{--}35\text{cm}^3$ TiCl_4 in each

Bubbler 2:

N_2 setting: 0.525 $575\text{cm}^3\text{min}^{-1}$

O_2 setting: 0.375 $375\text{cm}^3\text{min}^{-1}$

Back pressure: 72mm Hg

Sandbath: 29°C

Run time: 6 mins.

Thermocouple Readings

No.	mV	$^{\circ}\text{C}$	
1	4.32	104	
2	4.41	106	Ambient temperature: 23°C
3	4.14	101	Variac 1 setting: 80
4	2.19	67	Variac 2 setting: 110
5	3.79	96	
6	2.19	64	
7	3.05	80	

Voltage Across Coils

Coil No.	Initial Value	Final Value
1	3.28	4.10
2	2.91	4.00
3	2.89	3.90
4	3.42	4.10
5	3.14	3.87
6	2.80	3.76

Run DT41

Temperature of coils 800°C , 18.92% O_2 , 2mm ID baffled reactors

Coil No.	Dial Reading	R_m/Ω	R_t/Ω	Dial Setting
1	1.620	3.24	12.352	6.175
2	1.510	3.02	11.513	5.760
3	1.430	2.86	10.903	5.450
4	1.955	3.91	14.906	7.450
5	1.620	3.24	12.352	6.175
6	1.740	3.48	13.267	6.630

Bubbler 1: Approximately $30\text{--}35\text{cm}^3$ TiCl_4 in each

Bubbler 2:

N_2 setting: 0.700 $750\text{cm}^3\text{min}^{-1}$

O_2 setting: 0.175 $175\text{cm}^3\text{min}^{-1}$

Back pressure: 72mm Hg

Sandbath: 29°C

Run time: $4\frac{1}{2}$ mins.

Thermocouple Readings

No.	mV	$^{\circ}\text{C}$	
1	4.52	106	
2	4.75	111	Ambient temperature: 22°C
3	4.39	105	Variac 1 setting: 80
4	2.18	66	Variac 2 setting: 110
5	3.35	86	
6	2.38	67	
7	3.18	81	

Voltage Across Coils

Coil No.	Initial Value	Final Value
1	2.75	3.85
2	2.75	3.94
3	2.77	3.89
4	3.68 Becomes erratic	4.04 (average)
5	2.53	3.59
6	3.53	4.00

Run DT43

Temperature of coils 800°C , 59.64% O_2 , 2mm ID baffled reactors

Coil No.	Dial Reading	R_m / Ω	$R_t \Omega$	Dial Setting
1	1.605	3.21	12.259	6.130
2	1.855	3.71	14.169	7.085
3	1.450	2.90	11.076	5.540
4	1.760	3.52	13.419	6.710
5	1.595	3.19	12.161	6.080
6	1.820	3.64	13.877	6.940

Bubbler 1: Approximately $30\text{--}35\text{cm}^3$ TiCl_4 in each

Bubbler 2:

N_2 setting: 0.325 $360\text{cm}^3\text{min}^{-1}$

O_2 setting: 0.550 $532\text{cm}^3\text{min}^{-1}$

Back pressure: 72mm Hg

Sandbath: 29°C

Run time: $4\frac{1}{2}$ mins.

Thermocouple Readings

No.	mV	$^{\circ}\text{C}$	
1	4.54	106	
2	4.67	119	Ambient temperature: 21°C
3	4.30	102	Variac 1 setting: 80
4	2.23	66	Variac 2 setting: 110
5	3.67	91	
6	2.38	66	
7	3.10	79	

Voltage Across Coils

Coil No.	Initial Value	Final Value
1	2.88	4.07
2	3.38	4.10
3	2.42	3.58
4	3.34	4.06
5	2.35	2.25
6	3.38	4.00

Run DT45 Repeat of Run DT5

Temperature of coils 500°C, 18.92% O₂, 2mm ID baffled reactors

Coil No.	Dial Reading	R_m/Ω	R_t/Ω	Dial Setting
1	1.790	3.58	9.627	4.815
2	1.995	3.99	10.729	5.365
3	2.035	4.07	10.944	5.470
4	1.915	3.83	10.299	5.150
5	2.125	4.25	11.428	5.715
6	1.570	3.14	8.443	4.220

Bubbler 1: Approximately 30-35cm³ TiCl₄ in each

Bubbler 2:

N₂ setting: 0.700 750cm³min⁻¹

O₂ setting: 0.175 175cm³min⁻¹

Back pressure: 80mm rising to 265mm Hg

Sandbath: 32°C

Run time: 4 hours

Thermocouple Readings

No.	mV	°C	
1	4.68	111	
2	4.77	114	Ambient temperature: 24°C
3	4.41	107	Variac 1 setting: 80
4	2.16	68	Variac 2 setting: 110
5	3.48	91	
6	1.97	65	
7	3.20	84	

Voltage Across Coils

Coil No.	Initial Value	Final Value
1	1.83	2.00
2	2.19	2.95
3	1.81	1.95
4	3.05 Becomes erratic	3.97
5	2.00	2.29
6	1.45	1.62

Run DT49 Repeat of Run DT29

Temperature of coils 700°C, 18.92% O₂, 2mm ID baffled reactors

Coil No.	Dial Reading	R_m/Ω	R_t/Ω	Dial Setting
1	1.825	3.65	12.595	6.300
2	1.465	2.93	10.111	5.055
3	1.725	3.45	11.905	5.950
4	1.780	3.56	12.285	6.140
5	1.420	2.84	9.800	4.900
6	1.775	3.55	12.250	6.125

Bubbler 1: Approximately 30-35cm³ TiCl₄ in each

Bubbler 2:

N₂ setting: 0.700 750cm³min⁻¹

O₂ setting: 0.175 175cm³min⁻¹

Back pressure: 71mm rising to 92mm Hg

Sandbath: 29°C

Run time: 20 mins.

Thermocouple Readings

No.	mV	°C	
1	4.52	106	
2	4.62	109	Ambient temperature: 22°C
3	4.26	102	Variac 1 setting: 80
4	2.18	66	Variac 2 setting: 110
5	3.66	92	
6	2.04	61	
7	3.12	80	

Voltage Across Coils

Coil No.	Initial Value	Final Value
1	2.92	3.69
2	2.17	3.12
3	2.45	3.33
4	2.70	3.72
5	2.23	2.78
6	2.72	3.45

Run DT51 Repeat of Run DT35

Temperature of coils 750°C, 18.92% O₂, 2mm ID baffled reactors

Coil No.	Dial Reading	R_m/Ω	R_t/Ω	Dial Setting
1	2.025	4.05	14.708	7.355
2	1.985	3.97	14.417	7.210
3	1.720	3.44	12.492	6.245
4	2.090	4.18	15.180	7.590
5	1.740	3.48	12.638	6.320
6	1.900	3.80	13.800	6.900

Bubbler 1: Approximately 30-35cm³ TiCl₄ in each

Bubbler 2:

N₂ setting: 0.700 750cm³min⁻¹

O₂ setting: 0.175 175cm³min⁻¹

Back pressure: 72mm Hg

Sandbath: 30°C

Run time: 5 mins.

Thermocouple Readings

No.	mV	°C
1	4.68	109
2	4.63	109
3	4.22	102
4	2.14	66
5	3.36	86
6	2.22	64
7	3.08	79

Ambient temperature: 22°C

Variac 1 setting: 80

Variac 2 setting: 110

Voltage Across Coils

Coil No.	Initial Value	Final Value
1	3.32	4.03
2	3.19	3.99
3	3.03	3.96
4	3.71 Becomes erratic	4.00 (average)
5	2.85	3.45
6	3.32	4.00

A P P E N D I X 4


```

DIMENSION DENS(14,4),XF(3,4),XMOLWT(4),VEL(3),VIS(14,4),XA(3,3)
DIMENSION SC(3),CRO(3),DIFF(3)
DIMENSION T(14),DIF(14,12),F(4),PF(4,4),FF(4),HOLD(3),Z(3),XS(3,3)
DATA R/82.0575/
READ(5,10)((DENS(I,J),J=1,4),I=1,14)
READ(5,10)((VIS(I,J),J=1,4),I=1,14)
READ(5,10)((XF(I,J),J=1,4),I=1,3)
READ(5,10) (VEL(I),I=1,3)
READ(5,10)(XMOLWT(I),I=1,4)
READ(5,10)(T(I),I=1,14)
READ(5,10)((DIF(I,J),J=1,12),I=1,14)
READ(5,10)((XA(I,J),J=1,3),I=1,3)
READ(5,10)((XS(I,J),J=1,3),I=1,3)
10  FORMAT(V)
    WRITE(42,15)
15  FORMAT(5X,"I",3X,"DENS MIX",5X,"VISC MIX",3X)
    DO 5000 M=1,3
    DO 4000 I=1,14
    D=0.0025
    DO 300 J=1,4
    DENM=DENM+DENS(I,J)*XF(M,J)
    DO 200 K=1,4
    IF(K.EQ.J) GO TO 200
    ENIJ=(1.+(SQRT(VIS(I,J)/VIS(I,K))))*((XMOLWT(K)/XMOLWT(J))**0.25))*
& *2
    EIJ=ENIJ/(SQRT(8.0*(1.+(XMOLWT(J)/XMOLWT(K)))))
    SUM=SUM+EIJ*XF(M,K)
200 CONTINUE
    EQN=VIS(I,J)/(1.+(SUM/XF(M,J)))
    SUM=0.0
    VISM=VISM+EQN
300 CONTINUE
    WRITE(42,65)I,DENM,VISM
65  FORMAT(1X,I5,3X,F10.8,3X,F7.3)
    WRITE(42,21)
21  FORMAT(3X,"SCHMIDT",6X,"F(J)",9X,"FF(J)",8X,"CRO",10X,"DIFF",7X
& ,"J")
C  FLUX IN MOLES PER CM2 PER SEC
    F(1)=0.0004
    F(2)=0.0002
900 F(3)=-(2*F(1))
    F(4)=0.0
505 HOLD(1)=F(1)
    HOLD(2)=F(2)
    HOLD(3)=F(3)
    L=1
    DO 500 J=1,4
    DO 400 K=1,4
    IF(K.EQ.J) GO TO 400
    XIF=XF(M,J)/(XF(M,J)+XF(M,K))

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      CHI=F(J)/(F(J)+F(K))
      IF(CHI.EQ.0.0) GO TO 400
      PF(J,K)=((XF(M,J)+XF(M,K))*(CHI-XIF))/CHI
      IF(PF(J,K).LE.0.0) GO TO 400
      UNDER =UNDER+PF(J,K)
400  CONTINUE
      DO 411 K=1,4
      IF(K.EQ.J) GO TO 411
      IF(PF(J,K).LT.0.0) GO TO 206
      XII=PF(J,K)/UNDER
      BIT=XII/DIF(I,L)
      XSUM=XSUM+BIT
206  L=L+1
411  CONTINUE
      IF(XSUM.GT.1.0E05) GO TO 99
      DIFF(J)=1./XSUM
      RE=(D*VEL(M)*DENM)/VISM
      RE=RE*1.0E+06
      SC(J)=VISM/(DENM*DIFF(J))
      SC(J)=SC(J)*1.0E-06
      IF(D.GT.0.015) GO TO 100
      CRO(J)=D/(0.35+0.47*(SQRT(RE))*(SC(J)**0.3333333))
      GO TO 105
100  CRO(J)=D/(2.0+0.60*(SQRT(RE))*(SC(J)**0.3333333))
105  FF(J)=(DIFF(J)*XA(M,J)-XS(M,J))/(R*T(I)*CRO(J))
      Z(J)=ABS(HOLD(J)-FF(J))
99   UNDER=0.0
      XSUM=0.0
500  CONTINUE
      IF(Z(1).LT.1.0E-08) GO TO 700
      F(1)=FF(1)
      GOTO 900
700  IF(Z(2).LT.1.0E-08) GO TO 800
750  F(2)=FF(2)
      GO TO 900
800  IF(Z(3).LT.1.0E-03) GO TO 1000
      F(3)=FF(3)
      GO TO 900
1000 WRITE(42,901)SC(1),F(1),FF(1),CRO(1),DIFF(1),1
      WRITE(42,901)SC(2),F(2),FF(2),CRO(2),DIFF(2),2
      WRITE(42,901)SC(3),F(3),FF(3),CRO(3),DIFF(3),3
901  FORMAT(1X,5(F11.8,1X),3X,I3)
      GROWTH=(79.8998*F(1))/4.26
      THICKNES=THICKNES+(CRO(1)/2)
      TIME=TIME+(CRO(1)/GROWTH*2)
      RRATE=THICKNES/TIME
      RRATE=RRATE*60.0
      RRATE=RRATE*1.0E07
      RATE=ALOG(RRATE)
      WRITE(42,940)

```



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940 FORMAT(1X,"GROWTH",6X,"D",9X,"THICK(CM)",3X,"TIME(S)",2X,
&  "LN RATE(NM/MIN)",1X,"REYNOLDS"/)
WRITE(42,950)GROWTH,D,THICKNES,TIME,RATE,RE
950 FORMAT(1X,3(F10.8,1X,),F11.8,1X,F12.8,2X,F10.8//)
D=D+CRO(1)/2
IF(D.GT.0.1) GO TO 2000
GO TO 505
2000DENM=0.0
VISM=0.0
THICKNES=0.0
TIME=0.0
4000CONTINUE
5000CONTINUE

STOP

END

```

Table 11(a)

Mole Fractions at Edge of Boundary Layer (XA)

100% TiCl_4 conversion

	18.92% O_2	39.47% O_2	59.64% O_2
TiCl_4	0.01342577	0.01342561	0.01342621
O_2	0.18664918	0.38943725	0.58840499
Cl_2	0.0	0.0	0.0
N_2	0.79992506	0.59713714	0.3981688

Table 11(b)

Mole Fractions at Surface (XS)

	18.92% O_2	39.47% O_2	59.64% O_2
TiCl_4	0.0	0.0	0.0
O_2	0.17322341	0.37601164	0.57497878
Cl_2	0.02685153	0.02685122	0.02685242
N_2	0.79992506	0.59713714	0.3981688

Table 11(c)

Mean Mole Fractions Across Boundary Layer (XF)

	18.92% O_2	39.47% O_2	59.64% O_2
TiCl_4	0.00671289	0.00671281	0.00671311
O_2	0.1799363	0.38272445	0.58169189
Cl_2	0.01342577	0.01342561	0.01342621
N_2	0.79992506	0.59713714	0.3981688

Table 12(a)

Mole Fractions at Surface (XS)

18.92% O₂ concentration

	50% conversion	10%	1%
TiCl ₄	0.00671289	0.0120832	0.01329152
O ₂	0.17993629	0.18530661	0.18651492
Cl ₂	0.01342577	0.00268514	0.0002685
N ₂	0.79992506	0.79992506	0.79992506

Table 12(b)

Mean Mole Fractions Across Boundary Layer (XF)

18.92% O₂ concentration

	50%	10%	1%
TiCl ₄	0.01006933	0.01275449	0.01335865
O ₂	0.18329272	0.1859779	0.18658205
Cl ₂	0.00671289	0.00134257	0.00013425
N ₂	0.79992506	0.79992506	0.79992506

Table 13Mean Temperature (Bulk + Surface/2)

I	T(I)/K
1	573.15
2	583.15
3	595.65
4	608.15
5	620.65
6	633.15
7	645.65
8	658.15
9	670.65
10	683.15
11	695.65
12	708.15
13	720.65
14	733.15

Table 14Linear Velocity

% O ₂ Content	Velocity/cm.s ⁻¹
18.92	1.63575910
39.47	1.67996880
59.64	1.57740229

Table 15

X-Ray Powder Crystallograph

$2\theta/\text{mm}$	θ	d/nm	d/nm Rutile ¹¹⁷
55.3	13.825	0.3223	0.3245
72.3	18.075	0.2483	0.2489
78.5	19.625	0.2293	0.2297
79.5	19.875	0.2266	
83.0	20.75	0.2174	0.2188
88.5	22.125	0.2045	0.2054
109.0	27.25	0.1682	0.1687
111.3	27.825	0.1650	0.1624
126.0	31.50	0.1474	0.1480
138.5	34.625	0.1356	0.1360
140.5	35.125	0.1339	0.1347
151.0	37.75	0.1258	0.1305
153.0	38.25	0.1244	0.1243

Table 16

Experimental Rate18.92% O₂ Content

Run No. (DT)	1/T /10 ⁻⁴ K	Average Linear Thickness (arbitrary)	<u>ln (RATE)</u>		
			+ Error /nm.min ⁻¹	No Error /nm.min ⁻¹	- Error /nm.min ⁻¹
5	13.28	2.75	5.702	5.657	5.611
8	12.53	5.33	6.343	6.320	6.296
11	12.15	4.50	6.177	6.150	6.122
14	11.79	8.00	6.741	6.720	6.709
17	11.45	5.42	6.646	6.623	6.599
20	11.13	4.58	7.358	7.331	7.304
23	10.83	6.46	7.923	7.897	7.873
26	10.55	5.50	8.180	8.142	8.105
29	10.28	4.63	9.055	8.950	8.854
32	10.02	4.90	9.113	9.007	8.912
35	9.78	3.56	9.893	9.605	9.382
38	9.54	3.21	10.039	9.683	9.420
41	9.32	4.04	10.424	10.019	9.731
49	10.28	4.38	8.684	8.606	8.684
51	9.78	2.88	9.930	9.572	9.930

Table 17

Experimental Rate39.47% O₂ Content

Run No. (DT)	$1/T$ $/10^{-4}K$	Average Linear Thickness (arbitrary)	<u>ln (RATE)</u>		
			+ Error $/nm.min^{-1}$	No Error $/nm.min^{-1}$	- Error $/nm.min^{-1}$
6	12.93	3.33	5.886	5.850	5.811
9	12.53	4.17	6.102	6.073	6.042
12	12.15	9.65	6.925	6.913	6.900
15	11.79	7.54	6.970	6.954	6.937
18	11.45	7.67	7.680	7.663	7.647
21	11.13	6.05	7.857	7.832	7.807
24	10.83	6.58	8.171	8.140	8.109
27	10.55	4.50	9.028	8.922	8.827
30	10.28	4.75	9.082	8.976	8.881
33	10.02	4.04	9.383	9.220	9.081
36	9.78	3.10	9.754	9.466	9.243
39	9.54	4.83	10.198	9.910	9.687
42	9.32	4.44	10.112	9.825	9.601
46	12.15	5.67	6.402	6.380	6.358
47	11.45	5.65	7.380	7.358	7.336
48	10.83	6.63	8.393	8.354	8.316
50	10.28	5.06	9.040	8.945	8.858
52	9.32	3.42	10.102	9.746	9.483

Table 18

Experimental Rate59.64% O₂ Content

Run No. (DT)	1/T /10 ⁻⁴ K	Average Linear Thickness (arbitrary)	ln (RATE)		
			+ Error /nm.min ⁻¹	No Error /nm.min ⁻¹	- Error /nm.min ⁻¹
4/44	13.28	5.21	6.321	6.297	6.273
7	12.93	3.85	6.026	5.994	5.961
10	12.53	8.04	6.741	6.730	6.715
13	12.15	5.65	6.399	6.377	6.355
16	11.79	6.29	6.792	6.773	6.752
19	11.45	7.13	7.607	7.590	7.572
22	11.13	3.88	8.131	8.080	8.031
25	10.83	5.50	8.653	8.592	8.535
28	10.55	2.85	9.034	8.871	8.731
31	10.28	5.50	9.288	9.123	9.028
34	10.02	5.54	9.698	9.536	9.396
37	9.78	4.56	10.140	9.852	9.629
40	9.54	4.94	10.470	10.114	9.851
43	9.32	4.38	10.504	10.098	9.810

Table 19

Growth Profile

Time/min (±.75min)	Average Linear Thickness (arbitrary)	+ Error /10 ⁻³ cm	No Error /10 ⁻³ cm	- Error /10 ⁻³ cm
9.75	2.96	7.708	7.396	7.083
19.50	3.88	10.000	9.688	9.375
29.25	4.75	12.188	11.875	11.563
38.25	5.83	14.896	14.583	14.271
47.25	6.22	15.859	15.547	15.234
57.75	6.30	16.063	15.750	15.438

Table 20

Computed Density of Boundary Layer

Temperature/K	Density/g.cm ⁻³ 18.92% O ₂ only	
	100%	50%
573.15	0.00064620	0.00065190
583.15	0.00063513	0.00064073
595.65	0.00062179	0.00062728
608.15	0.00060901	0.00061439
620.65	0.00059675	0.00060202
633.15	0.00058497	0.00059013
645.65	0.00057364	0.00057870
658.15	0.00056275	0.00056771
670.65	0.00055226	0.00055713
683.15	0.00054216	0.00054694
695.65	0.00053241	0.00053711
708.15	0.00052301	0.00052763
720.65	0.00051394	0.00051848
733.15	0.00050518	0.00050963

Table 21

Computed Viscosity of Boundary Layer

Temperature/K	Viscosity/10 ⁻⁶ g.cm ⁻¹ s ⁻¹ 18.92% O ₂ only	
	100%	50%
573.15	385.660	285.153
583.15	288.970	288.451
595.65	293.734	293.208
608.15	297.192	296.678
620.65	301.214	300.696
633.15	305.224	304.714
645.65	309.162	308.648
658.15	313.089	312.583
670.65	316.949	316.442
683.15	320.794	320.294
695.65	324.578	324.076
708.15	328.348	327.853
720.65	332.059	331.561
733.15	335.753	335.264

Table 22

Computed Final Rate

Temperature/K	1n(Rate)/nm.min ⁻¹ 18.92% O ₂ concentration			
	100%	50% Conversion	10%	1%
573.15	10.3481	9.6549	8.0455	5.7429
583.15	10.3547	9.6615	8.0521	5.7495
595.65	10.3628	9.6697	8.0603	5.7567
608.15	10.3707	9.6775	8.0681	5.7655
620.65	10.3786	9.6854	8.076	5.7734
633.15	10.3863	9.6932	8.0837	5.7812
645.65	10.3937	9.7005	8.0911	5.7885
658.15	10.4013	9.7082	8.0987	5.7962
670.65	10.4089	9.7158	8.1063	5.8038
683.15	10.4158	9.7227	8.1132	5.8106
695.65	10.4227	9.7296	8.1201	5.8176
708.15	10.4298	9.7367	8.1273	5.8247
720.65	10.4369	9.7438	8.1349	5.8317
733.15	10.4440	9.7509	8.1414	5.8389

Table 23

Computed Growth Profile

10% Conversion

Temperature = 658.15K

Thickness/cm	Time/min
0.0031	2.48
0.0129	27.01
0.0193	37.42
0.0284	58.44
0.0411	100.15
0.0589	179.13

Table 24

Computed Flux (Final) 100% Conversion

18.92% O₂ Only

Temperature/K	Flux/10 ⁻⁵ mol.cm ⁻² s ⁻¹		
	TiCl ₄	O ₂	Cl ₂
573.15	0.18771	0.45680	-0.37541
583.15	0.18885	0.45925	-0.37769
595.65	0.19028	0.46214	-0.38057
608.15	0.19168	0.46545	-0.38335
620.65	0.19309	0.46837	-0.38618
633.15	0.19450	0.47127	-0.38900
645.65	0.19584	0.47431	-0.39167
658.15	0.19724	0.47713	-0.39448
670.65	0.19865	0.48009	-0.39731
683.15	0.19994	0.48323	-0.39987
695.65	0.20124	0.48623	-0.40248
708.15	0.20259	0.48912	-0.40518
720.65	0.20394	0.49210	-0.40788
733.15	0.20532	0.49485	-0.41063

Table 25

Computed Final Flux 50% Conversion

18.92% O₂ Only

T Temperature/K	Flux/10 ⁻⁵ mol.cm ⁻² s ⁻¹		
	TiCl ₄	O ₂	Cl ₂
573.15	0.093938	0.22902	-0.18788
583.15	0.094507	0.23024	-0.18901
595.65	0.095226	0.23169	-0.19045
608.15	0.095922	0.23334	-0.19184
620.65	0.096628	0.23480	-0.19326
633.15	0.097331	0.23625	-0.19466
645.65	0.098000	0.23777	-0.19600
658.15	0.098702	0.23918	-0.19740
670.65	0.099407	0.24066	-0.19881
683.15	0.10005	0.24223	-0.20010
695.65	0.10070	0.24373	-0.20140
708.15	0.10137	0.24518	-0.20275
720.65	0.10205	0.24667	-0.20410
733.15	0.10274	0.24804	-0.20547

Table 26

Effective Diffusion Coefficients (All Conversions)

Temperature/K	$\text{TiCl}_4/\text{cm}^2\text{s}^{-1}$	$\text{O}_2/\text{cm}^2\text{s}^{-1}$	$\text{Cl}_2/\text{cm}^2\text{s}^{-1}$
573.15	0.22284	0.56886	0.38301
583.15	0.22979	0.58586	0.39462
595.65	0.23867	0.60731	0.40961
608.15	0.24754	0.62938	0.42463
620.65	0.25663	0.65135	0.43983
633.15	0.26585	0.67238	0.45549
645.65	0.27509	0.69509	0.47116
658.15	0.28457	0.71780	0.48691
670.65	0.29423	0.74102	0.50314
683.15	0.30379	0.76478	0.51942
695.65	0.31351	0.78862	0.53561
708.15	0.32345	0.81262	0.55246
720.65	0.33353	0.83706	0.56955
733.15	0.34378	0.86139	0.58652

Table 27

Boundary Layer Thickness and Characteristic Dimension

50% Conversion

δ/cm	δ/cm	
0.0025	0.006144	T=573.15K
0.00864402	0.018964	
0.02760840	0.012318	
0.03992595	0.017433	
0.05735872	0.024429	
0.08178820	0.033860	
0.0025	0.006313	T=733.15K
0.00881305	0.020196	
0.02900897	0.013186	
0.04219451	0.018826	
0.06102061	0.026645	
0.08766536	0.037340	

Table 28

Final Reynold's Number (50% Conversion)

Temperature/K	Re
573.15	0.30585536
583.15	0.29873751
595.65	0.28960362
608.15	0.28201748
620.65	0.27427136
633.15	0.26684367
645.65	0.25977155
658.15	0.25299434
670.65	0.24653840
683.15	0.24031826
695.65	0.23438397
708.15	0.22867857
720.65	0.22322990
733.15	0.21798103

Table 29

Final Schmidt Number (50% Conversion)

Temperature/K	TiCl ₄	Sc	
		O ₂	Cl ₂
573.15	1.96285	0.76791	1.14218
583.15	1.95908	0.76740	1.14093
595.65	1.95834	0.76866	1.14128
608.15	1.95064	0.76623	1.13731
620.65	1.94625	0.76583	1.13575
633.15	1.94219	0.76556	1.13373
645.65	1.93871	0.76494	1.13211
658.15	1.93465	0.76473	1.13091
670.65	1.93033	0.76418	1.12901
683.15	1.92763	0.76343	1.12755
695.65	1.92451	0.76282	1.12663
708.15	1.92102	0.76241	1.12487
720.65	1.91731	0.76175	1.12293
733.15	1.91352	0.76150	1.12176

Table 30

Surface Growth Rate

$\ln(R_s)/\text{nm}\cdot\text{min}^{-1}$

T/°C	20% O ₂	40% O ₂	60% O ₂
480	12.47878		16.085011
500		13.447065	14.233052
525	16.199886	14.670448	19.197767
550	15.111192	20.734203 16.579816*	16.559571
575	19.063082	21.074808	19.495856
600	18.278763	29.225654 25.236073*	28.191547
625	24.878773	31.777126	36.297316
650	32.799214	37.441554	49.393675
675	37.385531	62.457596	60.04119
700	63.597642	64.934181	73.501979
725	66.311553	79.901307	112.09076
750	121.45767	102.43674	117.83744
775	134.05026	196.29846	326.90854
800	246.20837	165.77121	304.80828

*Repeat experiments.

Table 31

Corrolation Coefficients for Surface Growth Rate Curves

Percentage O ₂ Content	Corrolation Coefficient
20	-0.903
40	-0.990
60	-0.659

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