

THE KINETICS AND MECHANISM OF THE
OXIDATION OF CHROMIUM(III) CHLORIDE

by

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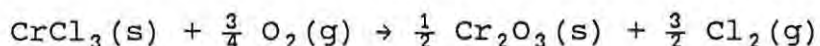
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ABSTRACT

The kinetic behaviour of anhydrous CrCl_3 in gaseous oxidising atmospheres has been examined in the temperature range 350 to 630°C in order to identify optimum reaction conditions and to establish the mechanism by which the reaction is controlled. The reaction under consideration is



The main experimental techniques used were isothermal and programmed-temperature thermogravimetry, supplemented by scanning electron-microscopy, surface-area determinations and porosity measurements. The effects of sample pelletisation, gas flowrate, temperature, oxygen partial pressure, pellet porosity and the addition of other oxide species on the rate and extent of reaction have been studied.

The reaction is shown to occur in a single step, starting at ~350°C under non-isothermal conditions, and exhibiting a deceleratory rate over most of the reaction. Isothermal thermogravimetric curves were fitted to a number of kinetic rate expressions, and a series of statistical analyses used to identify the rate equation which best describes the experimental data. Supporting evidence was provided by scanning electron-microscopic examination of partially-reacted samples.

It is concluded that the reaction is under chemical control, and that reaction occurs by means of a linearly-advancing reactant-product interface. The reaction kinetics can be described by a contracting-geometry rate expression.

To my parents

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LIST OF SYMBOLS

(s)	solid phase
(l)	liquid phase
(g)	gas phase
(aq)	aqueous phase
ΔH^θ	enthalpy of reaction at standard conditions
ΔH_r	enthalpy of reaction
ΔS_r	entropy of reaction
ΔG^θ	Gibbs free energy at standard conditions
ΔG_r	Gibbs free energy of reaction
R	universal gas constant
T	absolute temperature
K_p^θ	equilibrium constant at constant pressure and standard conditions
K	equilibrium constant
a_x	activity of species x
p_x	partial pressure of species x
k	apparent rate constant
v	rate of reaction
E_A	apparent activation energy
A	pre-exponential (frequency) factor
α	fractional conversion
ρ_0	absolute density
ρ_b	bulk density
t	time
t_{red}	reduced-time
$t_{0,5}$	time at which $\alpha = 0,5$
m_0	initial mass of sample
m_f	final mass of sample
m_i	mass of sample at time t_i

r_0	initial radius of pellet
r_c	radius of unreacted core of pellet
r	thickness of the product layer on the sides of pellet
h_0	initial height of pellet
h_c	height of unreacted core of pellet
h	thickness of the product layer on the ends of pellet
a	ratio of height to diameter of pellet
D	diffusion coefficient
C	concentration of reactant gas
r	correlation coefficient
$s_{y.x}$	standard error of the linear regression
$\%s_b$	percentage standard error of the slope of the regression line

1. INTRODUCTION

1.1 Chromium in South Africa

The primary source of chromium and chromium chemicals is the mineral chromite, which has the idealised formula $\text{FeO} \cdot \text{Cr}_2\text{O}_3$. Current world production of this ore is estimated at 10 million tonnes per annum¹, of which South Africa produces approximately one third. South Africa also possesses about 68% of the total world reserves of this ore², and therefore chromium is considered to be a valuable and strategic metal in this country.

The four major products resulting from the beneficiation of chromite are ferrochromium, sodium dichromate, chromic oxide (Cr_2O_3) and chromium metal itself. South Africa currently produces ~28% of world output of ferrochromium, but only ~4% of world sodium dichromate and virtually no Cr_2O_3 or chromium metal.

The economic importance of beneficiation becomes more apparent when the relative costs of these products are considered¹. The value of chromite is typically R0,38 per kilogram of contained chromium, whereas the unit cost of chromium increases to R2,20 for high carbon ferrochromium, R3,90 for low carbon ferrochromium, R4,10 for sodium dichromate, R9,40 for chromic acid, R12,30 for chromic oxide and R18,00 for chromium metal.

These facts clearly show that it would be economically advantageous for South Africa to produce chromium products in the highest stage of beneficiation possible, rather than to export the raw materials and then to re-import the upgraded products at inflated prices. In addition, the ever-present threat of sanctions and the unstable political climate in South Africa emphasize the need for this country to be as self-sufficient as possible, particularly in the field of technologically-strategic materials.

At present the most widely used route for the production of chromium chemicals is via sodium dichromate. This process is shown schematically in Figure 1.1. Chromite ore is calcined with soda ash and lime at 1100 to 1200°C to yield iron as hematite and chromium as sodium chromate. The calcine product is then milled and the soluble Na_2CrO_4 leached in water, leaving most of the constituents of the ore as an insoluble residue. Sodium chromate is converted to the dichromate by the action of sulphuric acid. This is the major starting material for the production of chemicals such as Cr_2O_3 , chromic acid (CrO_3), chromium sulphate and chromium metal. Cr_2O_3 is produced by reacting sodium dichromate with elemental sulphur; the oxide precipitates out and is washed, calcined and reground to yield the final product.

This conventional process has, however, certain disadvantages in the South African context; the most significant of these is the non-availability of a local source of soda

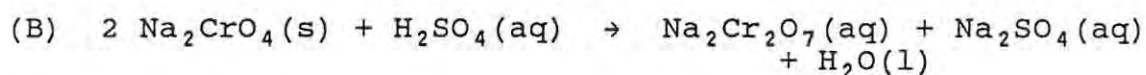
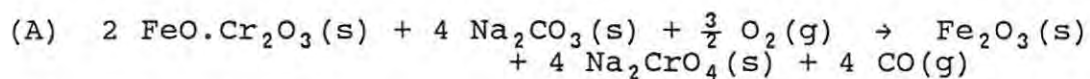
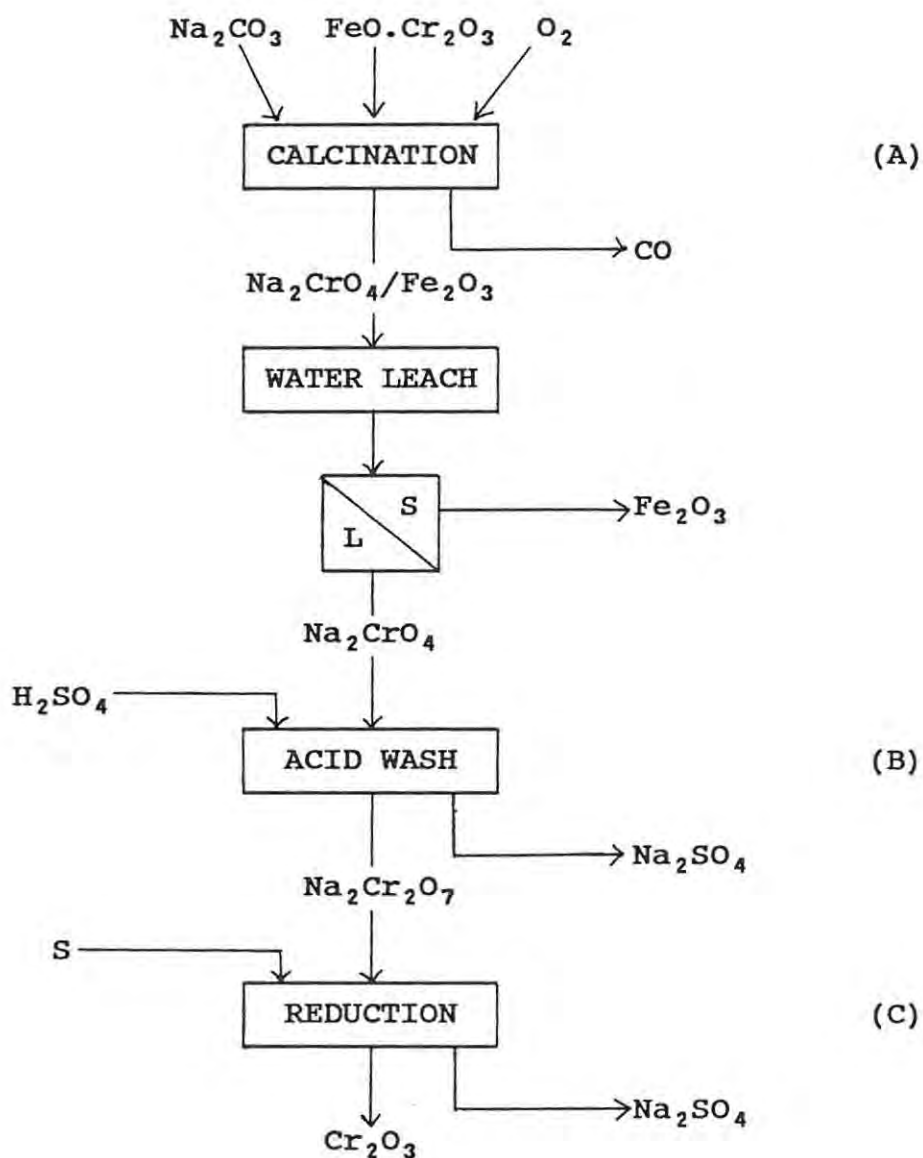


Figure 1.1 Simplified representation of the most widely used commercial process for the production of Cr_2O_3

ash, Na_2CO_3 . The current world-wide focus on the use of carcinogenic chemicals also means that processes involving toxic chromium(VI) chemicals are losing favour. Alternative processes for the manufacture of chromium(III) chemicals in this country are therefore always of interest.

1.2 International Cr_2O_3 production

The world production of Cr_2O_3 is estimated at 100 000 to 150 000 tonnes per annum¹. In South Africa most of the oxide produced is destined for use as a pigment in paint production, while the major Western European producers supply Cr_2O_3 predominantly to the metallurgical industry for use either as a refractory material or for the production of chromium metal by the aluminothermic reduction (thermite) process. For the latter applications, the specifications on oxide purity are considerably more stringent. Some typical examples of specifications set by producers and users are given in Table 1.1.

1.3 Cr_2O_3 production in South Africa

Rolfe's Pigment Manufacturers, situated at Elandsfontein, Transvaal, are at present the only producers of commercial chromium oxide in South Africa. Over the past decade their production of Cr_2O_3 has averaged 300 to 330 tonnes per annum, which satisfies the current local demand. The

Table 1.1 Specifications for Cr_2O_3 set by European producers and users

	British Chrome & Chemicals	Bayer AG, FRG	Murex Ltd. England	Delachaux France	Russian Tech. grade
Cr_2O_3 (%)	99,7	99,7	>98,7	99,5	99.7
H_2O sol. (%)	-	0,16	-	0,02	-
H_2O (%)	<0,2	0,34	<0,2	0,10	-
Fe (ppm)	650	120	<1500	100	210
C (ppm)	<200	<200	<500	-	<200
S (ppm)	50	200	<150	40	30
Si (ppm)	500-700	500	<500	100	500
V (ppm)	100-200	50	<1200	-	<50
Pb (ppm)	<10	<10	<10	5	<10

product is sold mainly to paint producers for use as a pigment, with small amounts going into refractory production.

The oxide is manufactured from sodium dichromate from the Durban Bayer plant. This is then mixed with sulphuric acid to form a thick syrupy mixture which is reduced in the presence of carbon. The carbon, known as "hydrol", is a glucose derivative. Following reduction, small amounts of "crystallisation promoters" are added to the syrup to maintain the correct colour of the pigment. The nature of these additives is a closely-guarded trade secret. In the production of Cr_2O_3 for the metallurgical or refractories industries, these additives are omitted in order to keep the product as pure as possible, as the introduction of other oxides such as Fe_2O_3 or Al_2O_3 has a detrimental effect on the properties of the Cr_2O_3 . The syrup is then transferred to a rotary kiln where it is calcined at 800°C for about 1 hour. The product is manually removed and undergoes

repeated washing and filtering to remove soluble sodium sulphate and other impurities. After drying, the purified oxide is packaged and distributed. A typical product analysis is shown in Table 1.2.

It is somewhat surprising to note that the colour of the pigment, relative to a standard, is the most important criterion monitored on the plant. The chemical analysis is maintained at >95,0% Cr_2O_3 , but other specifications are not stringent. No other tests of physical or chemical properties are carried out, either by the pigment manufacturers themselves or by the end users.

Table 1.2 Typical chemical analysis of Cr_2O_3 produced commercially in South Africa
Delta Chrome Oxide Green D1110 - Rolfe's
Pigment Manufacturers

Matter soluble in water: predominantly Na_2SO_4 ; trace of Cr as Na_2CrO_4 may be present	Max. 1,0%
Moisture and volatile matter	Max. 1,0%
Silica and refractory material	$\pm 0,2\%$
Aluminium oxide	Max. 1,0%
Boron oxide	Max. 1,0%
Chromic oxide	Min. 95,0% Av. 96,0%

1.4 Cr_2O_3 as a pigment

Cr_2O_3 is widely used as a pigment, and since the characteristics of pigments depend largely on their physical properties, some of these are discussed briefly.

Cr_2O_3 has a dull green colour. Its physical properties include good resistance to ultra-violet radiation and colourfastness up to 1000°C , physical durability, resistance to weathering, and insolubility in water, acids and alkalis. Paint coloured by chromic oxide thus finds its main use on tennis courts, roofing, and for the camouflage of military vehicles and equipment.

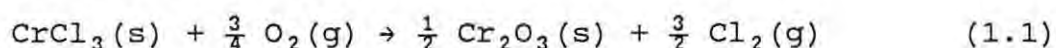
As with most pigments, the colour shade depends largely on the particle size and size distribution, with some dependence on particle shape. These factors also determine the homogeneity of dispersion (dispersivity) of the pigment in the paint product, which in turn influences the degree of gloss of the paint. In general, the smaller the pigment particle, the better the "tinting" of the paint. Tinting or tinctorial strength refers to the ability of a pigment to retain its colour on dilution with the white pigment, TiO_2 . For Cr_2O_3 , as the particles increase in size, the pigment becomes more bluish in colour and loses tinctorial strength.

1.5 Chromium chemicals from chromium(III) chloride

Of considerable recent interest in the minerals' processing industry is the use of chlorination technology for extractive metallurgy. Chloride routes are particularly attractive because of the ease of separation of the different metal chlorides by a variety of techniques, both chemical and physical.

At the Council for Mineral Technology (Mintek), work both of a hydrometallurgical and a pyrometallurgical nature is currently being carried out to investigate alternate routes to chromium chemicals and metal via a chromium chloride intermediate.

A pyrometallurgical route presently under consideration involves the high temperature chlorination of ferrochromium or the carbo-chlorination of chromite to produce chromium (III) chloride, CrCl_3 , and iron(III) chloride, FeCl_3 , as the major products. These chlorides can readily be separated by physical means on the basis of the difference between their sublimation temperatures - CrCl_3 sublimes at 945°C , while FeCl_3 sublimes at 315°C . The product of interest, CrCl_3 , has, however, little commercial value in its own right; rather it is a versatile intermediate from which more useful and valuable chromium chemicals can be manufactured. One such product is chromic oxide, Cr_2O_3 . This chemical can be produced by the solid-gas oxidation of chromium(III) chloride according to the reaction



1.6 Previous studies of the oxidation of CrCl_3

The earliest recorded accounts of the conversion of anhydrous chromium(III) chloride to chromic oxide are the qualitative results of Rose (1838)³ and of Burion (1910)⁴. Rose heated the chloride in air to form the oxide, while Burion found that CrCl_3 heated in atmospheres of both oxygen and steam produced Cr_2O_3 .

In more recent literature this reaction has been used in practice to produce aerosol-size oxide particles. A Swiss patent (1951)⁵ discusses the preparation of finely-divided metal oxides by the thermal decomposition of their chlorides which are solid at the decomposition temperatures. The conversion is carried out by injecting a suspension of the finely-divided chloride ($\sim 20 \mu\text{m}$) in oxygen into a reaction chamber and igniting the mixture. The oxide produced in this manner has an average particle size of $1 \mu\text{m}$.

A similar technique for producing oxides with a particle size of $<100 \text{ nm}$ is discussed in a British patent (1957)⁶. The oxides are prepared by the hydrolysis of their halides in a turbulent flame at temperatures greater than 600°C . These oxides find use as reinforcing agents in rubbers and plastics, as fillers for paints, coatings and cosmetics, and as coating agents for papers and fibres.

Juillet *et al* (1973)⁷ prepared metallic oxide aerosols in the size range 6 to 200 nm by the decomposition of anhydrous

chlorides in the diffusion flame of a hydrogen-oxygen reactor. The shape (spherical or polyhedral), dimensions and crystal structure of the oxide particles were found to be influenced by the flowrate of the chloride vapour through the reactor, the reaction temperature (1400 to 2700°C), and the residence time of the reagent in the flame. These finely-divided oxides exhibited unusual photocatalytic properties and, in particular, the surface activity of particles was found to vary according to their shape. Such particles are used to catalyse the photo-oxidation (in the ultra-violet range) of organic and inorganic compounds at room temperature.

Studies of a more fundamental nature have been carried out by Pechkovskii et al (1964)⁸. The techniques of differential thermal analysis and thermogravimetry were used to investigate the behaviour of anhydrous CrCl_3 in oxygen. These investigators found that the reaction is endothermic, starting at 350°C, and produces Cr_2O_3 and chlorine gas.

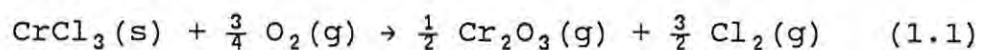
Bulatova and Vil'nyanskii (1961,1967)^{9,10} also carried out studies of a fundamental nature on this system. They undertook thermodynamic analyses of possible chromium/chloride/oxide systems, and determined the basic expressions for ΔH^θ , ΔG^θ and $\log K_p^\theta$ for the various reactions. Their subsequent experimental work comprised a quantitative investigation of the kinetics and mechanism of the oxidation of chromium(III) chloride, and examined the dependence of the rate of the reaction on the duration of the reaction,

the temperature, the oxygen concentration in the gas, and the gas flowrate. These investigators proposed that the reaction exhibits an autocatalytic topochemical mechanism, typical of many solid-gas reactions. From calculations of the "apparent activation energy", E_A , it was further concluded that the reaction is under chemical control in the temperature range 350 to 400°C, and under diffusion control from 500 to 600°C. Between these temperature ranges is a transition region of mixed control.

1.7 Objectives of this research

The production of chromium chemicals, and, in particular, chromic oxide, from chromium(III) chloride is a relatively novel approach; consequently insufficient fundamental information on the reaction system is available. However, if a suitable reactor for any potential technical process is to be designed, knowledge of the rate at which the reaction occurs and the factors which influence the rate are of importance.

In this thesis an analysis of the kinetic behaviour of the reaction



under various experimental conditions is undertaken.

The objectives of the work are as follows :

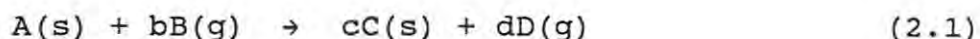
- (i) to identify the steps involved in the reaction;
- (ii) to identify any by-products or side-reactions, and the conditions under which they occur;
- (iii) to identify the factors affecting the rate and extent of the reaction;
- (iv) to identify the rate-controlling step under different experimental conditions;
- (v) to establish the mechanism by which the reaction progresses;
- (vi) to compare the chemical and physical properties of the oxide produced by this route with specifications for commercial Cr_2O_3 .

2. METHODOLOGY AND TECHNIQUES

2.1 Solid-gas reactions

Solid-gas reactions play a significant role in the technologies of most industrialised nations, and such reactions are represented in a wide range of disciplines. These include the extraction of metals from their ores (e.g. the reduction of iron oxide, the roasting of sulphide ores, or the chlorination of ilmenite), the combustion of solid fuels, coal gasification and the incineration of solid refuse.

The reaction under consideration in this investigation falls into the same category, and may be represented schematically by the equation



In general, the rate equation for a heterogeneous reaction should account for more than one process, since the overall reaction may involve a number of intermediate steps. These processes include mass transfer of reactant or product species to or from the reaction site, radiative or convective heat transfer through different layers of the product, and the chemical reaction itself. If $v_1, v_2, \dots, v_n$ are the rates of change for the individual processes which make up the overall rate, then, if the changes occur along parallel paths and the various processes are independent of one another, the overall rate of the reaction

will be given by the sum of these individual rates

$$V_{\text{overall}} = \sum_{i=1}^n V_i \quad (2.2)$$

This situation often arises in solid catalyst reactions. However, for most solid-fluid non-catalysed heterogeneous reactions, the overall reaction requires the individual processes to occur in succession. At steady-state, all these processes will occur at the same rate

$$V_{\text{overall}} = V_1 = V_2 = \dots = V_n \quad (2.3)$$

The rate of the overall reaction, under a particular set of (non-steady-state) experimental conditions, will be limited by the rate of the slowest individual process, v_i . It is this process which provides the greatest resistance to the overall reaction, and which is conventionally described as the rate-controlling, rate-limiting, or rate-determining step of the reaction.

Five possible steps are usually identified during a solid-gas reaction; any one, or a combination, may be rate-controlling. The description of these processes was first given by Yagi and Kunii¹¹. For a single particle in a moving gas stream, reacting according to equation (2.1), these steps may be described as follows :

- (i) diffusion of gaseous reactant B through the gas film surrounding the particle to the surface of the solid A - known as film diffusion or fluid-phase mass transfer;
- (ii) diffusion of the gaseous reactant B through the product layer C to the surface of the unreacted core A

- known as ash- or product-layer diffusion;
- (iii) chemical reaction of gaseous reactant B with solid reactant A at the reaction interface;
- (iv) diffusion of product gas D through the product layer C to the surface of the particle;
- (v) diffusion of the product gas D through the boundary gas layer surrounding the pellet back into the bulk gas stream.

When studying solid-gas reactions, all of these processes must be taken into account. Earlier workers in this field (prior to the 1960's) usually treated the solid reactant as being completely "solid" and non-porous, in order to simplify the mathematical representation of the system. The classic model for solid-gas reactions is thus the "unreacted shrinking-core model"^{12,13,14}. More recently, structural parameters, such as porosity of the solid reactant and product, surface area and pore-size distribution, have also been taken into account. It has also been realised that it is often not appropriate to identify a single rate-controlling step, since the rate can be determined by a number of factors acting concurrently. The rate-controlling step may also change during the reaction, depending on experimental conditions. For example, an increase in reaction temperature often corresponds to a change in the rate-controlling step from a chemical to a mass-transfer process. This is because the apparent activation energy, E_A , of a chemical reaction is typically 40 to 200 kJ mol⁻¹, and so the rate increases significantly with increasing

temperature; the rate of gas diffusion through a partially-reacted sample is, however, not affected substantially by temperature ($E_a \approx 5$ to 20 kJ mol^{-1}). Therefore, at lower temperatures, the rate of the chemical reaction will present greater resistance to the overall reaction than the rate of diffusion of the reactant gas to the reaction site. At higher temperatures this situation is reversed. Similarly, as the pellet size of the sample increases, the diffusion distance to the unreacted core within the pellet increases, and so mass transfer of the reactant gas provides the greatest resistance to reaction. A qualitative representation of the combined effect of these two parameters on the rate-controlling step is illustrated in Figure 2.1.

Much of the theoretical treatment of the kinetics of solid-gas reactions closely follows the theory developed for the simplest reverse reaction - the decomposition of simple solids according to the equation



Reactions of this type are usually studied experimentally by measuring the product yield or fractional conversion, α , as a function of time or temperature, depending on whether isothermal or non-isothermal (programmed-temperature) techniques are employed. The extent of conversion can be determined from measurements of the pressure of evolved gas(es), the mass loss, by analysis of the evolved gas(es), or by measurements of evolved or absorbed energy. Changes in other physical properties may also provide useful information on the progress of the reaction, depending on

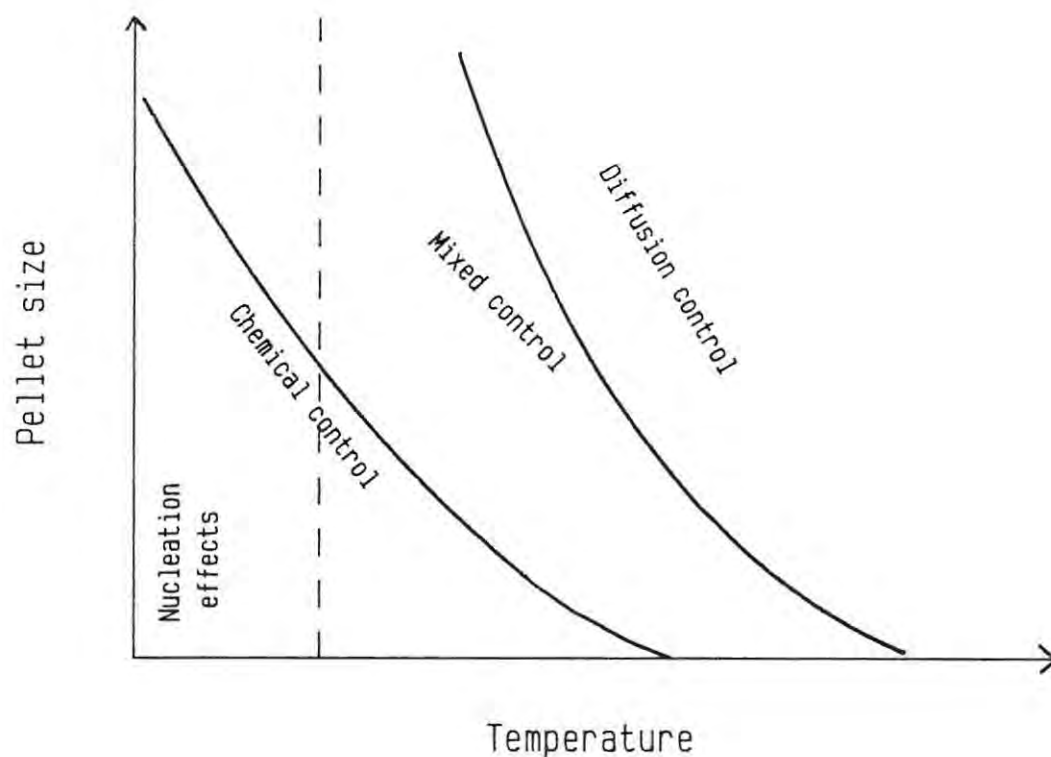


Figure 2.1 Representation of how temperature and pellet size determine the rate-limiting step in solid-gas reactions
(Adapted from Szekeley *et al*¹²)

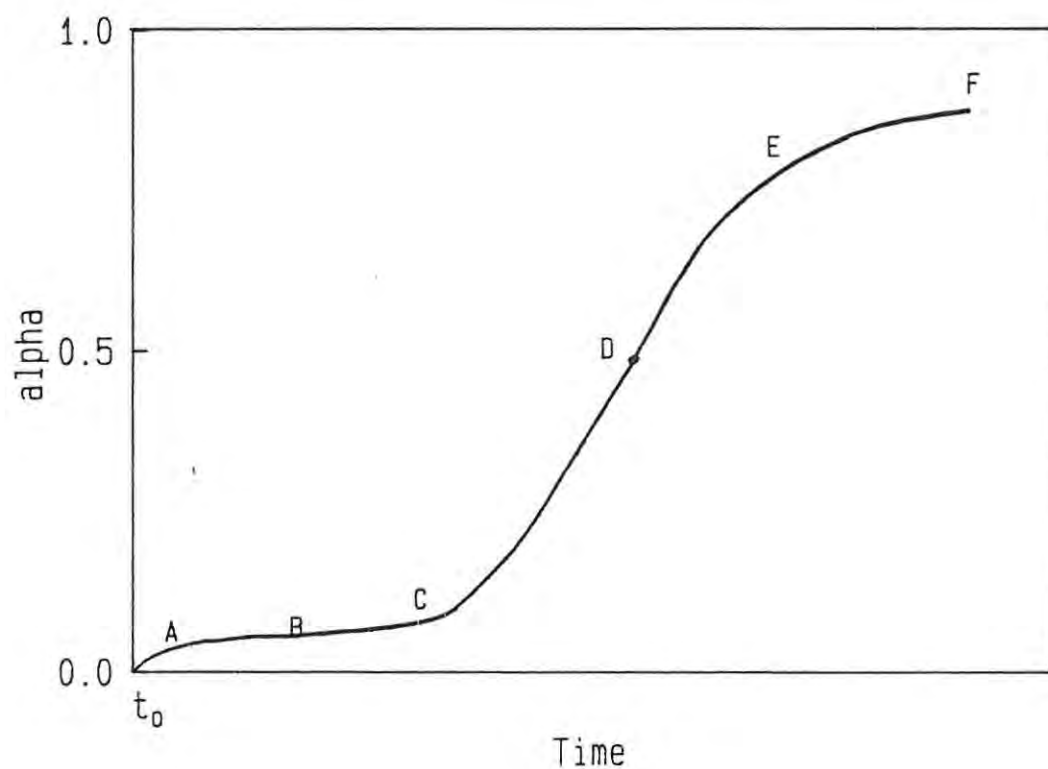
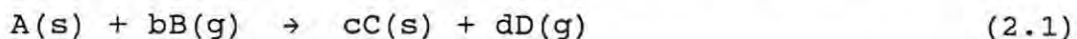


Figure 2.2 Generalised α -time plot summarising characteristic behaviour observed for the isothermal decomposition of solids
(Adapted from Young¹⁵)

the particular reaction system under consideration.

A generalised plot of an isothermal α -time curve for the decomposition of a solid is shown in Figure 2.2¹⁵. Section A of the curve represents the initial reaction, often associated with the decomposition of impurities or the evaporation of moisture from the sample. Section B is known as the induction period, during which the formation of the first product nuclei (germ nuclei) occurs. Once stable nuclei have formed, section C results from the acceleratory period of growth of these nuclei, which continues until the maximum rate of reaction is achieved at point D. Thereafter, the rate decelerates, section E, since the growth of individual nuclei is no longer possible and they start to coalesce. Completion of the reaction occurs at point F. In many reactions some of these processes may exhibit different degrees of significance, while some may be completely absent.

Extending these ideas to the more general solid-gas reaction



all processes, other than reactant-gas diffusion, will be closely related to those occurring during the simple decomposition of a solid. Nuclei of solid product C will form and grow on the surface of solid reactant A; for further reaction to occur, diffusion of the reactant gas B through the solid product layer must take place. The physical properties of this product layer will obviously be important in determining whether further reaction will be

limited by the rate of diffusion through this layer.

When undertaking a kinetic analysis of a reaction, an attempt is usually made to describe the experimental α -time data in terms of a mathematical model. The mathematical modelling of a solid-gas reaction system is usually simplified by choosing a shape for the solid reactant that can be well-defined geometrically. Such shapes commonly include spheres or cylinders. Experimental conditions are then identified under which the various steps of the reaction are rate-controlling. The particular mechanism operating can then be postulated. Further discussion of the methods of kinetic analysis may be found in Chapter 8.

2.2 Some physical and chemical properties of CrCl_3

The starting material, CrCl_3 , for the production of the oxide, Cr_2O_3 , has certain physical and chemical properties which influence its behaviour in the reaction system. Two of these properties are discussed below.

2.2.1 Crystal structure

Anhydrous CrCl_3 crystallises in a flaky or leaf-like form. The unusual crystal structure¹⁶⁻²⁰ can be described as a cubic close-packed stacking of chlorine ions, where between every second pair of chlorine layers, two-thirds of the

octahedral interstices are filled by chromium ions. The structure can also be considered as a stacking of Cl-Cr-Cl sandwiches, as shown in Figure 2.3. The chromium ions are therefore arranged in layered rings, similar to those found in graphite. CrCl_3 is the only substance known to have this exact structure.

The alternate layers of chlorine atoms with no metal atoms between them are held together only by van der Waals forces; crystal cleavage therefore occurs predominantly parallel to these planes^{17,18}, as bonding within the sandwiches is much stronger than between sandwiches.

A practical consequence of this structure is that comminution of the crystals is extremely difficult. The chromium (III) chloride tends to remain as platelets or flakes, even under severe grinding or milling conditions. Thus a wide distribution of particle sizes may exist and it is often necessary to work with relatively large crystals (up to 6 mm diameter) rather than with a fine powder which is generally preferred for kinetic experiments.

2.2.2 Vapour pressure

Anhydrous CrCl_3 does not exhibit a liquid phase, but sublimes on heating. Sublimation is quoted in various sources²¹⁻²⁴ as occurring at temperatures from 945 to 1300°C. However, the equilibrium temperature at which

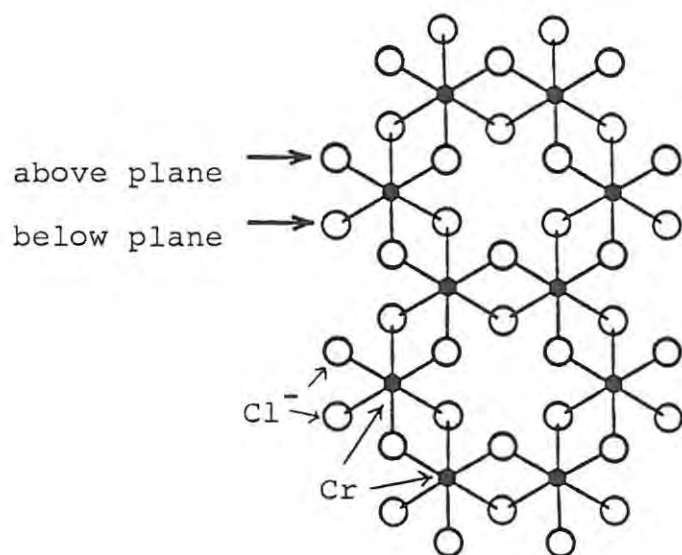


Figure 2.3 The crystal structure of CrCl_3
(Adapted from Amelinckx and Delavignette¹⁷)

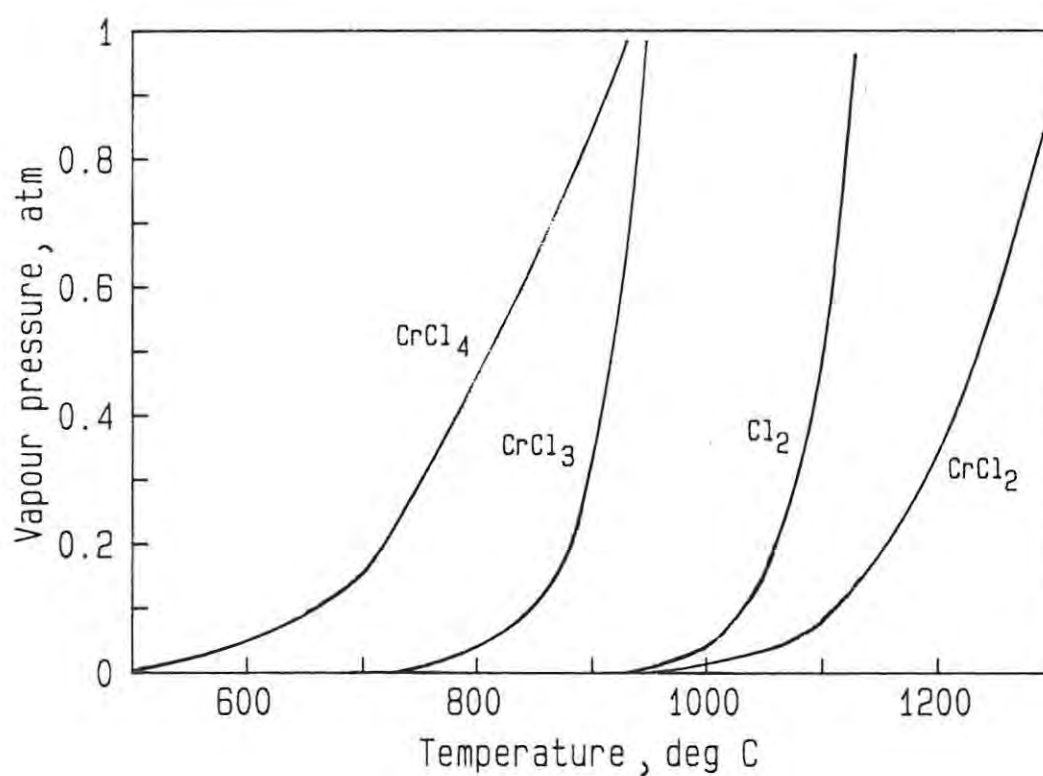
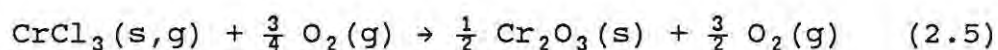


Figure 2.4 The dependence of the vapour pressure of chromium chlorides on temperature
(Adapted from Doerner²⁵)

sublimation occurs is not of importance here, since it has been found that vaporisation of CrCl_3 may begin at temperatures as low as 400°C^{25} . A plot of the equilibrium vapour pressure of CrCl_3 as a function of temperature is shown in Figure 2.4. Under non-equilibrium conditions, e.g. in the absence of chlorine, the vapour pressure curves shift to lower temperatures.

This high vapour pressure at relatively low temperatures can complicate the reaction mechanism by allowing parallel side-reactions to occur. In particular, the major reaction competing with the oxidation of CrCl_3



will be the vaporisation of CrCl_3



Since the rate of vaporisation is directly proportional to the surface area available, the effects of this reaction can be minimised by minimising the surface area of the chloride.

2.3 Experimental methods

2.3.1 Choice of sample configuration

As discussed in Section 2.2, CrCl_3 is not an easy material to handle, particularly in kinetic studies. Its flaky nature means that it is extremely difficult to achieve reproducible sample preparations, while its high vapour pressure results in competition from undesirable side-

reactions. The CrCl_3 starting material has therefore been used in the form of pressed pellets so as to minimise the effects of these factors.

By using a slightly larger mass than conventionally employed, and compressing the crystals under standard conditions, better uniformity in sample preparation can be achieved. The effective surface area of the chloride is also considerably reduced, and therefore the rate of chloride sublimation is correspondingly diminished. A further advantage is that a well-defined geometry for the starting material is established, which simplifies the setting up of a mathematical model for the kinetic analysis of the reaction.

The shape of the pellet should be such that the results of the present kinetic analysis can be extrapolated to describe a more realistic larger scale situation. Since CrCl_3 crystals are a flaky plate-like shape, the shape chosen for the pellets was a flat plate or disc, with a height-to-diameter ratio of $\sim 0,2$.

2.3.2 Choice of experimental techniques

If a kinetic analysis of a particular system is to be undertaken, it is necessary to measure continuously, and under isothermal conditions, the fractional conversion, α , of the material with time. In the case of a solid-gas

reaction of this nature, several options are available. The measurement of the evolution of product chlorine gas as a function of time, or of the mass loss as a function of time are the most practical approaches.

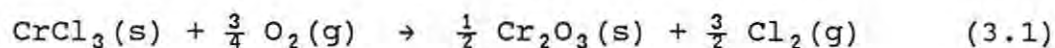
For convenience of experimental procedure and ease of data analysis, thermogravimetry (TG) was chosen. This was supplemented by the use of other experimental techniques for confirmation or clarification of conclusions drawn from the TG results.

3. THERMODYNAMIC ANALYSIS OF THE Cr-O-Cl SYSTEM

A thermodynamic analysis of the system of interest was carried out to predict the reaction conditions under which the reaction is expected to be favourable, and to identify potential by-products or side-reactions. All thermodynamic data quoted are from References 21 and 22, and all calculations have been carried out on the basis of one mole of CrCl_3 .

3.1 Extent of reaction

The extent to which the reaction



will go can be predicted from consideration of the equilibrium constant and equilibrium concentrations of the reactant species.

An Ellingham diagram, depicting the Gibbs free energy of the reaction, ΔG_r , as a function of temperature for various oxidation reactions, is shown in Figure 3.1. Reaction (3.1) (line F) has a negative free energy over the entire temperature range, becoming more negative with increasing temperature. It is therefore expected that the oxidation of CrCl_3 will occur spontaneously in this temperature range.

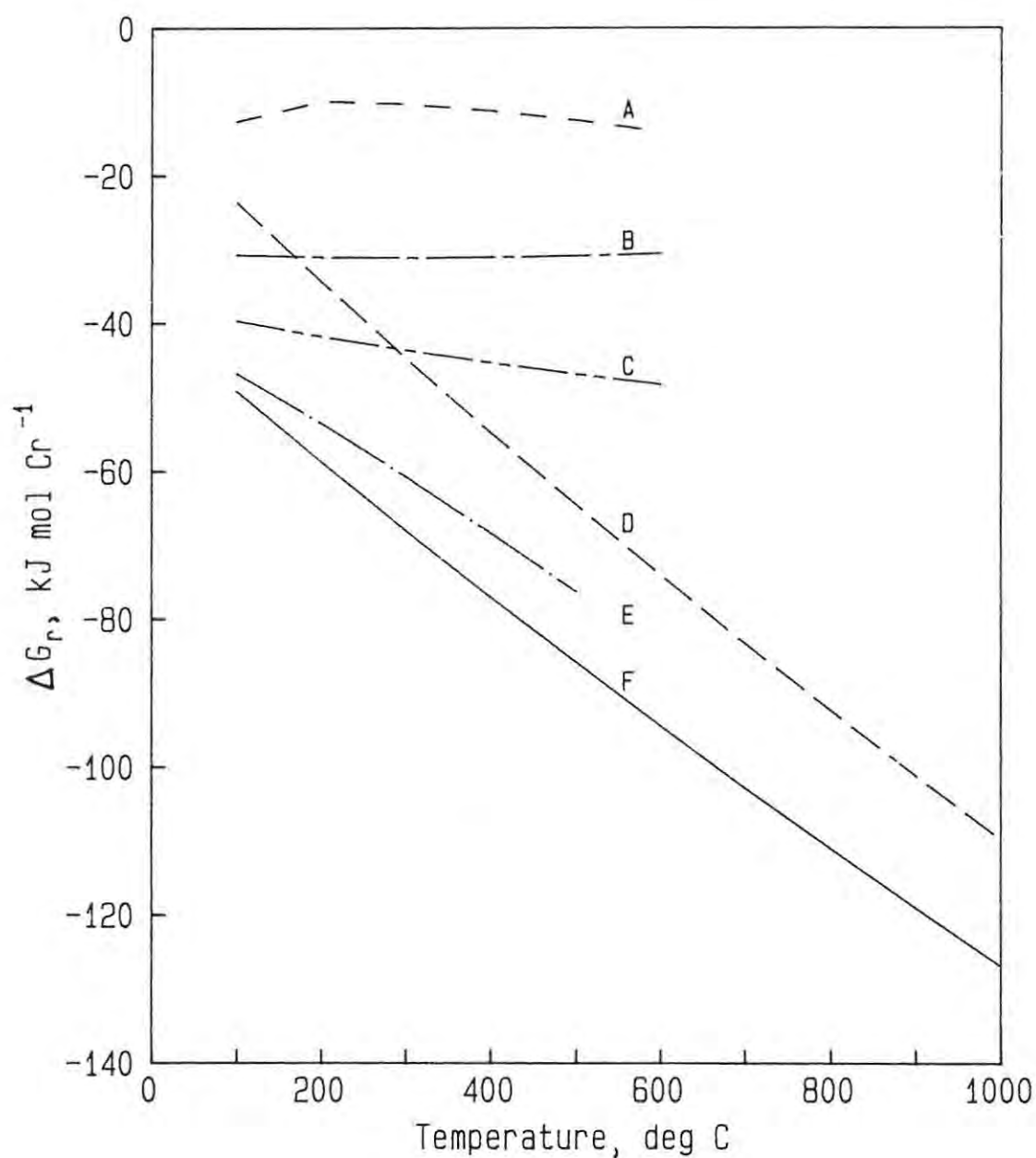
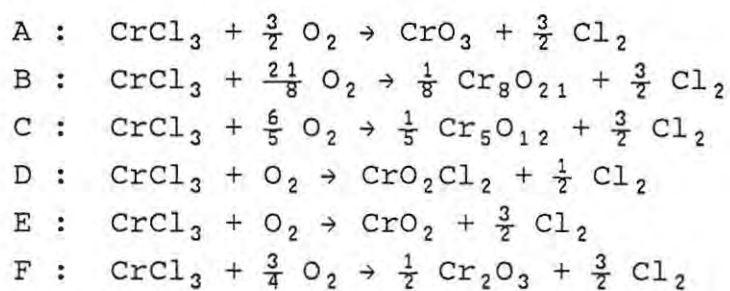
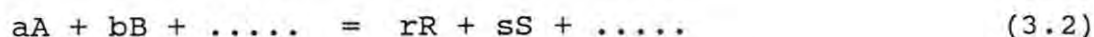


Figure 3.1 Ellingham diagram showing the dependence of the Gibbs free energy of reaction on temperature for the Cr-O-Cl system



For any reaction



the equilibrium constant, K , is given by

$$K = \frac{(a_R^r \cdot a_S^s \dots)}{(a_A^a \cdot a_B^b \dots)} \quad (3.3)$$

where a is the activity of each reaction species.

Since $\Delta G_r = -RT \ln K$

reaction (3.1) may be represented as

$$-\frac{\Delta G_r}{RT} = \ln \left[\frac{a_{Cr_2O_3}^{1/2} \cdot a_{Cl_2}^{3/2}}{a_{CrCl_3} \cdot a_{O_2}^{3/4}} \right] \quad (3.4)$$

If any of the reaction species are pure solids, they can be assumed to have unit activity; if any of the reaction species are gases, their activities are given approximately by their partial pressures (strictly fugacities) in the system.

$$\text{Therefore } -\frac{\Delta G_r}{RT} = \ln \left[\frac{p_{Cl_2}^{3/2}}{p_{O_2}^{3/4}} \right] \quad (3.5)$$

From Figure 3.1, at a typical reaction temperature of 500°C , $\Delta G_r = -85,83 \text{ kJ}$.

Hence equation (3.5) reduces to

$$p_{Cl_2}^2 = 1,662 \times 10^8 p_{O_2} \quad (3.6)$$

If the reaction occurs under atmospheric pressure

$$p_{Cl_2} + p_{O_2} \approx 1 \text{ atm} \quad (3.7)$$

Simultaneous solution of equations (3.6) and (3.7) shows that at equilibrium

$$\begin{aligned} p_{O_2} &\approx 1 \text{ atm} \\ p_{Cl_2} &\approx 0,02 \text{ ppm} \end{aligned} \quad (3.8)$$

This means that even in the presence of minute amounts of oxygen, the chloride will be substantially converted to the oxide. It also implies that the reaction is essentially irreversible, even in the presence of considerable amounts of chlorine. This reaction should therefore go readily to completion under suitable experimental conditions, and the rate should not be affected by equilibrium considerations.

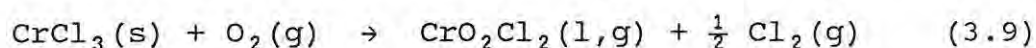
3.2 Formation of other chromium-chloride-oxide species

A number of Cr-O-Cl species have the potential to form from the reaction of $CrCl_3$ with oxygen. Species for which thermodynamic data is available include the oxides CrO_3 , Cr_8O_{21} , Cr_5O_{12} and CrO_2 , and the oxychloride CrO_2Cl_2 . The dependence of the Gibbs free energies of these reactions on temperature is shown on the Ellingham diagram in Figure 3.1. This data indicates that the thermodynamic probability of the various products forming decreases in the order

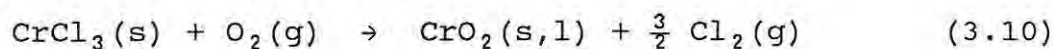


Inspection of the magnitude of these free energies in the temperature range of interest (300 to 600°C), suggests that, besides the $CrCl_3$ volatilisation discussed in Section 2.2.2, the only side-reactions which may interfere with the desired

oxidation reaction are the formation of chromyl chloride



or the formation of CrO_2



All other chromium chlorides are far less stable and are unlikely to form.

Under strongly oxidising conditions the formation of the higher oxide species may become more favourable, but the existence of such species is likely to be transient. At temperatures of 250 to 450°C these higher oxides decompose to form Cr_2O_3 and, under conditions of high pressures of oxygen, CrO_2 ^{23,26}.

3.3 Enthalpy of reaction

The temperature dependence of the enthalpy of reaction, ΔH_r , is shown in Table 3.1. The discontinuity between 1000 and 1100°C is due to the sublimation of CrCl_3 , which occurs at 1007°C with an enthalpy of sublimation of 236,4 kJ mol⁻¹²¹. The calculations assume that all reactants and products are at the temperature indicated. On this basis it can be seen that the reaction is slightly exothermic over the temperature range considered.

The energy balance for a potential process involving this reaction is detailed in Appendix A. A "reactor" is envisaged into which oxygen enters at ambient temperature;

oxygen then reacts with CrCl_3 at the reaction temperature, and the product gases leave the reactor at the reaction temperature. If it is assumed that the efficiency of oxygen utilisation is less than 100% (as would be expected in a solid-gas reaction) and that (say) 50% excess oxygen is used, it can be shown that the process would require an input of thermal energy. At a temperature of (say) 600°C , the oxidation reaction itself is insufficiently exothermic to provide the energy required to raise the temperature of the oxygen, and an energy input of $11,80 \text{ kJ mol}^{-1} \text{ CrCl}_3$ is required. Since the energy change for the process is small ($+20 \text{ kJ mol}^{-1} \text{ CrCl}_3$), this suggests that whatever process configuration may be used on a large scale, control of heat transfer in the system should be straightforward, and the energy requirements small.

Table 3.1 Temperature dependence of the enthalpy of reaction for the reaction
 $\text{CrCl}_3(\text{s}) + \frac{3}{2} \text{O}_2(\text{g}) \rightarrow \frac{1}{2} \text{Cr}_2\text{O}_3(\text{s}) + \frac{3}{2} \text{Cl}_2(\text{g})$

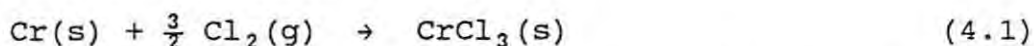
Temperature ($^\circ\text{C}$)	ΔH_r (kJ mol^{-1})	Temperature ($^\circ\text{C}$)	ΔH_r (kJ mol^{-1})
100	-13,13	700	-22,08
200	-14,21	800	-23,99
300	-15,51	900	-25,99
400	-16,97	1000	-28,09
500	-18,56	1100	-266,7
600	-20,27	1200	-268,9

4. EXPERIMENTAL PROCEDURES

4.1 Reagents

4.1.1 CrCl_3

Anhydrous chromium(III) chloride was produced on a batch scale by the high temperature chlorination of chromium metal according to the reaction



Details of the procedure may be found in Appendix B. Each batch of CrCl_3 was analysed by the Wet Chemistry Section of the Analytical Science Division at Mintek. Since CrCl_3 is insoluble in water, the sample was solubilised by fusion with Na_2O_2 in a zirconium crucible. This procedure also oxidised the Cr(III) to Cr(VI). The sample was then acid-leached in H_2SO_4 , residual Cr(III) oxidised with KMnO_4 , and then the permanganate destroyed by HCl . The chromium content was determined volumetrically by titration with iron(II) ammonium sulphate using ferroin as the indicator. The chloride content was determined gravimetrically by precipitation of the chloride as AgCl , after reaction with AgNO_3 . The CrCl_3 starting material used in this work was >98% pure.

4.1.2 Gases

The oxygen, nitrogen and air used in this work, both as the pure gases and in gas mixtures, were high-purity grade

gases, supplied by Afrox, South Africa, and were employed without further purification.

4.1.3 Other reagents

Other reagents used were AR grade Cr_2O_3 supplied by Saarchem, South Africa; ER grade SiO_2 from PAL Chemicals, South Africa; CP grade Al_2O_3 from Riedel-de-Haen, Germany; and Fe_2O_3 supplied by Kanto Chemical Co, Inc., Japan.

4.2 Sample preparation

The CrCl_3 oxidation was generally carried out with the starting material in pellet form. The pellets were usually prepared by compressing 1 g CrCl_3 in a 13 mm diameter uniaxial die under a load of 5 tons for 3 minutes, using a hydraulic press. Typical dimensions and physical characteristics of the pellets are given in Table 4.1.

Table 4.1 Dimensions and properties of CrCl_3 pellets

Diameter (d)	13,0 mm
Height (h)	2,5 mm
$a = h/d$	0,192
Bulk volume	331,8 mm ³
Measured surface area	0,100 m ² g ⁻¹
Absolute density	2,96 g cm ⁻³
Porosity	11,9 %
Mass	1 g

4.3 Thermogravimetric experiments

Both isothermal and programmed-temperature (non-isothermal) thermogravimetric (TG) experiments were carried out using a Netzsch Simultaneous Thermal Analyser, Model STA429. This instrument is capable of carrying out TG and DTA (differential thermal analysis) measurements simultaneously, to a maximum temperature of 1750°C. A schematic representation of the balance-furnace system is shown in Figure 4.1. The balance is a highly-sensitive top-loading Sartorius substitution model which has been slightly modified for use in the present configuration. Samples are held in alumina crucibles, balanced on an alumina sample-holder pedestal which plugs into the top of the balance box. A single-head TG sample holder was used in both the isothermal and programmed-temperature experiments. Changes in mass of the sample are compensated electromagnetically by an inductive displacement transducer; this means that any sample will always remain in the same vertical position in the furnace, irrespective of its mass. The furnace is heated by Super Kanthal molybdenum disilicide elements. The furnace temperature is measured and controlled by a P.I.D. (proportional-integral-differential) controller using a B-type (Pt30%Rh-Pt6%Rh) thermocouple held inside the alumina sample holder. The sample temperature was also measured using a B-type thermocouple. All experiments were carried out under atmospheric pressure (~84 kPa on the Witwatersrand) in dynamic gas atmospheres. Gas flowrates were controlled by the use of needle valves and measured using calibrated rotameters.

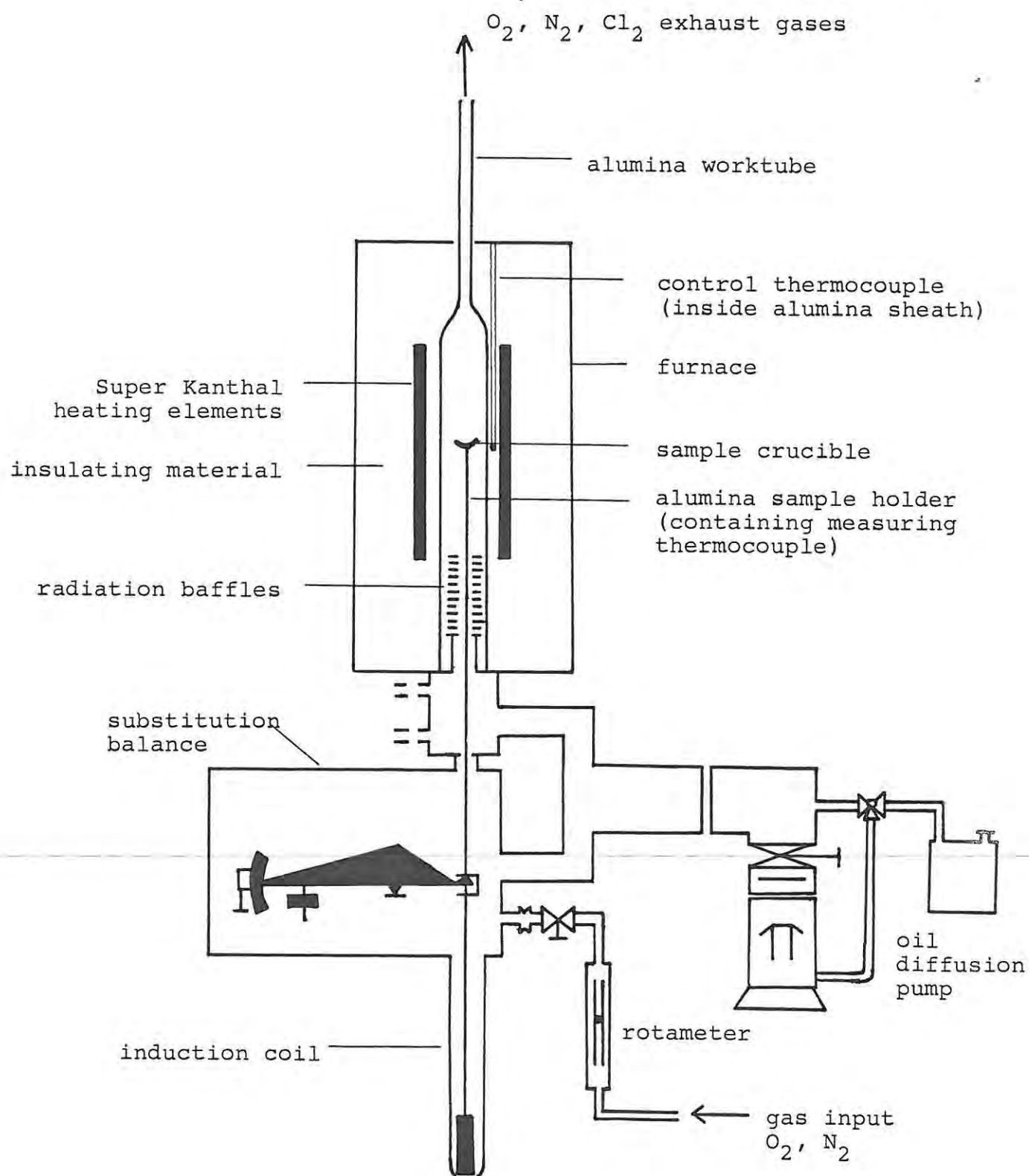


Figure 4.1 Representation of the Netzsch STA429 simultaneous thermal analyser as used for the oxidation of $CrCl_3$

The experimental data from each run were captured by a datalogger (built in the Mintek laboratories²⁷) coupled to an Apple II Plus microcomputer. The rate of data acquisition varied from 1 reading (time, temperature and mass) per second to 1 reading per 90 seconds, depending on the length of the experimental run. Most experiments used an acquisition rate of 1 reading every five seconds, collecting a maximum of 1668 raw data points for each experiment. The data were then manipulated as desired using a series of computer programs collectively called STA429, which are readily available within the High Temperature Chemistry Group at Mintek²⁷. Further details of programs designed for use in this work are discussed in Chapter 8.

Two different configurations for the pelletised samples were tested; these are illustrated in Figure 4.2. This was to ensure that all parts of the pellet were equally exposed to the reaction atmosphere, thereby avoiding asymmetric reaction of the pellet. Results of experiments carried out under identical conditions showed that there appeared to be no differences between these two configurations which could be attributed to mass-transfer effects.

4.3.1 Programmed-temperature TG experiments

Programmed-temperature TG experiments were carried out at heating rates of from 2 to 20°C min⁻¹. The heating rates discussed in the text refer to the programmed heating rate; the actual rates observed are somewhat lower. This is

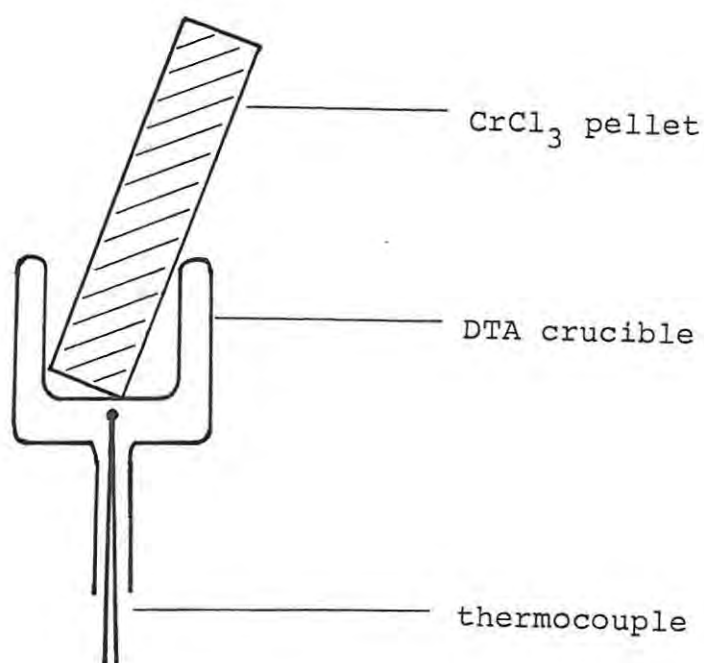
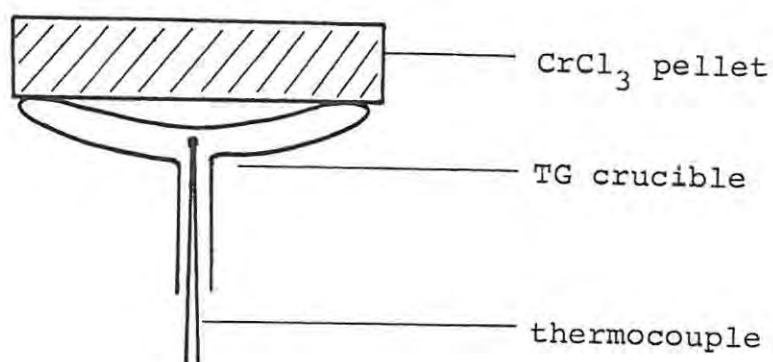


Figure 4.2 Sample configurations used for TG experiments
(a) Pellet held horizontally on a perforated TG crucible
(b) Pellet held vertically in a sectioned DTA crucible

because the temperature controller is regulated by the furnace temperature, rather than by the sample temperature. There is typically a 50 to 100°C lag between the furnace and sample temperatures. The temperatures shown in the experimental results are, however, the measured sample temperatures.

4.3.2 Isothermal TG experiments

In the isothermal experiments, the samples were introduced into the furnace while it was at room temperature. The furnace was then programmed to heat up at 99,9°C min⁻¹ (the maximum permissible heating rate) to the required temperature, after which the temperature was held constant until the reaction was complete. This practice resulted in non-isothermal conditions during the first few minutes of each experiment. However, as isothermal reaction times usually ranged from 2,5 to 40 hours, the effect of this initial heating on the rate of reaction was assumed to be negligible. This assumption was justified at temperatures up to ~600°C, as the onset of mass loss (corresponding to the onset of oxidation) did not occur until after the isothermal temperature had been reached.

4.4 Scanning electron-microscopy (SEM)

4.4.1 Back-scattered electron images

Chemical compositions across pellet cross-sections were determined by observing the back-scattered electron image on a Joel JSM-840M scanning electron - microscope. Back-scattered electron emission occurs from a depth of ~100 nm into the sample. The intensity of emission is related to the atomic number of the scattering atoms; high atomic number samples scatter the electrons more strongly, thereby giving rise to a brighter image.

The experimental technique used was as follows. CrCl_3 pellets, made in the conventional manner, were heated in air in a Kanthal-wound 1,5 kW tube furnace. The pellets were balanced vertically in a fire-clay crucible so that all parts of the pellet were equally exposed to the reaction atmosphere. Reaction was allowed to proceed at the selected temperature for times of between 2 and 60 minutes. The fractional reaction, α , was then calculated by comparing the mass of the sample before and after the reaction.

The partially-reacted pellets were then prepared for SEM observations. They were first impregnated with epoxy resin under vacuum because the porosity of Cr_2O_3 is considerably greater than that of CrCl_3 and so the product pellets tended to break up on sectioning unless they had been impregnated. A resin found to be suitable for this purpose was Araldite M

mixed in a 5:1 mass ratio with Hardener HY 956, both supplied by Ciba-Geigy, South Africa. The pellets were then mounted in Perspex sample holders using the epoxy resin. After rough sectioning, the exposed cross-section was polished to a fine finish, first using 1000# carborundum paper, then on a polishing disc with paraffin, and finally with a series of diamond polishing pastes (Hyprez spray for 6, 0,25 and 0,1 μm , supplied by Engis Ltd., Kent, England, and DP-Spray for 3 and 1 μm from Struers, Denmark). Attempts were made to ensure that the final surface exposed corresponded as closely as possible with a section taken directly across a diameter of the pellet.

4.4.2 Secondary-electron images

A Hitachi scanning electron-microscope, Model S-450, was used to identify crystal topology, sizes and shapes by observing the secondary-electron images. Secondary-electron emission is confined to emission from the surface of the sample (to a depth of ~ 10 nm); such electrons have typical energies of 0 to 50 eV. This emission is produced as a result of the interaction between the energetic beam electrons and the weakly-bound conduction band electrons of the sample. The topographic contrasts arise because the intensity of electron generation depends on the angle of incidence of the beam.

The samples used for these analyses were products from the TG experiments. The pellets were gently crushed to a fine

powder using an agate mortar and pestle. These powders were then observed directly after conventional SEM sample preparation.

4.5 X-ray diffraction analysis

Determinations of product purities and identification of unknown species were carried out by X-ray diffraction (XRD) analysis, using a Phillips diffractometer, Model DY 678, operating with x-rays of Cu-K α radiation ($\lambda = 0,1541$ nm).

4.6 Surface-area measurements

Surface areas were measured using the B.E.T. (Brunauer, Emmett and Teller) method with krypton gas as the adsorbate. The apparatus used was built in the Mintek laboratories.

4.7 Measurements of density, porosity and pore-size distribution

The absolute densities, ρ_0 , of various species were measured using a Quantachrome stereo-pycnometer, with helium gas as the adsorbate. The bulk densities, ρ_b , of CrCl $_3$ and Cr $_2$ O $_3$ pellets were measured using a simple mercury-displacement porosimeter. By measuring the volume of mercury displaced by a given mass, the porosity of the pellets could then be

calculated from the relation

$$\text{Porosity (\%)} = \frac{\rho_o - \rho_b}{\rho_o} \times 100 \quad (4.2)$$

The measurements of pore-size distribution were carried out on a Quantachrome Autoscan Porosimeter, using mercury pressures of up to 4×10^5 kPa.

4.8 Residual chloride analysis

Concentrations of residual chloride in the oxide product were determined by the Chromatography Section of the Analytical Science Division at Mintek using the technique of ion-exclusion chromatography.

4.9 Colour measurements

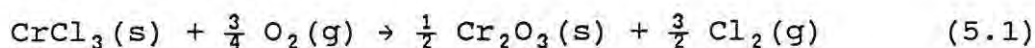
The measurements of the colour of Cr_2O_3 were carried out using a Pacific Scientific Spectrogard Colour System. The most satisfactory measurements were made with the sample in powdered form. Cr_2O_3 samples, prepared under different experimental conditions, were gently crushed and then pressed into Perspex sample holders and covered with a glass microscope coverslip. Illumination of the sample was achieved using artificially-produced "average daylight". Because the oxide is opaque, the instrument was operated using the "spectral exclude" mode, which excludes the

effects of reflectance from the sample. A quantitative value for the colour of a sample was obtained from its x,y coordinates on a CIE (Commission Internationale de L'Eclairage) chromaticity diagram, while the brightness of the colour was determined from a plot of the reflectance spectrum in the visible wavelength region. Comparisons with a standard were made to facilitate interpretation of the data. The standard chosen was pigment-grade Cr_2O_3 , Delta Chrome Oxide Green D1110, obtained from Rolfe's Pigment Manufacturers, Elandsfontein, South Africa.

5. THERMOGRAVIMETRY

5.1 Effect of pelletising the sample

For the reaction



the theoretical mass loss expected is 52,00%, assuming pure reactants and no side-reactions.

Figure 5.1 shows the programmed-temperature TG curves for CrCl_3 flakes and a CrCl_3 pellet in air. For the unpelletised sample, the onset of mass loss is seen to occur at $\sim 310^\circ\text{C}$, and the mass loss measured on completion of the reaction is 57,0%. The oxidation of the CrCl_3 pellet begins at $\sim 413^\circ\text{C}$, and the final mass loss measured is 52,8%. The observed mass loss for CrCl_3 flakes is therefore much greater than that theoretically predicted.

As discussed in Section 2.2.2, CrCl_3 has a significant vapour pressure, particularly in the absence of chlorine. The high mass loss can thus be explained in terms of sublimation of the chromium chloride occurring simultaneously with its oxidation. This explanation is supported by the observation that amounts of Cr_2O_3 are found deposited outside of the crucible and on the walls of the furnace tube, suggesting that a gas-phase process has occurred. The lower temperature at which the initial mass loss of the flakes occurs can also be ascribed to sublimation of the chloride, since the oxidation starts at a higher temperature.

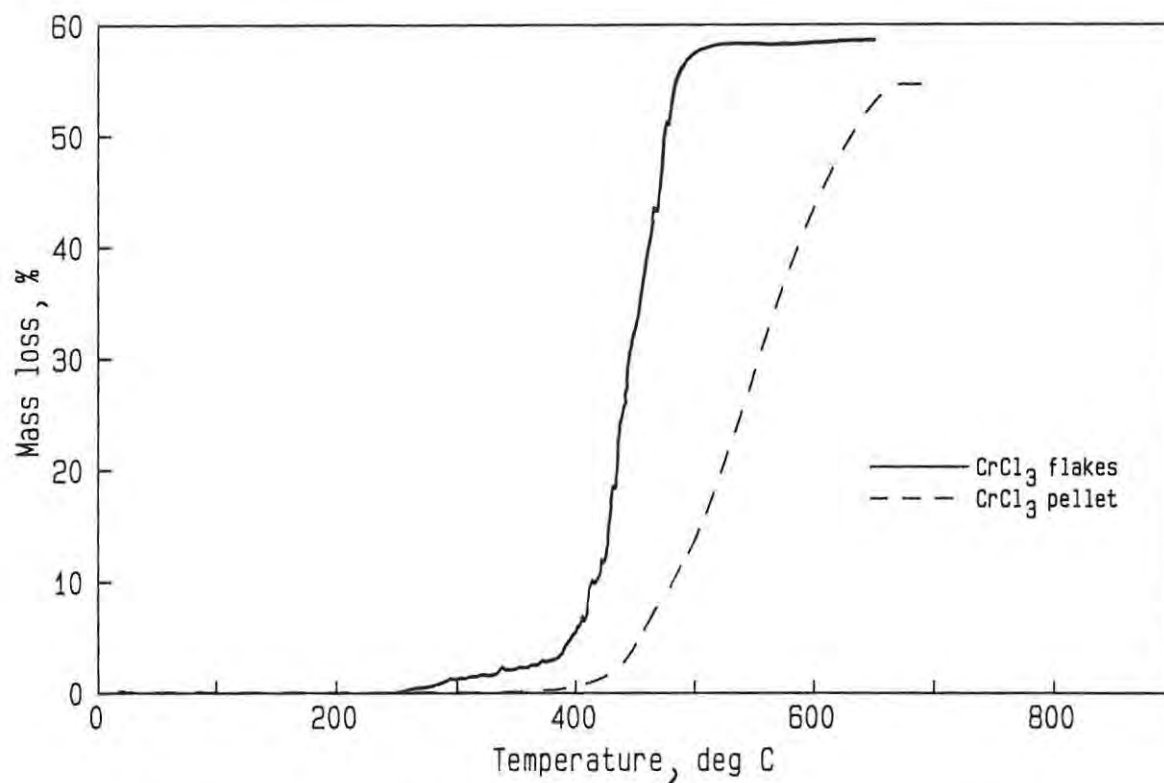


Figure 5.1 The effect of sample preparation on the non-isothermal oxidation of CrCl_3 in oxygen
 Conditions : Programmed-temperature TG
 $10^\circ\text{C min}^{-1}$ heating rate
 $200 \text{ cm}^3 \text{ min}^{-1}$ oxygen

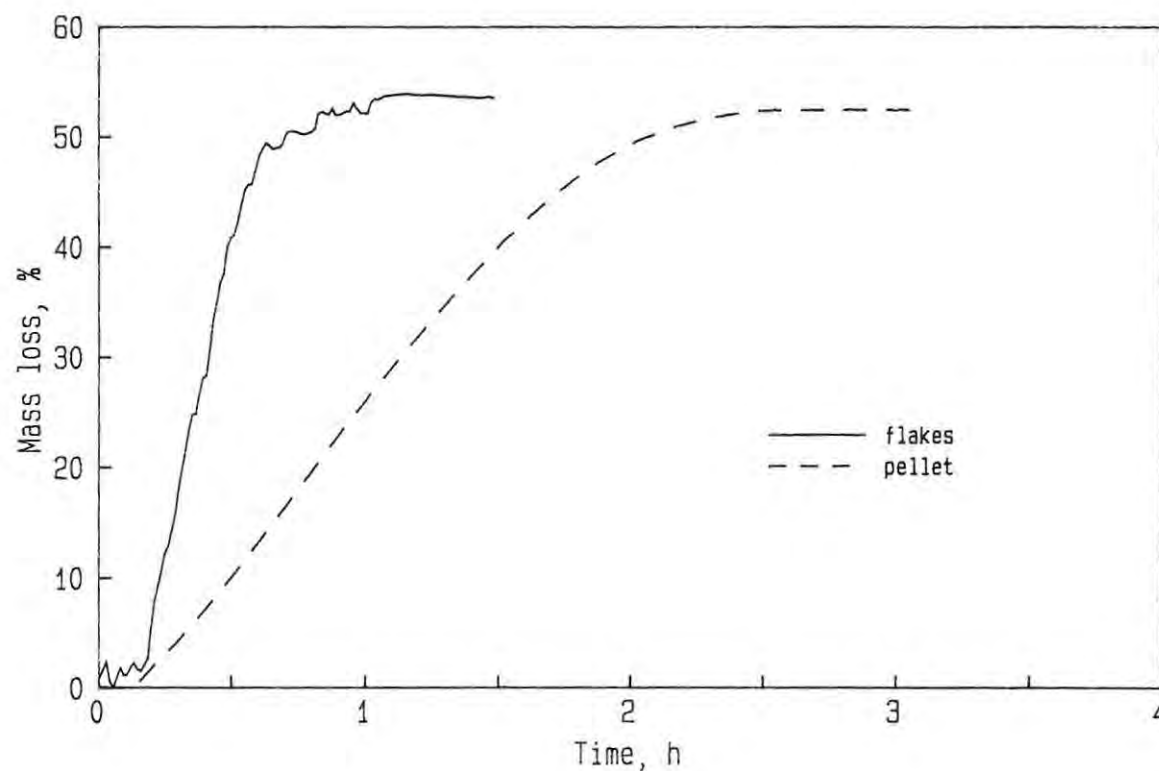


Figure 5.2 The effect of sample preparation on the isothermal rate of oxidation of CrCl_3 in air
 Conditions : Isothermal TG
 500°C
 $200 \text{ cm}^3 \text{ min}^{-1}$ air

These results show that in order to eliminate the competing side-reaction



from the reaction system, it is necessary to reduce the volatility of the chloride. One way in which this can conveniently be done is to reduce the surface area available by compacting the sample into a suitable pellet.

The isothermal oxidations of CrCl_3 pellets and CrCl_3 flakes are compared in the TG traces of Figure 5.2. For CrCl_3 flakes, the observed mass loss exceeds the theoretical value due to the removal of chromium from the sample by volatilisation of the chloride prior to and during its oxidation. The oxidation of the flakes is complete in less than an hour, while the pellet takes ~2,5 hours for complete conversion. This is to be expected for heterogeneous reactions where contact between the solid and gaseous reactants is important. The surface area of the flakes has been measured to be $1,613 \text{ m}^2 \text{ g}^{-1}$, while CrCl_3 pellets only have a surface area of $0,100 \text{ m}^2 \text{ g}^{-1}$. A far greater degree of solid-gas contact thus occurs in the flakes, giving rise to an enhanced reaction rate.

For kinetic analysis of the TG curves, however, the use of pellets is preferable. Oxidation of a pellet gives rise to a smooth and well-defined TG curve which can readily be described by a mathematical function. In contrast, the curve for the oxidation of flakes shows a number of irregularities due to flakes of different sizes reacting at different rates, and is far more difficult to interpret.

Figure 5.3 shows a comparison of isothermal TG experiments carried out in air and in nitrogen. In both experiments, the CrCl_3 was pressed into pellets. It is reasonable to assume that any mass loss observed in the nitrogen atmosphere can be attributed to the sublimation of the chloride, rather than to oxidation. Only a slight mass loss is observed in nitrogen, and it is therefore concluded that the use of the samples in the form of pellets reduces the rate of volatilisation of CrCl_3 satisfactorily. The observed mass loss for the CrCl_3 pellet reacted in air corresponds closely with that predicted theoretically, showing no evidence of CrCl_3 volatilisation occurring as a competing side-reaction.

All further TG experiments were carried out using the sample in the form of a pellet. Typical reproducibility which can be achieved under identical experimental conditions is illustrated in Figures 5.4(a) and (b) and summarised in Table 5.1. The tabulated rates have been expressed in terms of the time required to reach a particular extent of conversion, e.g. $t_{0,25}$ is the time at which $\alpha = 0,25$.

The sensitivity of TG measurements means that a very high degree of reproducibility is usually obtained for experiments of this nature. The higher-than-expected experimental errors measured in this work (~2 to 7%) can be ascribed to the variation in particle size of the CrCl_3 and the inability of the crystals to be ground into a fine powder (Section 2.2.1).

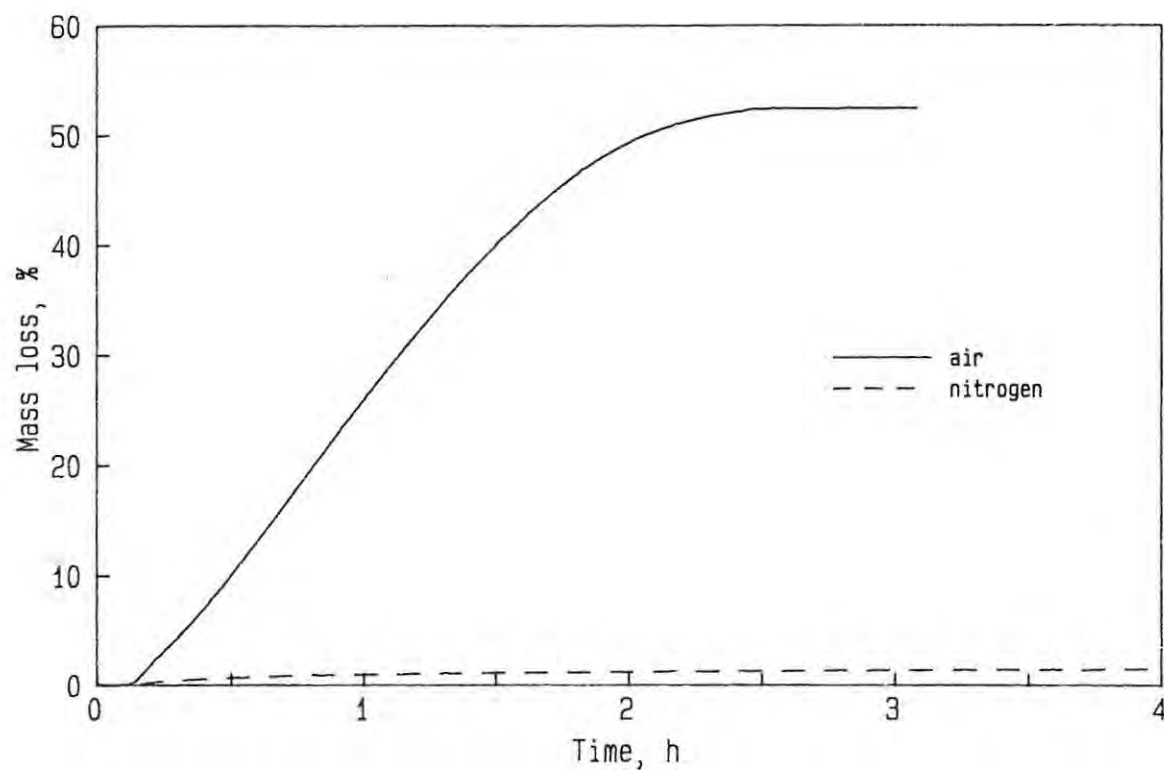


Figure 5.3 The effect of reaction atmosphere on the rate of sublimation of CrCl_3
Conditions : Isothermal TG
1 g CrCl_3 pellet
500°C
200 $\text{cm}^3 \text{ min}^{-1}$ gas flowrate

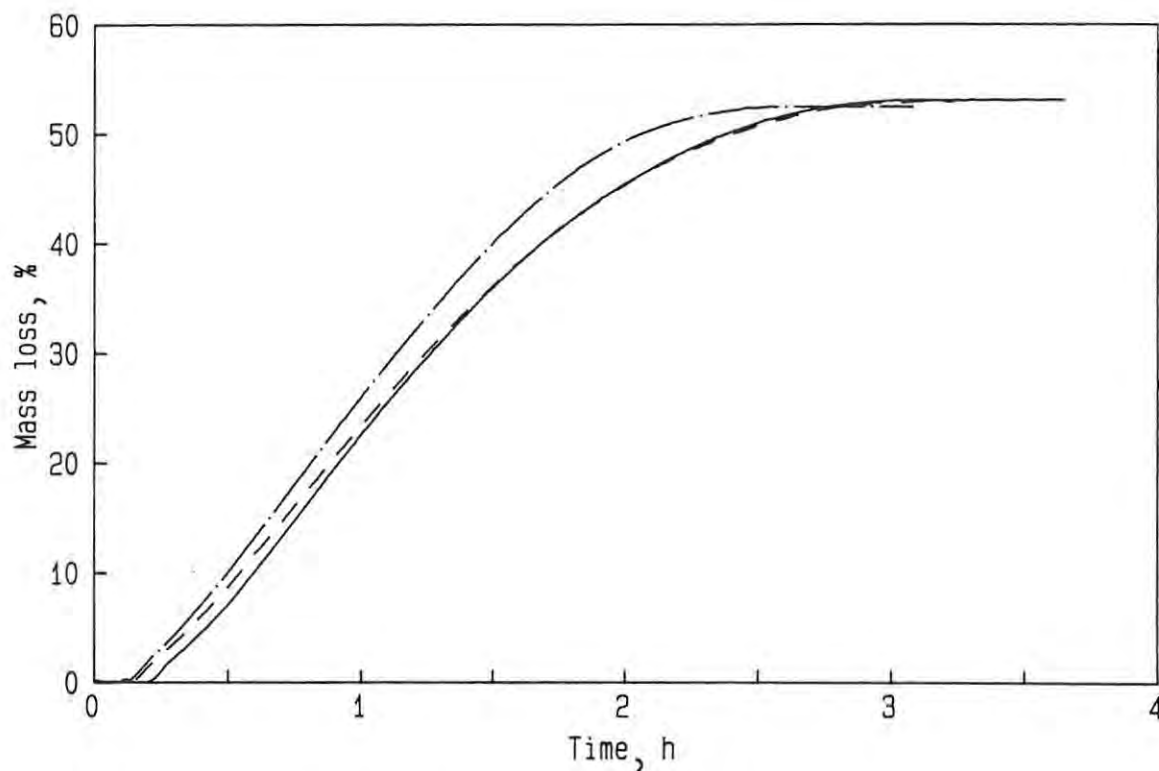


Figure 5.4(a) Typical reproducibility of isothermal TG curves for the oxidation of CrCl_3
 Conditions : Isothermal TG
 1 g CrCl_3 pellet
 $200 \text{ cm}^3 \text{ min}^{-1}$ air
 500°C

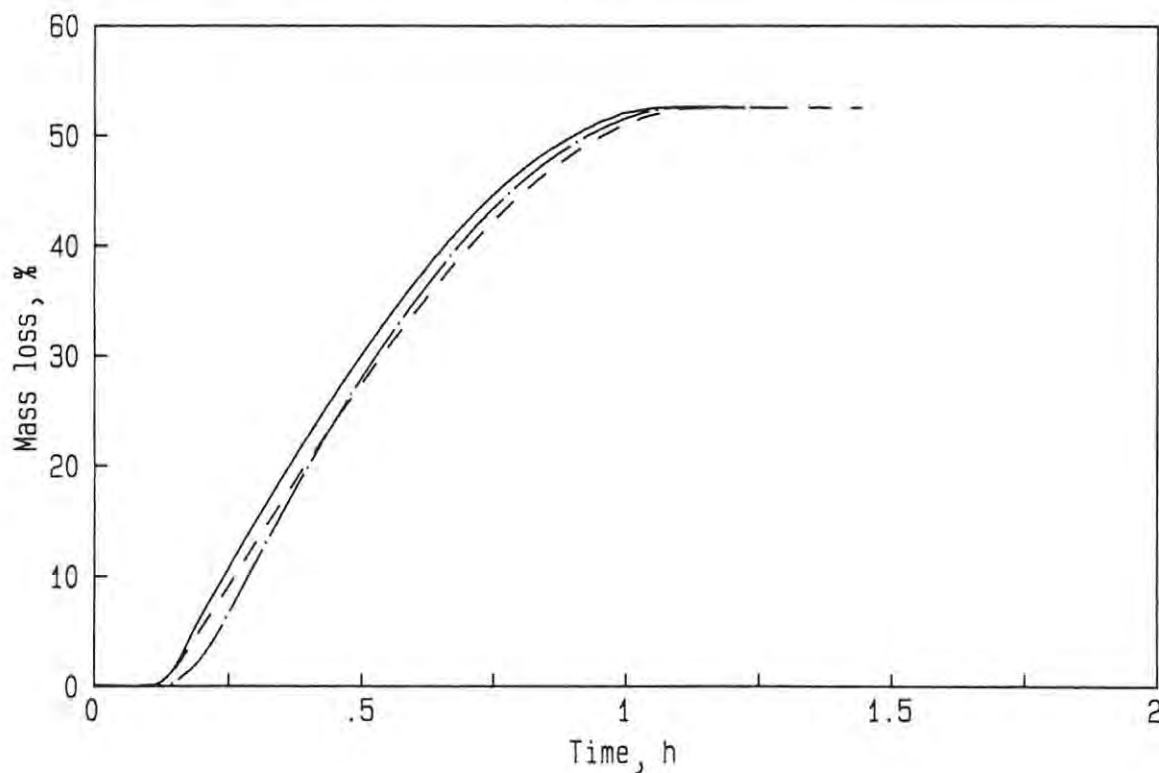


Figure 5.4(b) Typical reproducibility of isothermal TG curves for the oxidation of CrCl_3
 Conditions : Isothermal TG
 1 g CrCl_3 pellet
 $200 \text{ cm}^3 \text{ min}^{-1}$ air
 600°C

Table 5.1 Typical reproducibility of isothermal TG experiments

Conditions : Isothermal TG
1 g CrCl_3 pellet
200 $\text{cm}^3 \text{min}^{-1}$ air

Temperature ($^{\circ}\text{C}$)	Replicate No.	$t_{0,25}$ (h)	$t_{0,5}$ (h)	$t_{0,75}$ (h)
500	1	0,68	1,16	1,68
	2	0,70	1,14	1,67
	3	0,62	1,01	1,48
600	1	0,30	0,48	0,70
	2	0,28	0,44	0,65
	3	0,32	0,48	0,68

5.2 Effect of gas flowrate

Figures 5.5(a) to (d) and Table 5.2 show the effect of the gas flowrate on the rate of reaction under isothermal conditions at temperatures from 400 to 600 $^{\circ}\text{C}$. Due to the sensitive nature of the TG balance, 200 $\text{cm}^3 \text{min}^{-1}$ is the maximum flowrate permitted.

Although increasing the flowrate does result in an increase in the reaction rate at all temperatures, at the lower temperatures the effect is small and falls close to within the observed experimental reproducibility (Figure 5.4 and Table 5.1). This indicates that fluid-phase mass-transfer (film diffusion) is not significant in affecting the reaction rate under these experimental conditions. However, for faster reaction rates at higher temperatures (Figure 5.5(c)), the gas flowrate may have some effect on the reaction rate. Since apparatus considerations precluded the use of a higher flowrate, a constant and fastest-possible

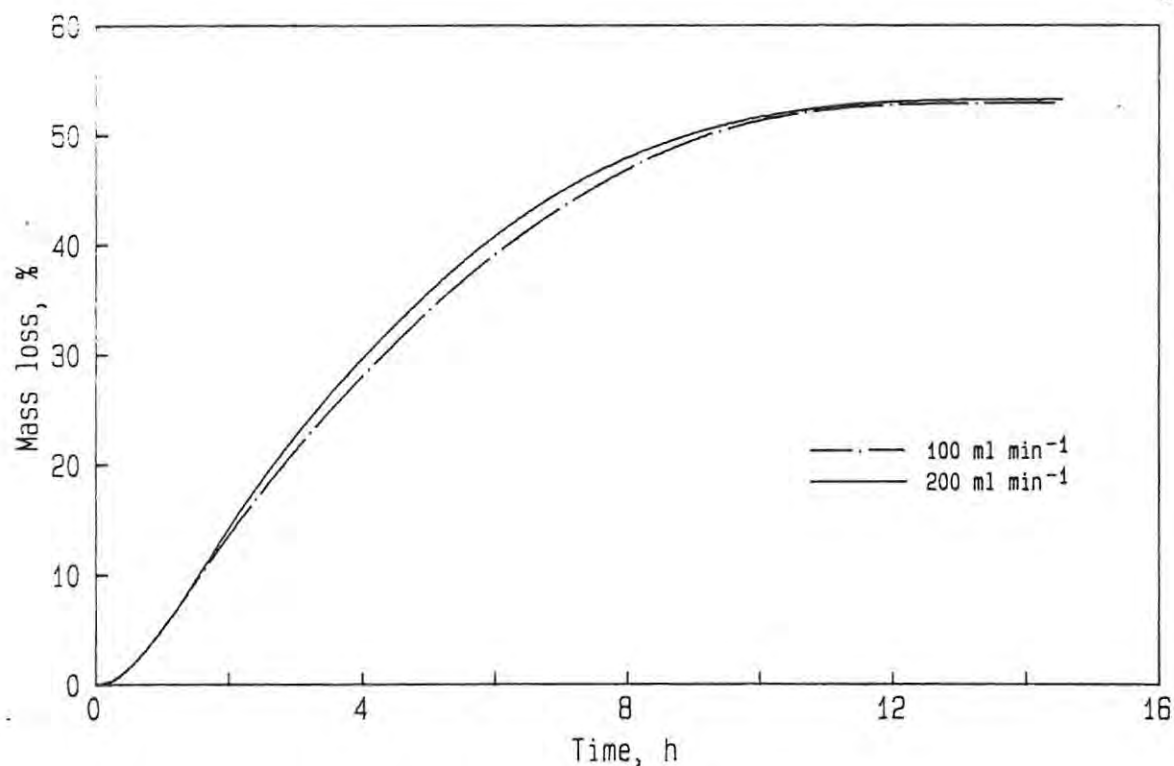


Figure 5.5(a) The effect of gas flowrate on the rate of oxidation of CrCl_3
 Conditions : Isothermal TG
 1 g CrCl_3 pellet
 Air
 400°C

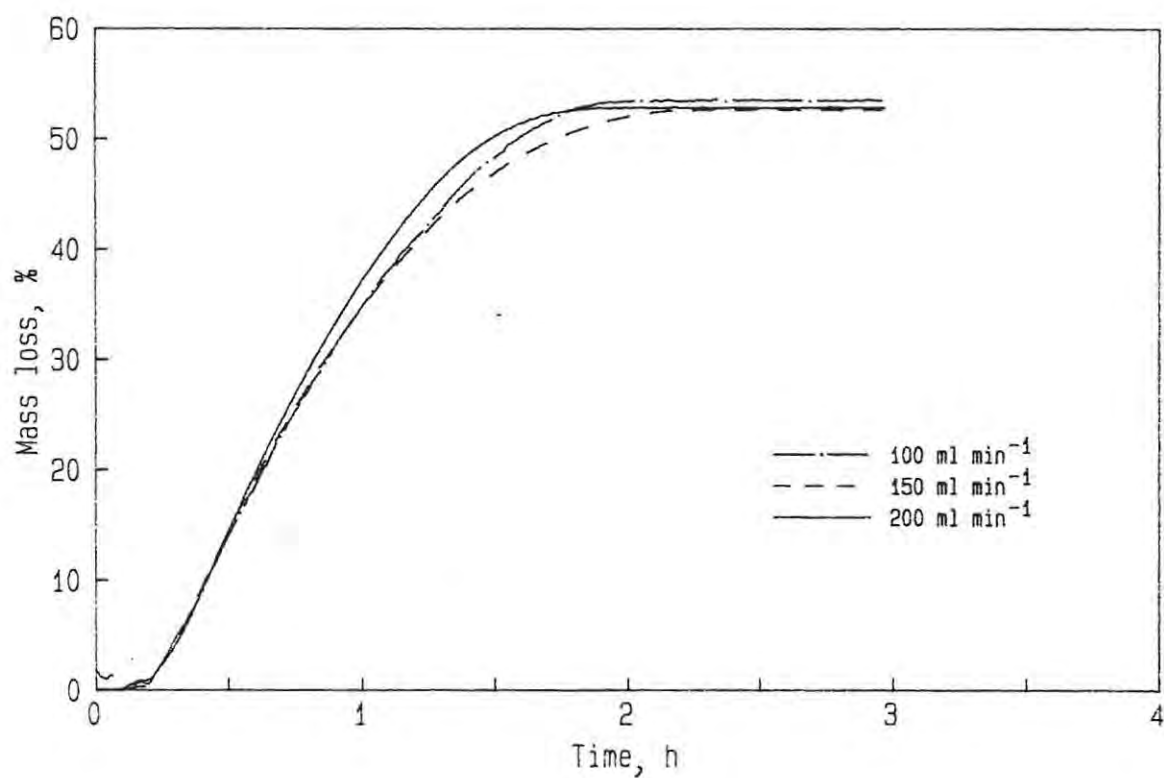


Figure 5.5(b) The effect of gas flowrate on the rate of oxidation of CrCl_3
 Conditions : Isothermal TG
 1 g CrCl_3 pellet
 Air
 530°C

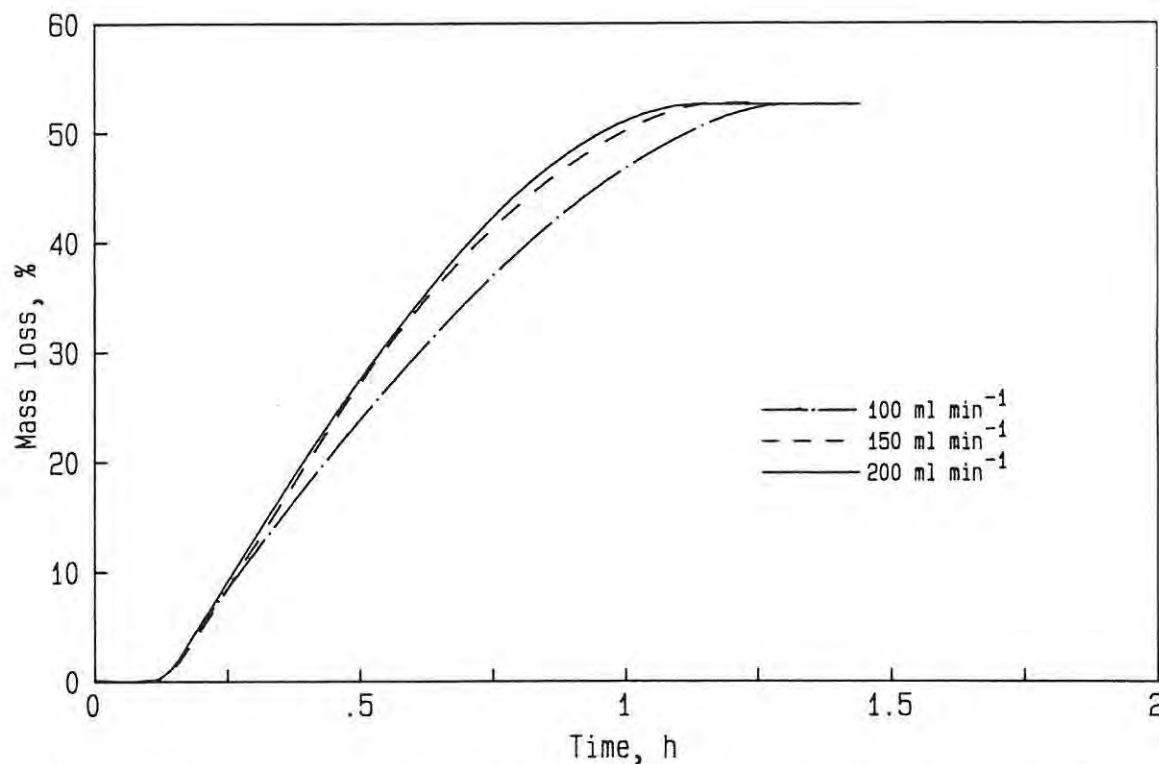


Figure 5.5(c) The effect of gas flowrate on the rate of oxidation of CrCl_3
 Conditions : Isothermal TG
 1 g CrCl_3 pellet
 Air
 600°C

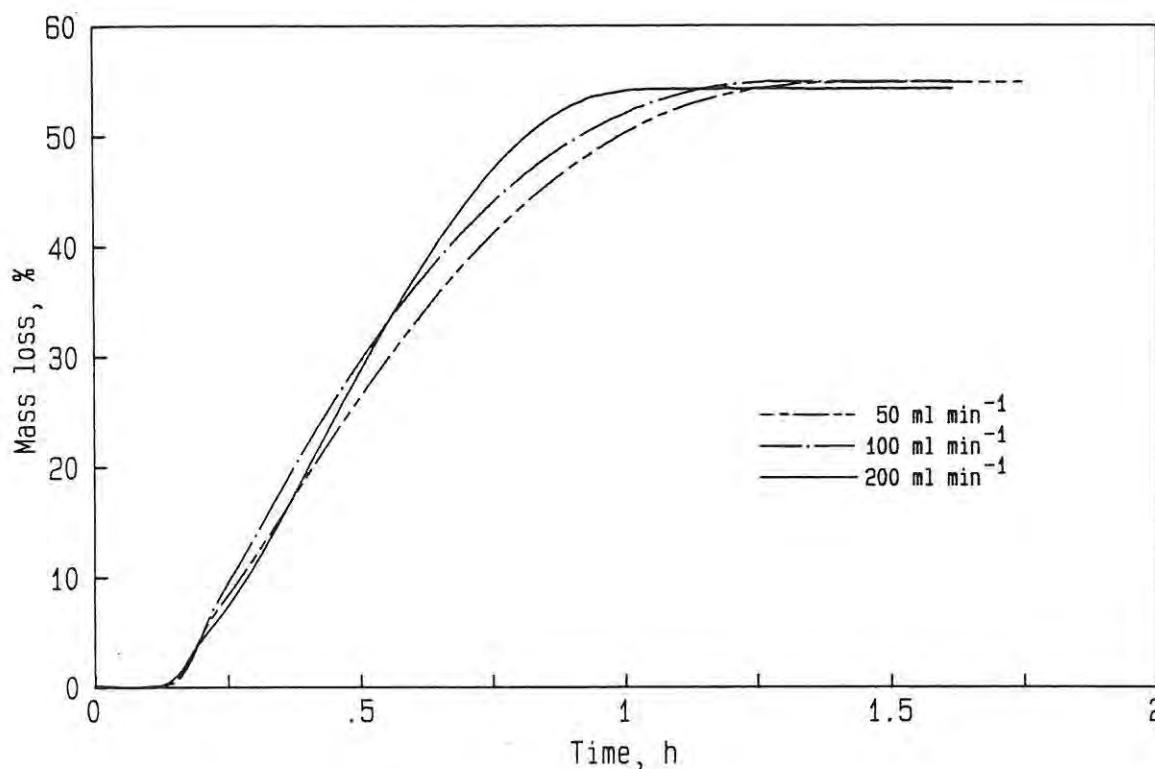


Figure 5.5(d) The effect of gas flowrate on the rate of oxidation of CrCl_3
 Conditions : Isothermal TG
 1 g CrCl_3 pellet
 Oxygen
 500°C



Table 5.2 Effect of gas flowrate on the rate of reaction
 Conditions : Isothermal TG
 1 g CrCl_3 pellet

Atmosphere		Temperature (°C)	Flowrate (cm ³ min ⁻¹)	Reaction time (h)		
				t _{0,25}	t _{0,5}	t _{0,75}
Air	400	100	1,98	3,80	6,13	
		200	1,90	3,55	5,83	
	530	100	0,50	0,78	1,17	
		150	0,47	0,77	1,16	
		200	0,47	0,74	1,07	
	600	100	0,32	0,54	0,80	
		150	0,31	0,49	0,71	
		200	0,31	0,48	0,71	
	Oxygen	500	50	0,33	0,52	0,75
100			0,30	0,47	0,70	
200			0,33	0,48	0,65	

flowrate was therefore chosen. Subsequent experiments were all carried out using a flowrate of $200 \text{ cm}^3 \text{ min}^{-1}$, and it is expected that under these conditions, the effects of film diffusion will be minor, or at least constant, at all temperatures considered.

5.3 Effect of temperature

5.3.1 Reaction in air

The results of isothermal experiments carried out at temperatures from 350 to 630°C in an air atmosphere are shown in Figures 5.6(a) to (c). This temperature range was chosen because the reaction goes to completion in a reasonable time under isothermal conditions. Below 350°C ,

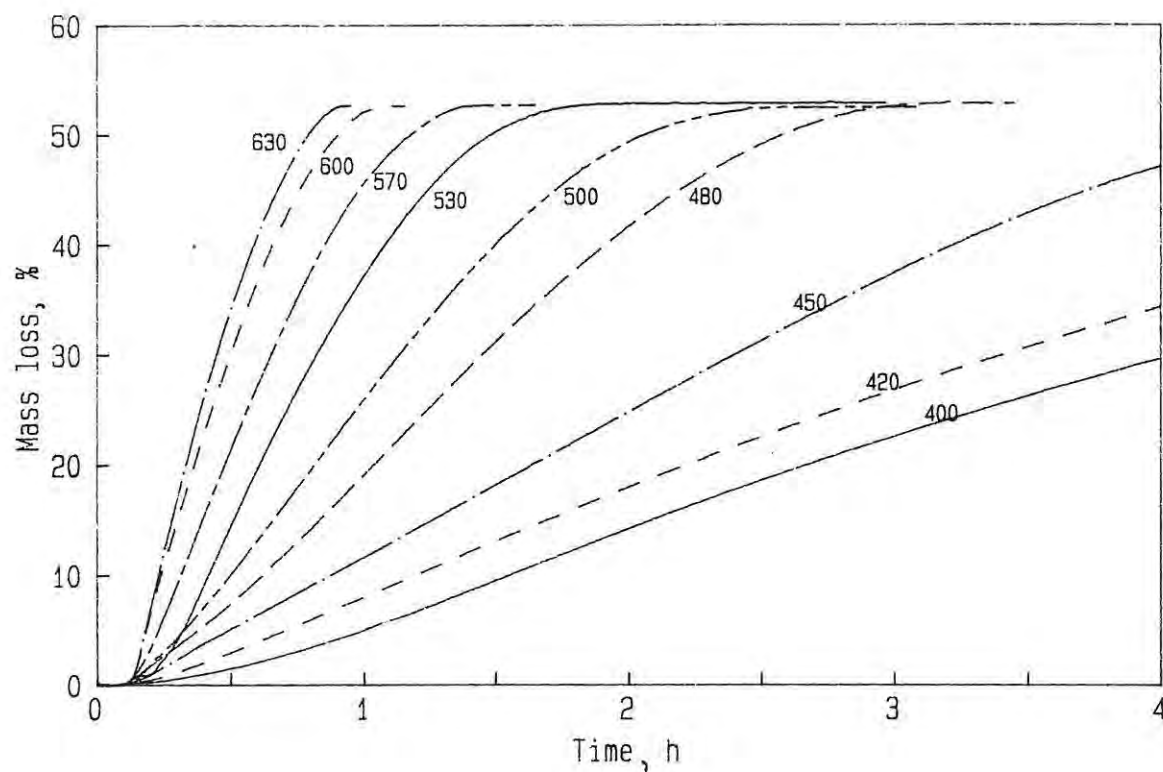


Figure 5.6(a) The effect of reaction temperature on the rate of oxidation of CrCl_3 in air
 Conditions : Isothermal TG
 1 g CrCl_3 pellet
 $200 \text{ cm}^3 \text{ min}^{-1}$ air
 $400 - 600^\circ\text{C}$

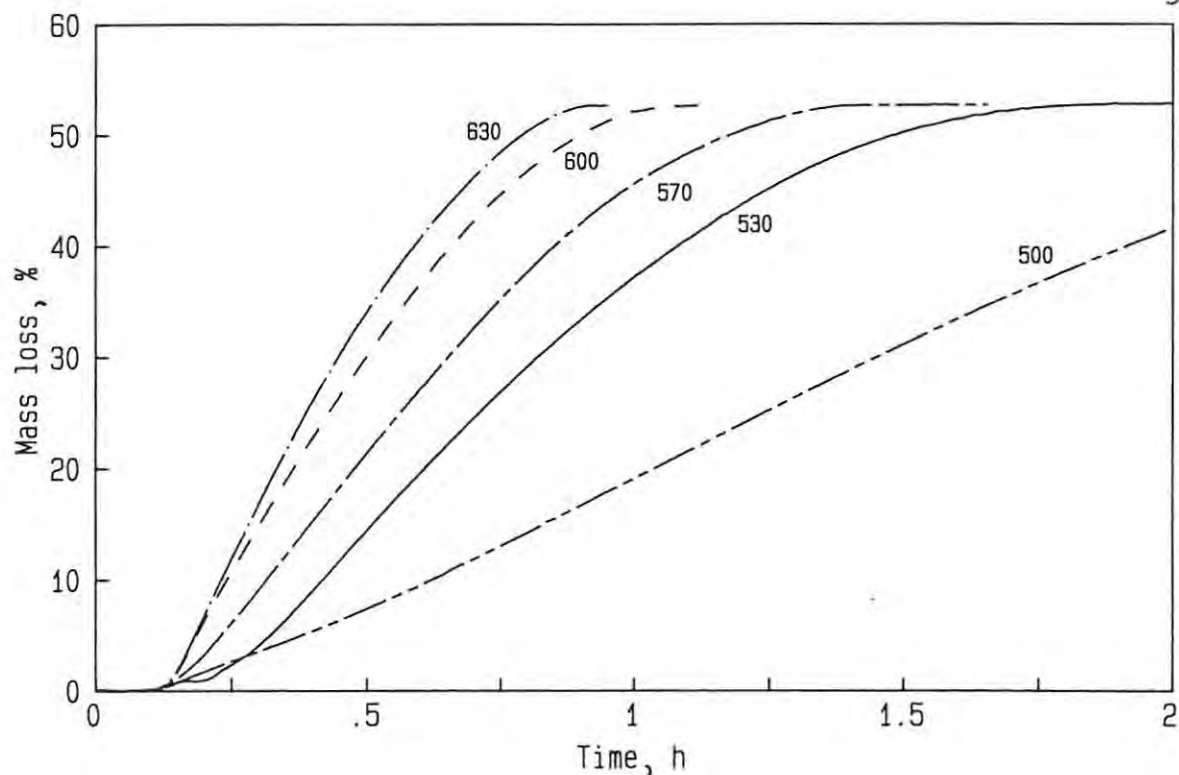


Figure 5.6(b) The effect of reaction temperature on the rate of oxidation of CrCl_3 in air
 Conditions : Isothermal TG
 1 g CrCl_3 pellet
 $200 \text{ cm}^3 \text{ min}^{-1}$ air
 500 - 630 °C

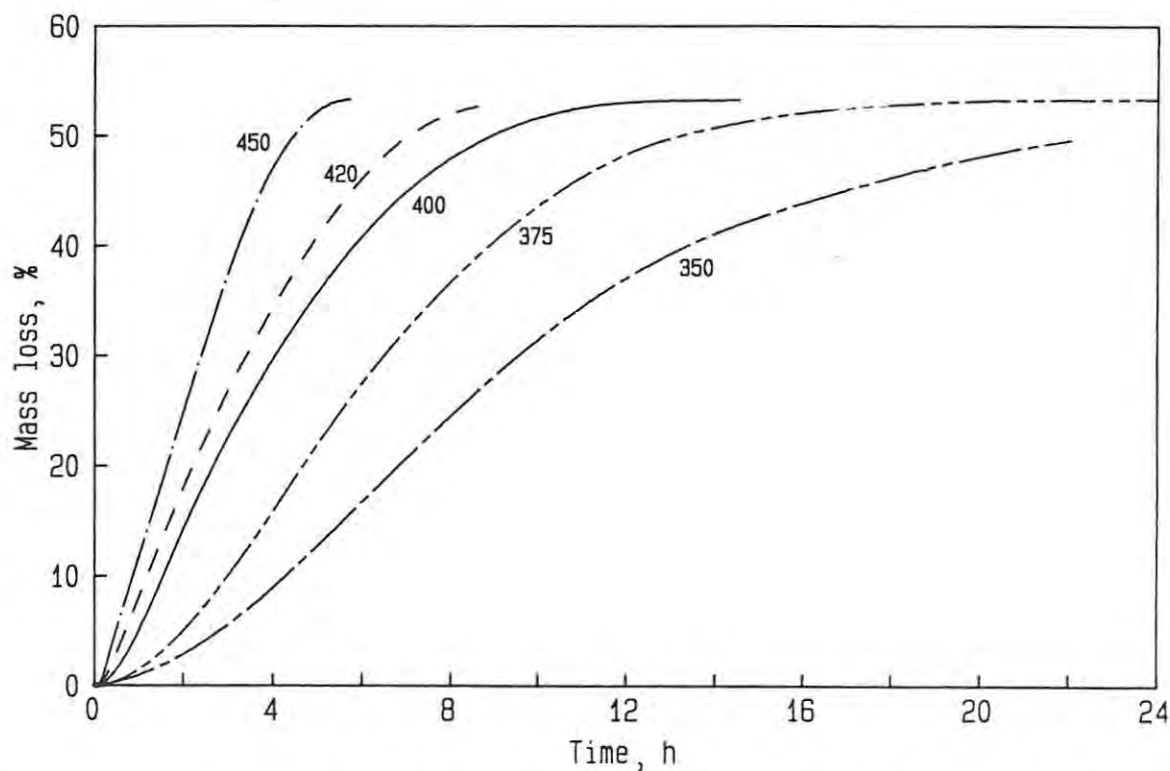


Figure 5.6(c) The effect of reaction temperature on the rate of oxidation of CrCl_3 in air
 Conditions : Isothermal TG
 1 g CrCl_3 pellet
 $200 \text{ cm}^3 \text{ min}^{-1}$ air
 350 - 450 °C

the reaction is extremely slow and takes up to two days to reach completion; above 600°C, the reaction time is of the order of 30 minutes which means that a significant fraction of the reaction takes place under non-isothermal conditions, due to the time required for the furnace and sample to heat up (Section 4.3.2).

At all temperatures studied, the TG curves show the theoretically-predicted mass loss of 52,0%. The shape of the TG curves suggests that, following an initial induction period, the overall reaction rate is deceleratory. The induction period is not a characteristic feature of the reaction, but arises because of the finite time required to heat the furnace from room temperature to a temperature at which oxidation occurs at a measurable rate (Section 4.3.2). However, at temperatures of 400°C and below, the rate is acceleratory at low fractional conversions ($\alpha < \sim 0,2$), followed by an approximately linear region, before the final deceleratory region ($\alpha > 0,5$). The acceleratory region is probably the reaction period during which the first (germ) nuclei of Cr_2O_3 form and grow. Once these nuclei have covered the surface, they start to coalesce and the rate becomes deceleratory, giving rise to an asymmetric sigmoid TG curve. With increasing reaction temperature, the α -range over which the acceleratory and linear regions are observable decreases, and deceleratory rate behaviour dominates the reaction. This will be discussed further in Chapter 8.

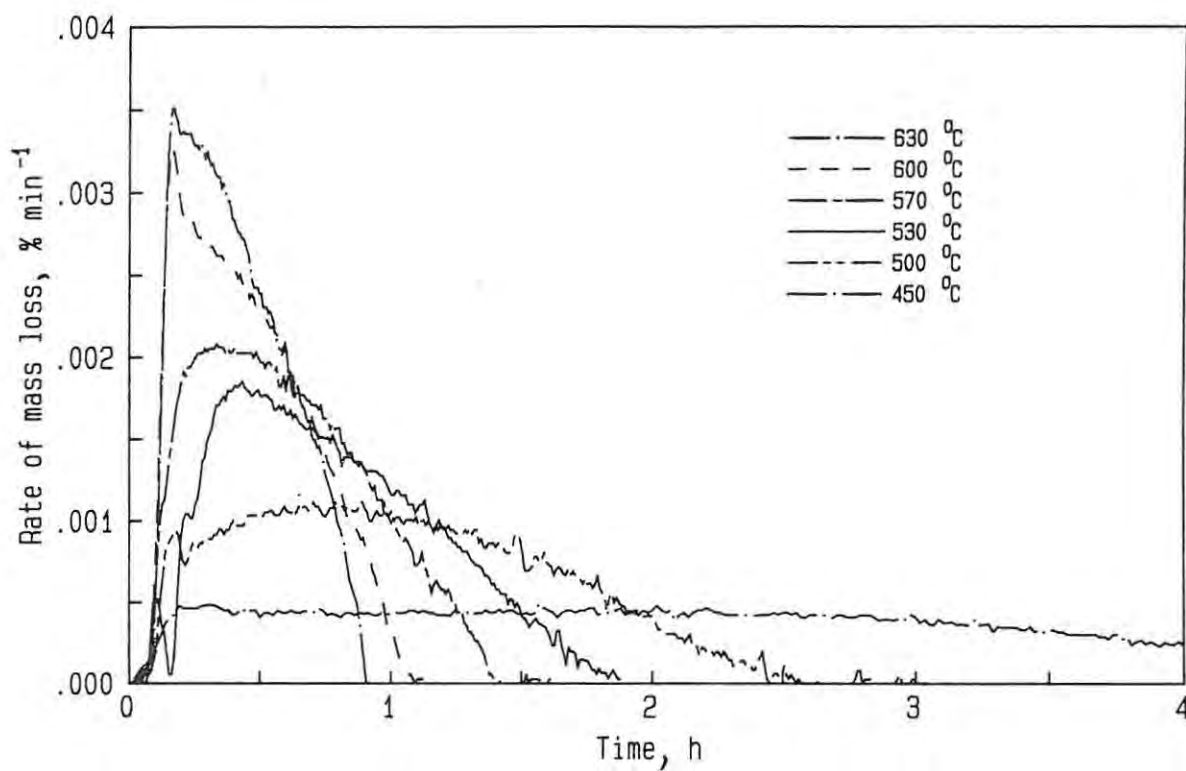


Figure 5.7 The effect of reaction temperature on the first derivative of isothermal TG curves (DTG curves)
 Conditions : Isothermal TG
 1 g CrCl₃ pellet
 200 cm³ min⁻¹ air

Figure 5.7 shows the first derivative of the mass loss with respect to time for some of the TG traces of Figure 5.6(a). These DTG plots give a better indication of the effect of temperature on the reaction rate. At the beginning of each reaction, the rate increases rapidly, reaches a peak, and then decreases until the end of the reaction. The higher the temperature, the greater the maximum rate and the shorter the time to the peak maximum. The higher the temperature, the wider the range of rates over the reaction, while at low temperatures, the peak becomes more indistinct and the rate is almost constant over the entire reaction.

5.3.2 Reaction in oxygen

Analogous isothermal experiments carried out in pure oxygen at various temperatures are shown in Figures 5.8(a) to (c). The shapes of the curves are similar to those measured in air. The overall rates of the reactions in oxygen (as measured by the time to reach 50% conversion) are, however, considerably higher than those in air (molar fraction $O_2 = 0.21$) at the same temperatures. This effect is summarised in Table 5.3. It can be seen that the reaction time is reduced by ~65% when the reaction is carried out in oxygen.

Another significant difference between the curves measured in air and those in oxygen is that in oxygen the observed mass loss increases with decreasing temperature (longer reaction time), as shown in Table 5.4.

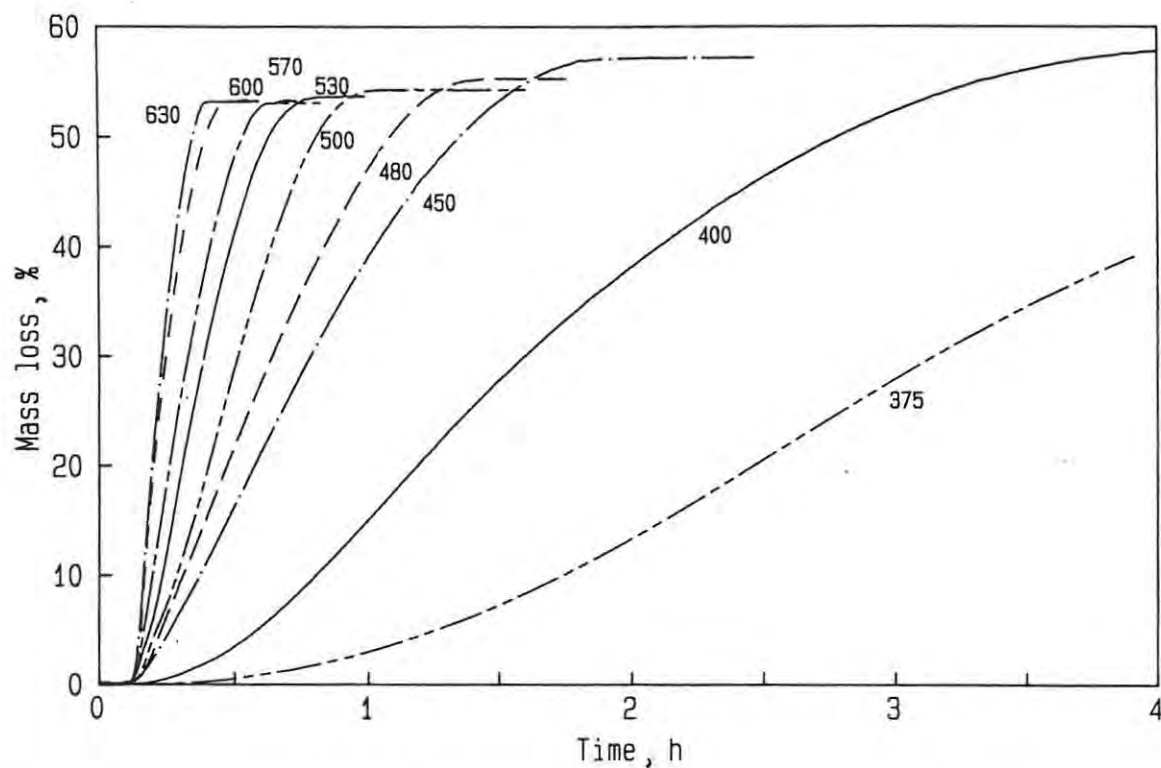


Figure 5.8(a) The effect of reaction temperature on the rate of oxidation of CrCl_3 in oxygen
 Conditions : Isothermal TG
 1 g CrCl_3 pellet
 $200 \text{ cm}^3 \text{ min}^{-1}$ oxygen
 $375 - 630^\circ\text{C}$

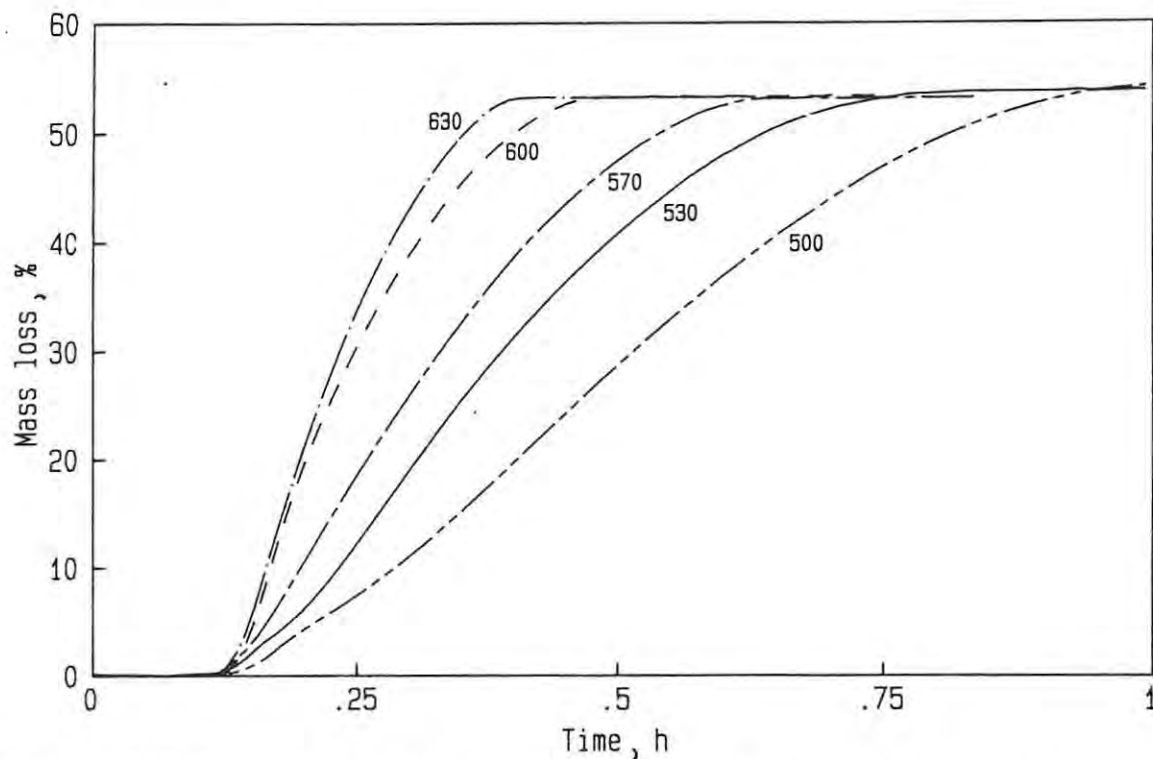


Figure 5.8(b) The effect of reaction temperature on the rate of oxidation of CrCl_3 in oxygen
 Conditions : Isothermal TG
 1 g CrCl_3 pellet
 $200 \text{ cm}^3 \text{ min}^{-1}$ oxygen
 $500 - 630^\circ\text{C}$

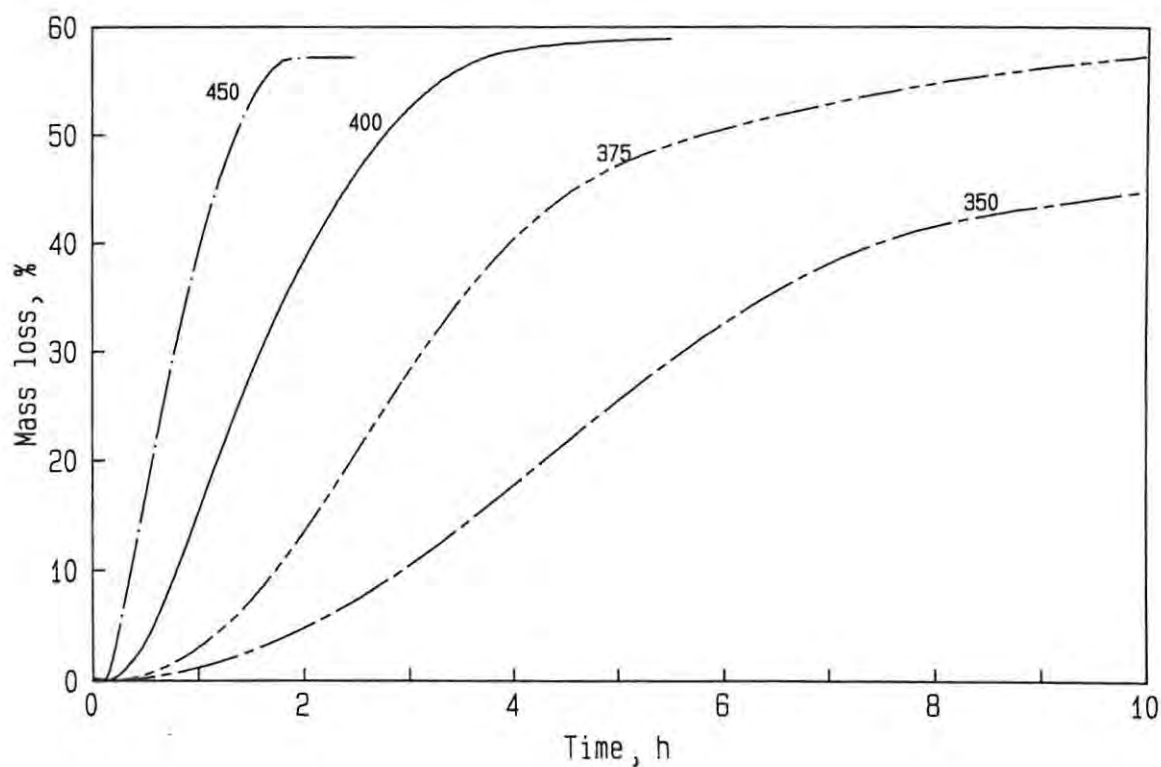


Figure 5.8(c) The effect of reaction temperature on the rate of oxidation of CrCl_3 in oxygen
 Conditions : Isothermal TG
 1 g CrCl_3 pellet
 $200 \text{ cm}^3 \text{ min}^{-1}$ oxygen
 $350 - 450^\circ\text{C}$

Table 5.3 Effect of temperature on the rate of reaction in air and in oxygen

Conditions : Isothermal TG
1 g CrCl_3 pellet
200 $\text{cm}^3 \text{min}^{-1}$ gas flowrate

Temperature ($^{\circ}\text{C}$)	$t_{0,5}$ (h)	
	Air	Oxygen
350	8,11	5,61
375	5,68	3,16
400	3,57	1,55
450	2,14	0,76
480	1,30	0,60
500	1,01	0,48
530	0,74	0,36
570	0,59	0,31
600	0,44	0,23
630	0,41	0,22

Initially it was thought that higher oxides of chromium, such as CrO_2 or CrO_3 , were forming; however, calculations of the mass losses expected for such reactions show that these should be less, not greater, than for the formation of Cr_2O_3 .

XRD analysis of the products of these reactions showed that Cr_2O_3 was the only species present.

To clarify this behaviour, a pellet reacted to completion at 400°C was heated to 570°C and held at the higher temperature for 3 hours; no mass change occurred. A pellet reacted at 570°C was then held at that temperature for three hours after the reaction was complete; no further mass change occurred. In a final experiment, a pellet reacted to completion at 570°C was held at 400°C for 3 hours; no mass change occurred. It was therefore concluded that once Cr_2O_3 forms, no further conversion of the product occurs. The

Table 5.4 Effect of temperature on the mass loss
for oxidation in pure oxygen

Conditions : Isothermal TG
1 g CrCl_3 pellet
200 $\text{cm}^3 \text{min}^{-1}$ oxygen

Temperature ($^{\circ}\text{C}$)	Mass loss (%)	Temperature ($^{\circ}\text{C}$)	Mass loss (%)
350	59,9	500	54,4
375	62,0	530	53,7
400	59,8	570	52,9
450	57,3	600	53,5
480	55,0	630	53,4

additional mass loss must therefore arise from a parallel secondary reaction involving the CrCl_3 reactant. The lower the reaction temperature, the more significant the rate of this competing reaction becomes in comparison with the rate of the main reaction. It is therefore suggested that the additional mass loss occurring is due to the loss of chromium from the sample by a vapour-phase process.

A similar effect has been reported by Pechkovskii *et al*⁸. They attributed the higher-than-expected mass loss to the formation of chromyl chloride, CrO_2Cl_2 . Thermodynamic predictions (Section 3.2) also suggest that chromyl chloride would be the most likely by-product to form in this reaction system.

The observation of brownish-red drops of liquid CrO_2Cl_2 which condensed on the plastic tubing of the furnace outlet confirmed the validity of these predictions. In pure oxygen atmospheres and under slow reaction conditions, chromyl chloride formation will thus compete with chromic oxide

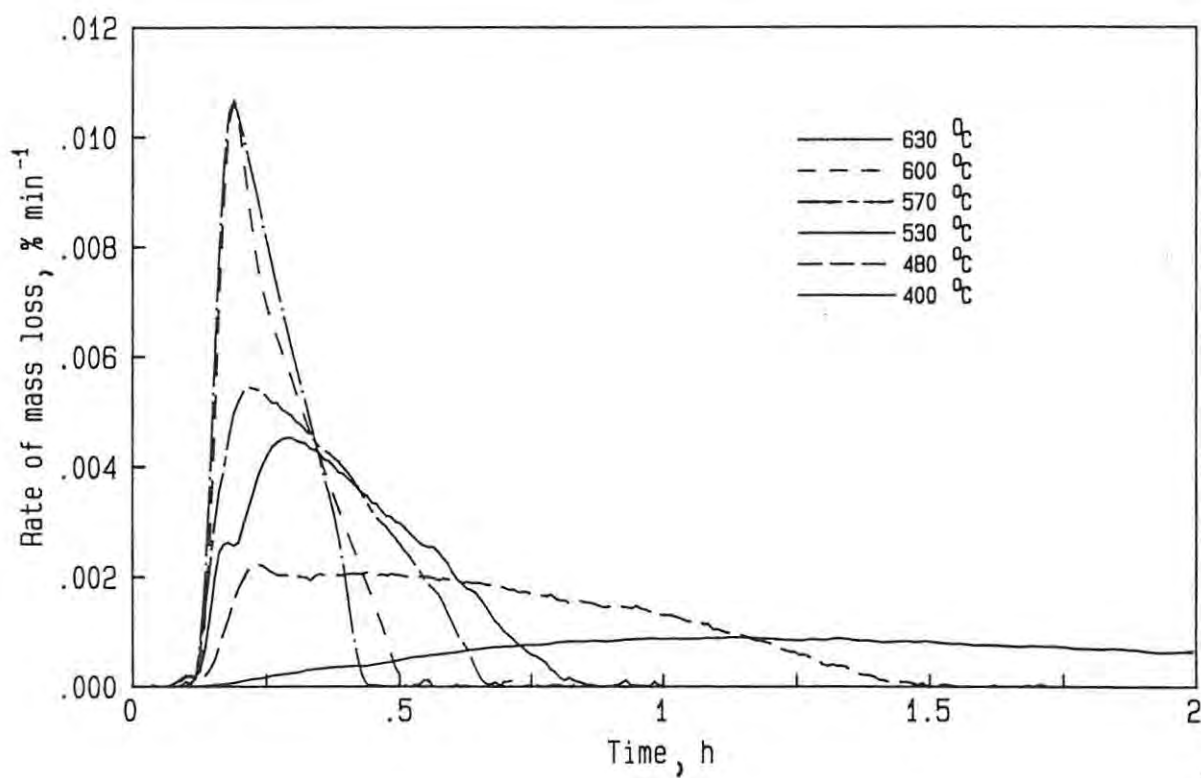
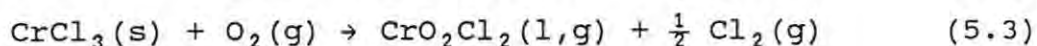
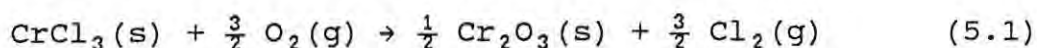


Figure 5.9 The effect of reaction temperature on the first derivative of isothermal TG curves
 Conditions : Isothermal TG
 1 g CrCl₃ pellet
 200 cm³ min⁻¹ oxygen

formation. The two reactions are



The DTG curves for isothermal TG experiments in oxygen are shown in Figure 5.9. Similar effects to those for reactions carried out in air (Figure 5.7) are observed; however, it can be seen that the peak maxima occur at rates approximately three times higher than those in air. This is in agreement with the results of Table 5.3.

5.4 Effect of pellet porosity

Pellets of varying porosities were produced by compressing the CrCl_3 under different pressures and for different lengths of time. The effect of pellet porosity on the rate of reaction is shown in Figure 5.10 and Table 5.5.

The pelletising conditions used represent a change in CrCl_3 porosity from 11,9% (compressed at 5 tons for 3 minutes) to 5,4% (compressed at 10 tons for 10 minutes). The difference in rate within these limits is not significant in comparison with the reproducibility of the experimental results (Figure 5.4). The pellet porosity thus has little effect on the reaction rate.

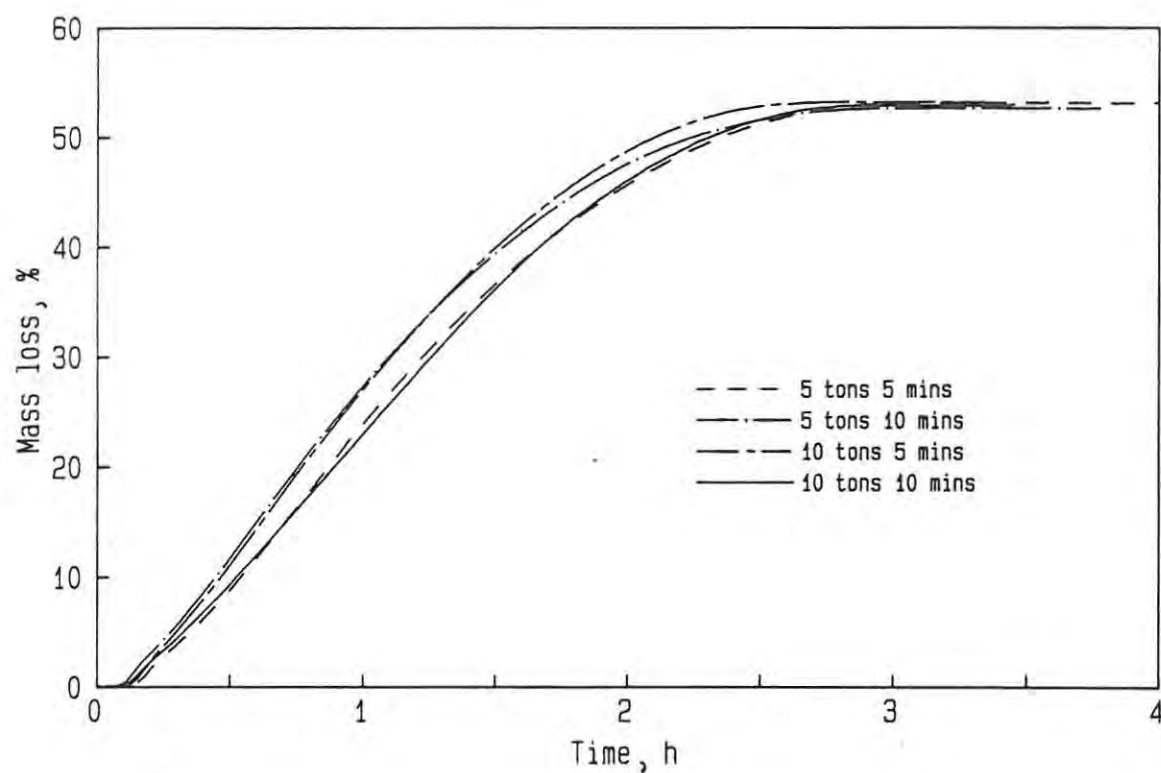


Figure 5.10 The effect of pellet porosity on the rate of oxidation of CrCl_3
 Conditions : Isothermal TG
 1 g CrCl_3 pellet
 $200 \text{ cm}^3 \text{ min}^{-1}$ air
 500°C

Table 5.5 Effect of pellet porosity on the rate of reaction

Conditions : Isothermal TG
 1 g CrCl_3 pellet
 $200 \text{ cm}^3 \text{ min}^{-1}$ air
 500°C

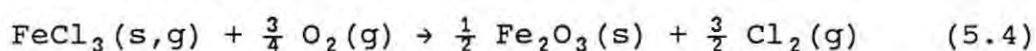
Pelletising Load (tons)	Conditions Time (min)	Porosity (%)	$t_{0,5}$ (h)
5	3	11,9	1,01
5	5	-	1,10
5	10	6,11	0,97
10	5	-	0,99
10	10	5,35	1,13

Two explanations for this are possible. If the reaction occurs uniformly throughout the pellet, then the independence of the rate on CrCl_3 porosity suggests that the reaction rate is limited by the rate of the chemical reaction. If, however, the reaction occurs at a well-defined reactant-product interface, then no diffusion of the reactant gas through the unreacted core of the CrCl_3 pellet will occur; the rate of reaction will therefore be expected to be limited either by the rate of gas diffusion through the Cr_2O_3 product layer, or by the rate of the chemical reaction at the interface. In the present system CrCl_3 is converted by a solid-gas reaction to Cr_2O_3 , so the structure of the product is pseudomorphic with that of the reactant. This means that increasing the porosity of the CrCl_3 starting material would be expected to result in increased porosity of the product layer, leading to less inhibited gas

mobility in this layer. Since the reaction rate is unaffected by these changes, this suggests that the reaction is under chemical control.

5.5 Effect of adding Cr_2O_3 to CrCl_3 pellets

In the analogous $\text{FeCl}_3/\text{Fe}_2\text{O}_3$ reaction



the reaction mechanism is known to be autocatalytic, i.e. the addition of Fe_2O_3 enhances the rate of oxidation of FeCl_3 ²⁸⁻³¹. Bulatova and Vil'nyanskii¹⁰ have also reported evidence of autocatalytic behaviour in their study of the oxidation of CrCl_3 powder. Experiments were therefore undertaken to determine whether a similar effect would be observed in the present $\text{CrCl}_3/\text{Cr}_2\text{O}_3$ system.

Intimate mixtures of CrCl_3 and commercial Cr_2O_3 were pelletised in the usual manner. The isothermal oxidation of these pellets is shown in Figure 5.11. The reaction rate increases markedly as the Cr_2O_3 content of the starting material is increased.

Two explanations of this effect are possible. The first is that the reaction *does* show autocatalytic behaviour, as found in the $\text{FeCl}_3/\text{Fe}_2\text{O}_3$ system. The presence of Cr_2O_3 provides nucleation sites for the formation of further Cr_2O_3 , and so the added Cr_2O_3 catalyses the reaction. The

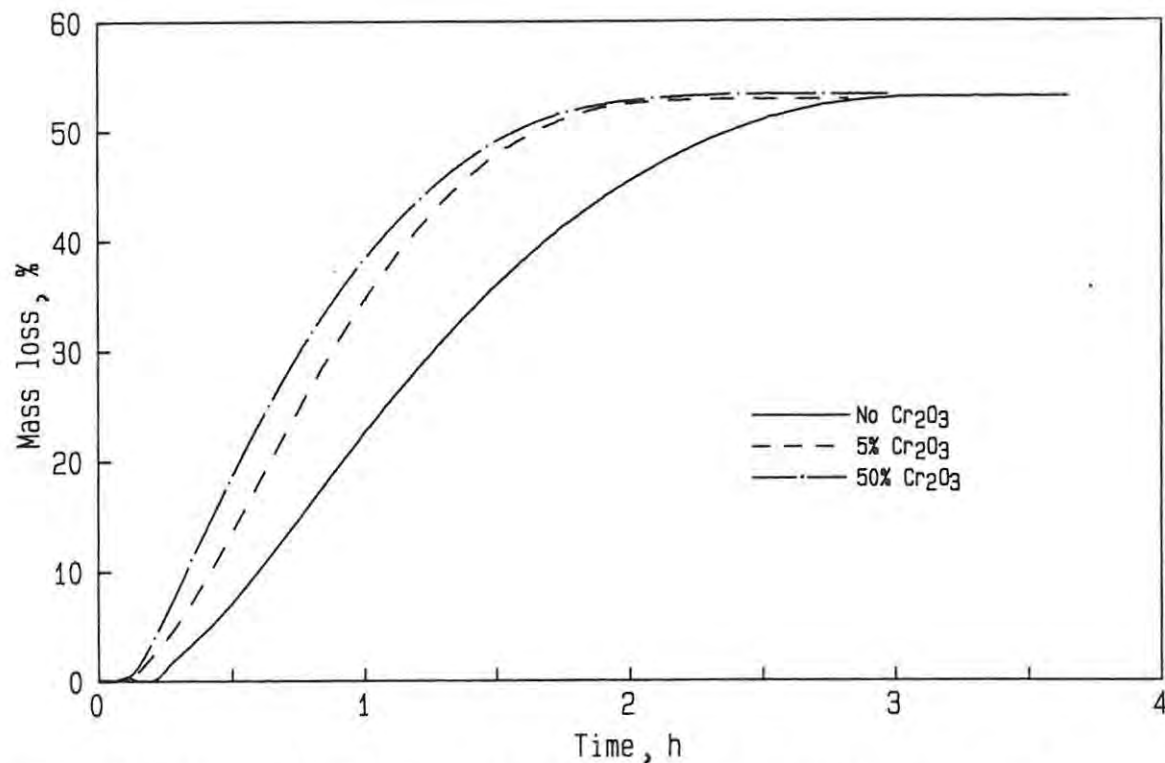


Figure 5.11 The effect of adding Cr_2O_3 on the rate of oxidation of CrCl_3
 Conditions : Isothermal TG
 1 g CrCl_3 pellet
 $200 \text{ cm}^3 \text{ min}^{-1}$ air
 500°C

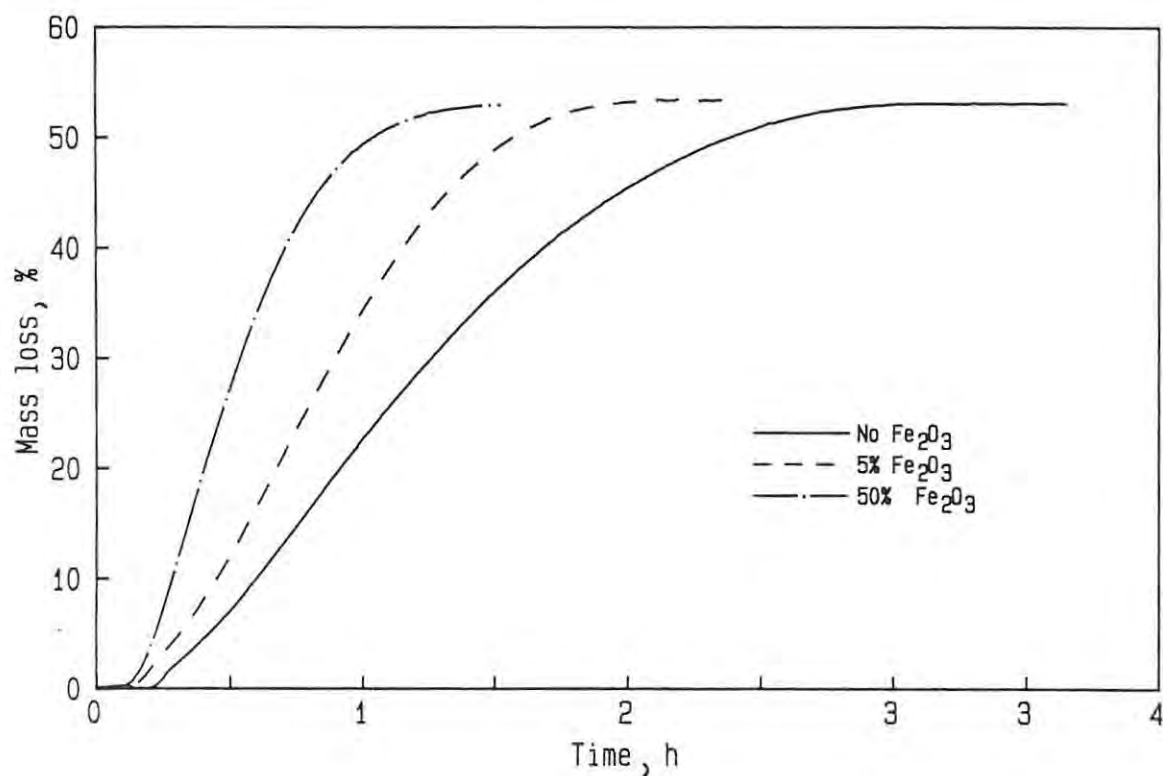


Figure 5.12 The effect of adding Fe_2O_3 on the rate of oxidation of CrCl_3
 Conditions : Isothermal TG
 1 g CrCl_3 pellet
 $200 \text{ cm}^3 \text{ min}^{-1}$ air
 500°C

second explanation of this effect is that it is merely a porosity effect. Cr_2O_3 is assumed to act as an inert diluent, thereby decreasing the effective density of the CrCl_3 in the pellet, and increasing its effective porosity. The reactant and product gases then penetrate and diffuse through the pellet more readily and so the reaction rate increases. This explanation would be consistent with a suggestion that the rate of gas diffusion through the product layer of the pellet is the rate-limiting step of the reaction.

To establish which, if either, of these postulations holds, similar experiments were carried out using other additives.

5.6 Effect of other additives

Analogous experiments to those shown in Figure 5.10 were carried out using Fe_2O_3 , Al_2O_3 and SiO_2 additives. The effects of these additives on the oxidation of CrCl_3 pellets are shown in Figures 5.12 to 5.14 and summarised in Table 5.6.

The addition of Fe_2O_3 (50% by mass) enhances the rate of oxidation to a greater extent than the corresponding addition of Cr_2O_3 (Figure 5.11). Silica and alumina additions at levels of 50% by mass increase the rate of reaction to a slightly lesser extent than the addition of Cr_2O_3 ; except in the case of Fe_2O_3 , 5% additions do not affect the reaction rate significantly.

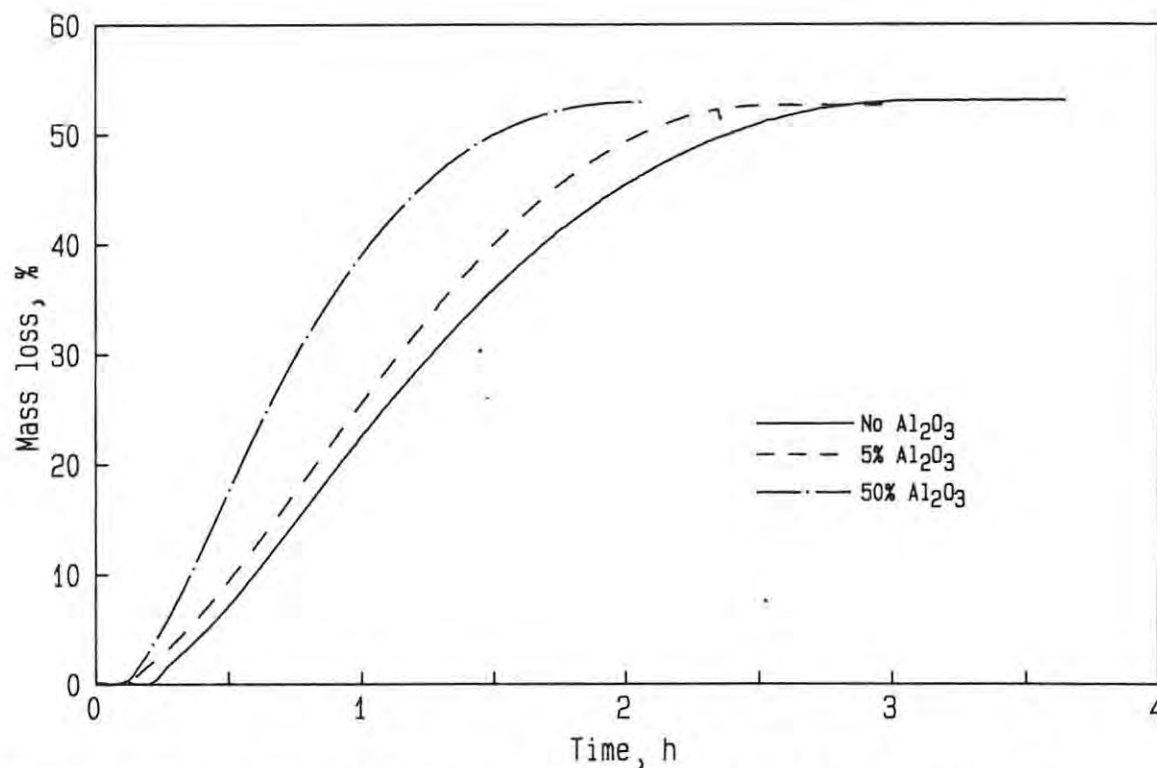


Figure 5.13 The effect of adding Al_2O_3 on the rate of oxidation of CrCl_3
 Conditions : Isothermal TG
 1 g CrCl_3 pellet
 200 $\text{cm}^3 \text{min}^{-1}$ air
 500°C

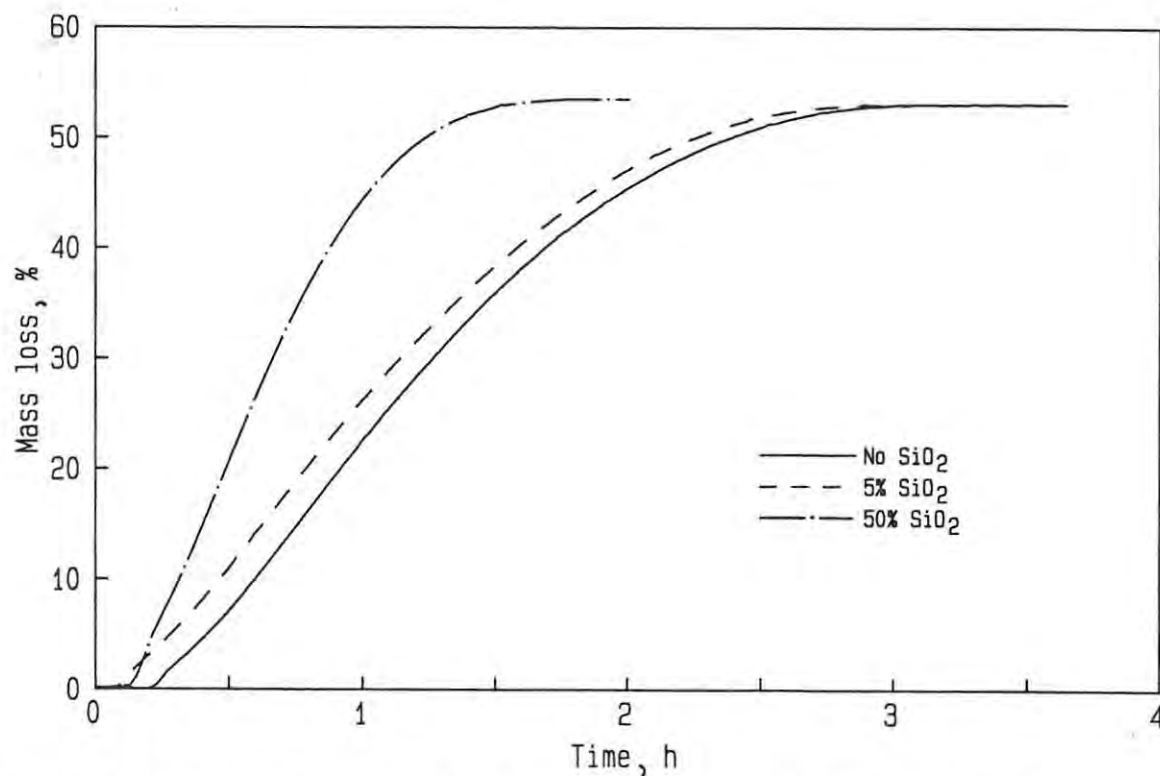


Figure 5.14 The effect of adding SiO_2 on the rate of oxidation of CrCl_3
 Conditions : Isothermal TG
 1 g CrCl_3 pellet
 200 $\text{cm}^3 \text{min}^{-1}$ air
 500°C

Table 5.6 Effect of additive concentration and density on the pellet porosity and the rate of reaction

Conditions : Isothermal TG
 1 g CrCl_3 pellet
 $200 \text{ cm}^3 \text{ min}^{-1}$ air
 500°C

Additive	Absolute density (g cm^{-3})	$t_{0,5}$ (h)		Pellet Porosity	
		5%*	50%	5%	50%
Cr_2O_3	5,22	0,79	0,68	10,0	23,4
Fe_2O_3	5,27	0,82	0,49	10,2	22,4
Al_2O_3	3,92	1,03	0,68	10,2	19,0
SiO_2	2,67	1,01	0,61	10,7	18,8

* additive concentrations

The analogous isothermal TG curve for a CrCl_3 pellet with no additive (porosity = 11,9%) has $t_{0,5} = 1,01\text{h}$.

Table 5.6 also indicates that for additive additions of 5%, the observed pellet porosity decreases as the absolute density of the additive increases. Since the additions were made on a mass percent basis, the densities of the additives at low concentrations are inversely proportional to the volumes they occupy in the pellet. Therefore under identical conditions of pellet preparation, and assuming that all additives have similar pore volumes, the lower the additive density, the greater the porosity within the pellet. At the higher additive concentrations, however, the size of the pellet itself increases due to the substantial mass increase of the sample, and the pellet porosity increases with increasing additive density. If the rate of reaction is limited by the rate of diffusion of reactant or product gases through the sample, it would be expected that greater enhancement of the rate of reaction would be achieved for pellets having greater porosity. The magnitudes of the rate changes which could be expected on the

basis of changes in porosity have been discussed with reference to Figure 5.9; however, the rate changes observed on the addition of the above additives are much larger and are therefore not compatible with varying porosity being mainly responsible for changes in reaction rate.

It is therefore concluded that although the effect of additives on the reaction rate may involve some contribution from the porosity factor, it is likely that the effects are mainly chemical. The transition metal oxides are well known to be catalysts and the metal oxides studied are thought to exert a catalytic effect on the reaction by facilitating the growth of the Cr_2O_3 product layer.

5.7 Effect of oxygen partial pressure

The different rates of reaction observed in air and oxygen atmospheres have already been discussed in Section 5.3. Figure 5.15 and Table 5.7 show the effect of the oxygen partial pressure on the reaction rate at constant temperature.

At constant total gas flowrate (constant film-diffusion mass-transfer effects) a marked increase in the reaction rate occurs on increasing the oxygen partial pressure. If the reaction rate is directly proportional to the oxygen molar fraction, this would be a strong indication that the

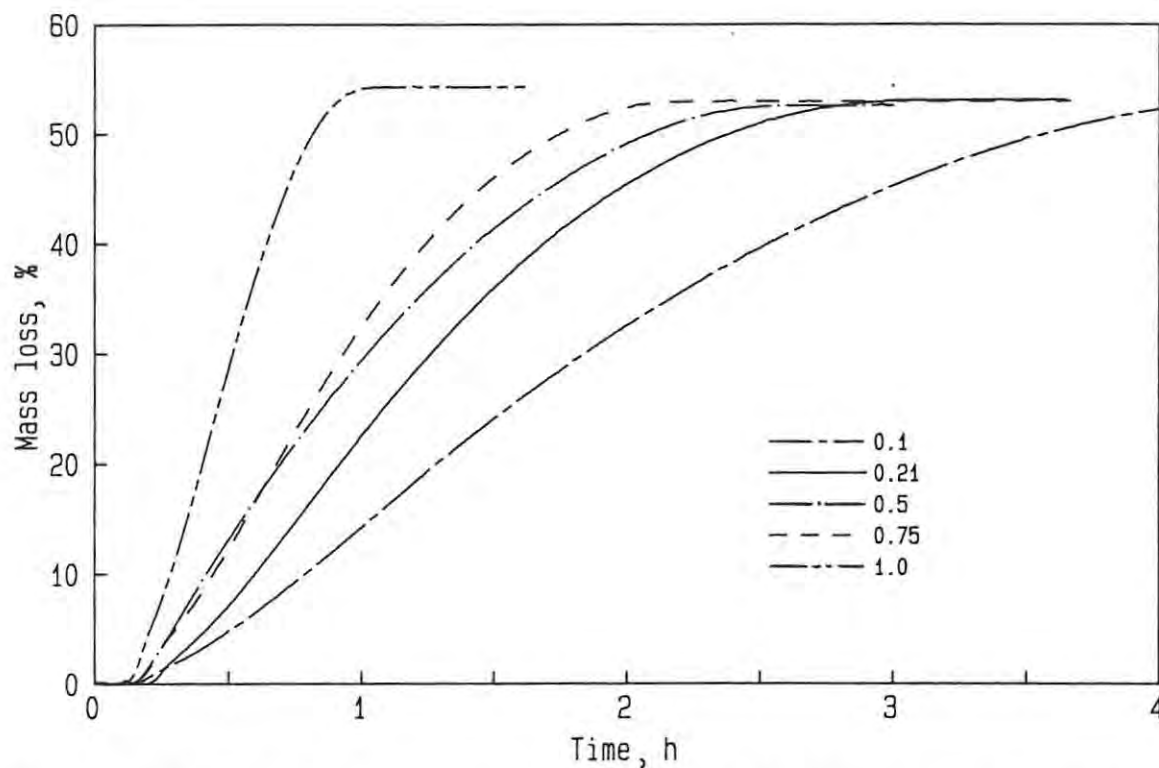


Figure 5.15 The effect of molar fraction of oxygen on the rate of oxidation of CrCl_3
 Conditions : Isothermal TG
 1 g CrCl_3 pellet
 $200 \text{ cm}^3 \text{ min}^{-1}$ gas flowrate
 500°C

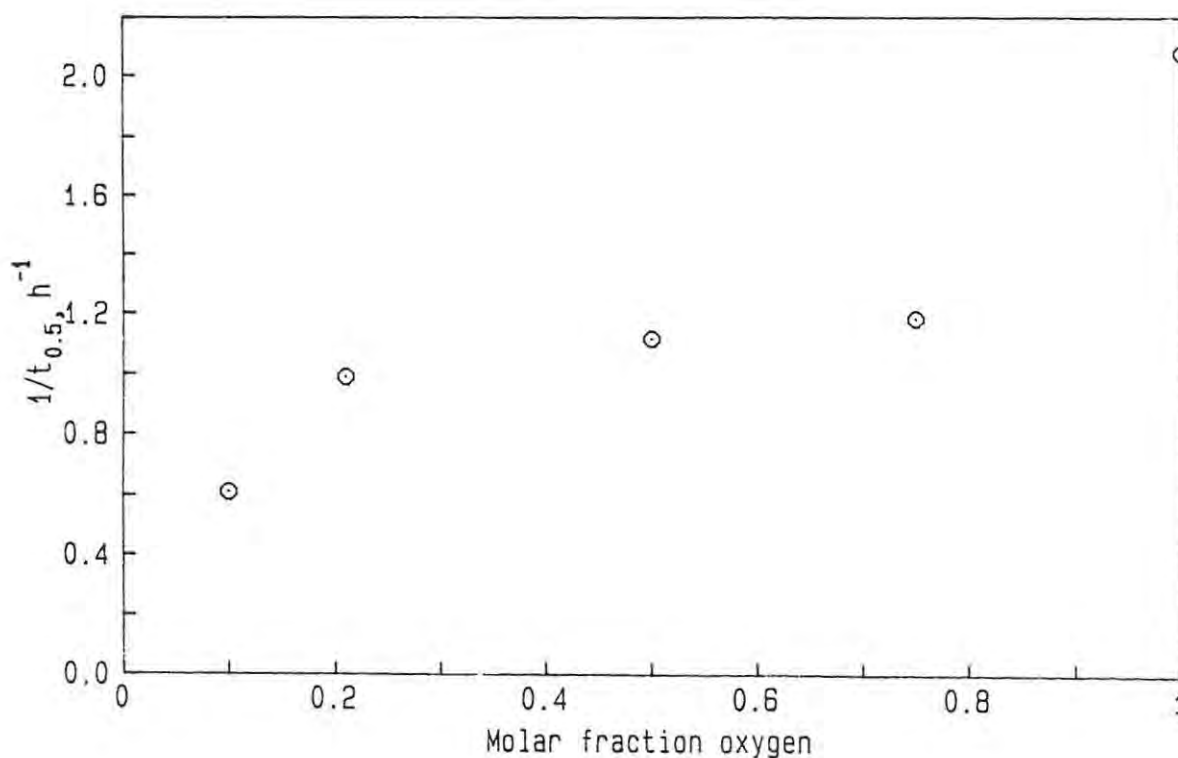


Figure 5.16 The dependence of the rate of reaction on the molar fraction of oxygen

Table 5.7 Effect of oxygen molar fraction on the rate of reaction

Conditions : Isothermal TG
 1 g CrCl_3 pellet
 200 $\text{cm}^3 \text{ min}^{-1}$ gas flowrate
 500°C

O_2 molar fraction	O_2 partial pressure* (kPa)	$t_{0,5}$ (h)
0,1	8,4	1,64
0,21	17,6	1,01
0,5	42,0	0,89
0,75	63,0	0,84
1,0	84,0	0,48

* corrected to atmospheric pressure on the Witwatersrand (~84 kPa)

reaction is under diffusion control. Diffusion of the reactant gas through a porous product layer is governed by Fick's first law of diffusion, which relates the rate of diffusion to the concentration gradient across which the diffusion occurs. The higher the molar fraction of oxygen, the higher will be the oxygen concentration at the surface of the pellet, and the greater the concentration gradient from the pellet surface to the unreacted CrCl_3 core.

The dependence of the rate of reaction on oxygen partial pressure could also be evidence for chemical control, as a higher oxygen partial pressure at the reaction site itself would result in a faster reaction rate. The experimentally-observed dependence of the rate of reaction on the molar fraction of oxygen is depicted quantitatively in Figure 5.16, where the reciprocal of the time at which $\alpha = 0,5$ has been taken as a measure of the reaction rate. It is evident that the dependency shown is not a linear relationship, and

that the increase in rate with increasing oxygen concentration is not very systematic. This may be as a result of poor gas mixing occurring at oxygen fractions of 0,21, 0,5 and 0,75, compared with fully-mixed gases at fractions 0,1 and 1,0. Although diffusion control of the reaction may occur at high oxygen partial pressures, the non-linearity of the relationship tends to negate the possibility of reactant-gas diffusion being the rate-limiting step of the reaction.

Of further significance in Figure 5.15 is that the reaction carried out in pure oxygen is accompanied by a mass loss of 54,4%, whereas all other experiments at lower partial pressures show mass losses very close to the theoretically-predicted value of 52,0%. This phenomenon has been described in Section 5.3.2 and explained in terms of the formation of chromyl chloride in the presence of excess oxygen.

5.8 Programmed-temperature TG experiments

5.8.1 Reaction in air

The effect of heating rate on the non-isothermal thermogravimetric behaviour of CrCl_3 in a dynamic air atmosphere is shown in Figure 5.17 and summarised in Table 5.8.

Table 5.8. Effect of heating rate on the oxidation of CrCl_3

Conditions : Programmed-temperature TG
 1 g CrCl_3 pellet
 200 $\text{cm}^3 \text{min}^{-1}$ air

Heating rate* ($^{\circ}\text{C min}^{-1}$)	Onset temp ($^{\circ}\text{C}$)	Completion temp ($^{\circ}\text{C}$)	Temp difference ($^{\circ}\text{C}$)	Mass loss (%)
2	377	618	241	53,0
10	413	813	400	52,8
20	443	850	407	34,9

* programmed heating rate - see Section 4.3.1

As expected, the lower the heating rate, the lower the temperatures at which the reaction starts and ends, and the smaller the temperature range over which the oxidation occurs. Lowering the heating rate results in the reaction system approaching closer to equilibrium conditions, and minimises the effects of heat transfer and thermal lag. This phenomenon is commonly observed in thermogravimetric experiments; it is therefore generally preferred to carry out non-isothermal experiments at as low a heating rate as possible, other factors being equal.

The most noteworthy feature of these programmed-temperature TG curves is, however, the mass loss observed at a heating rate of $20^{\circ}\text{C min}^{-1}$. A mass loss of only ~35% occurs, but from the external appearance of the pellet, the reaction appears to have gone to completion. Examination of a cross-section of a pellet, however, revealed three distinct zones - an outer layer of green Cr_2O_3 , an inner core of unreacted violet CrCl_3 , and, between these two zones, a shiny metallic-looking species. This species did not dissolve in

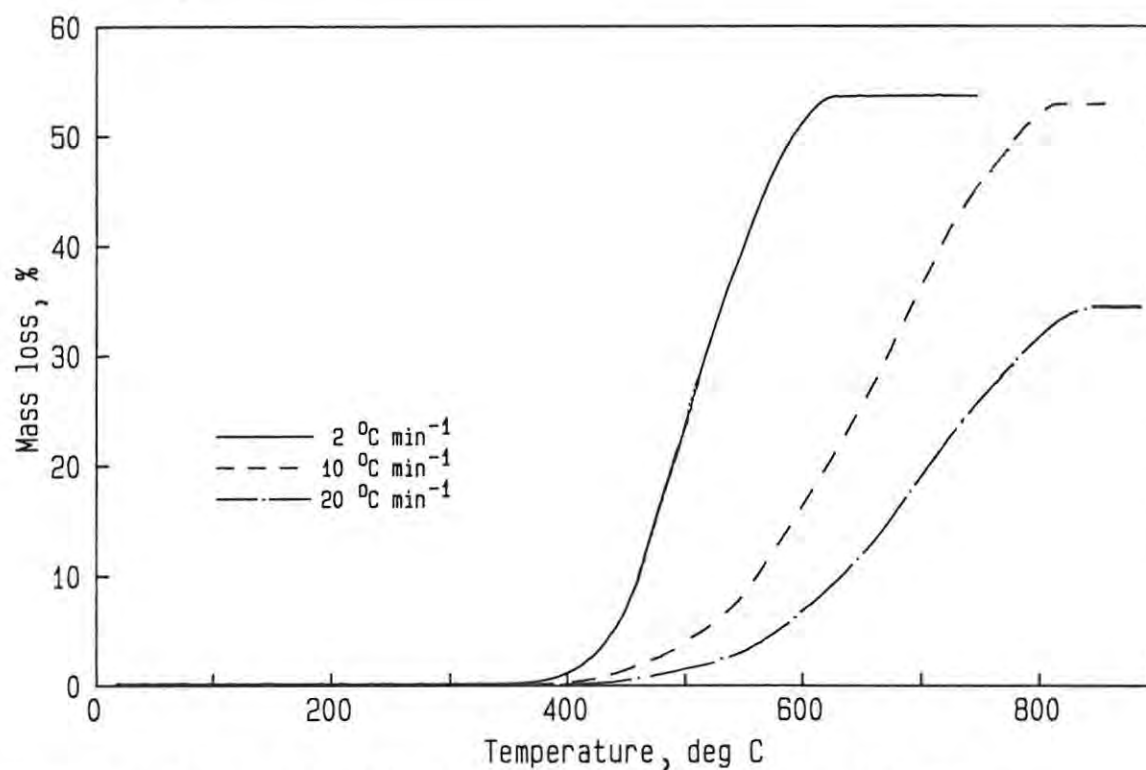


Figure 5.17 The effect of heating rate on the non-isothermal oxidation of CrCl_3 in air
 Conditions : Programmed-temperature TG
 1 g CrCl_3 pellet
 $200 \text{ cm}^3 \text{ min}^{-1}$ air

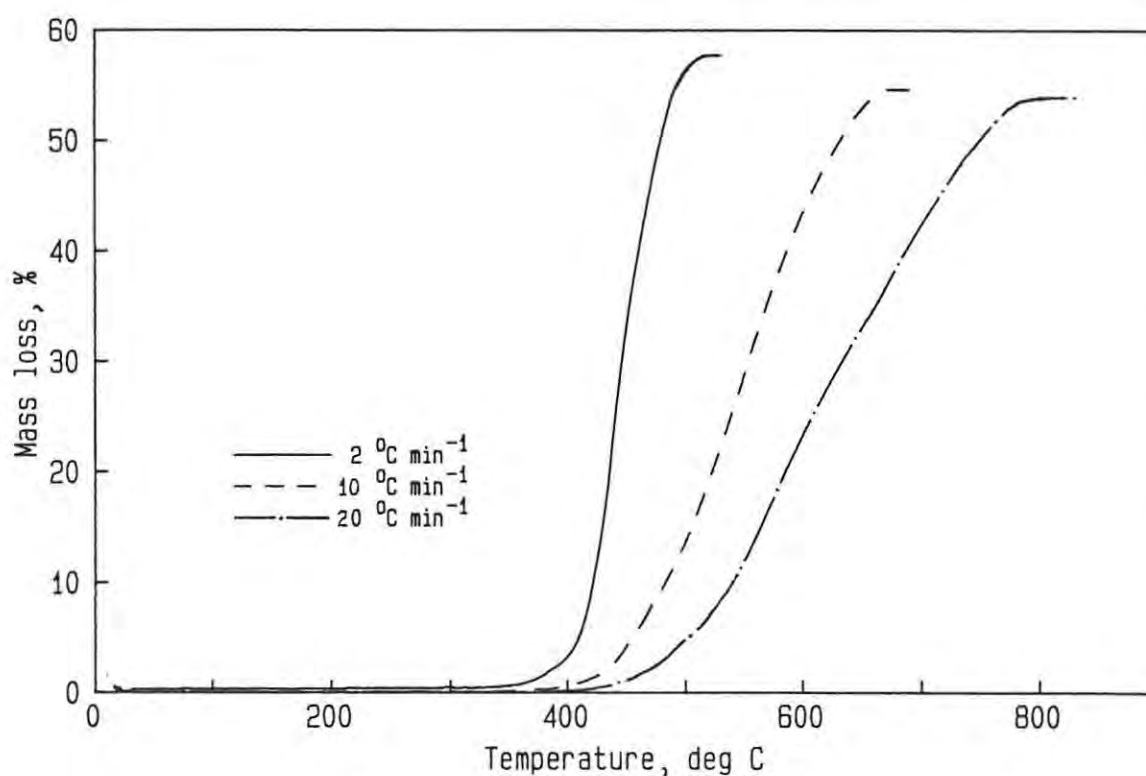


Figure 5.18 The effect of heating rate on the non-isothermal oxidation of CrCl_3 in oxygen
 Conditions : Programmed-temperature TG
 1 g CrCl_3 pellet
 $200 \text{ cm}^3 \text{ min}^{-1}$ oxygen

water or acetone, and it appeared that once this layer had formed, it did not oxidise further to Cr_2O_3 ; rather it inhibited the reaction, by preventing oxygen passing through to react with the CrCl_3 core. This species was identified by X-ray diffraction³² as CrOCl . The X-ray data is shown in Table 5.9.

Table 5.9 X-ray diffraction analysis of CrOCl

d_{th}^* (nm)	d_{obs} (nm)	$(I/I_0)_{th}$	$(I/I_0)_{obs}$	Plane (hkl)
0,769	0,781	100	856	001
0,345	0,345	100	100	101
0,246	0,245	100	100	110,012
0,234	0,233	80	28	111
0,213	0,213	40	11	103
0,207	0,206	40	11	112
0,200	0,200	60	35	013
0,193	0,193	80	56	200
0,187	0,187	60	9	201
0,178	0,177	60	40	113
0,172	0,172	40	13	104
0,159	0,158	80	7	020
0,156	0,154	60	19	021
0,152	0,151	80	44	212
0,145	0,144	80	22	121
0,139	0,139	60	11	213
0,127	0,128	40	13	301
0,123	0,124	60	19	220,024
0,122	0,122	40	11	302

* d_{th} - theoretical d-spacing³²

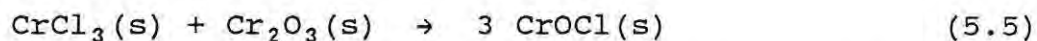
d_{obs} - observed d-spacing

I/I_0 - relative intensity of peak_i to major peak

The d-spacings measured for the species produced in the present study agree very closely with the literature values; however, there are large discrepancies between the relative intensities of the peaks. The major peak is ~8,5 times the intensity of the second-largest peaks. This major peak is assigned to diffraction occurring from the 001 plane³².

Because of the flaky nature of CrCl_3 crystals, their XRD pattern also shows a very high intensity peak from the 001 plane, and limited diffraction from other planes. Since the CrOCl examined in this work resulted from the reaction of CrCl_3 , it is likely that the crystal structures of these two species will be pseudomorphic, and hence the relative intensities measured can be explained.

Little reference to CrOCl can be found in the literature; however, it has been shown³²⁻³⁴ that CrOCl can be produced by the slow reaction of an intimate mixture of CrCl_3 and Cr_2O_3 according to the reaction



The product forms by vapour-phase transport along a temperature gradient, or on prolonged heating (~6 days) at 460°C .

CrOCl exhibits an orthorhombic crystal structure^{32,33}. The crystal lattice is two-dimensional, being built up from two layers of halide ions with a chromium-oxygen plane sandwiched between them. The weak van der Waals bonding between adjacent chloride layers allows them to be pulled apart easily. The similarity between this layer structure and that discussed for CrCl_3 (Section 2.2.1) is readily apparent.

In the present experimental system CrOCl is found to form on rapid heating of CrCl_3 in air. Unfortunately no thermo-

dynamic data for this species could be located, so the theoretical feasibility of this reaction occurring could not be determined. However, conditions obviously arise during the reaction such that the formation of CrOCl becomes more favourable than the oxidation of CrCl_3 . A possible reason is that at high heating rates the reaction occurs so rapidly that a situation of oxygen starvation develops within the pellet. Diffusion of the reactant gas through the Cr_2O_3 product layer then becomes the rate-limiting step. When the rate of the chemical reaction exceeds the rate at which oxygen can be provided at the reaction site, the alternative reaction occurs, resulting in the formation of CrOCl .

5.8.2 Reaction in oxygen

Figure 5.18 shows the results of TG experiments carried out under the same experimental conditions as Figure 5.16 except that a pure oxygen atmosphere was used. The main features of the curves are given in Table 5.10.

Similar effects to those discussed in Section 5.8.1 are observed, with the exception of the mass loss results. As in Section 5.3, it is seen that the reactions in pure oxygen occur far more rapidly and at lower temperatures than those in air. The experiments in oxygen, however, show a decreasing mass loss with increasing heating rate. Noting that a lower heating rate corresponds to a longer reaction time, this effect can be compared with that observed in

Table 5.10 Effect of heating rate on the oxidation of CrCl_3 .

Conditions : Programmed temperature TG
1 g CrCl_3 pellet
200 $\text{cm}^3 \text{min}^{-1}$ oxygen

Heating rate* ($^{\circ}\text{C min}^{-1}$)	Onset temp ($^{\circ}\text{C}$)	Completion temp ($^{\circ}\text{C}$)	Temp difference ($^{\circ}\text{C}$)	Mass loss (%)
2	355	523	168	57,8
10	400	672	272	54,6
20	410	797	387	54,5

* programmed heating rate

Section 5.3.2. This increased mass loss may therefore be attributed to the vapour-phase removal of chromium as CrO_2Cl_2 . CrOCl does not form in an oxygen atmosphere because the high oxygen partial pressure means that a situation of severe oxygen starvation is unlikely to arise.

5.9. Summary

The thermogravimetric results presented in this chapter have shown that the oxidation of CrCl_3 to Cr_2O_3 occurs at a measurable rate at temperatures above 400°C . Under certain experimental conditions, the formation of CrO_2Cl_2 or CrOCl may occur. It is uncertain whether these products arise as a result of competing side-reactions, or whether they form intermediate species in the oxidation reaction.

From the evidence presented so far, it appears that diffusion of oxygen through the product layer of the pellet may provide the major resistance to reaction under the

experimental conditions studied, although there is more evidence that the rate of the reaction is limited by the rate of the chemical process itself.

In the following two chapters, supplementary experimental techniques which provide further insight into the nature of the rate-limiting step of the reaction, are discussed.

6. SCANNING ELECTRON-MICROSCOPY STUDIES

The results of isothermal thermogravimetric experiments, discussed in Chapter 5, suggest that the rate of oxidation of CrCl_3 is probably limited by the rate of the chemical reaction, although there is some evidence that the reaction may be under diffusion control. In order to obtain further experimental evidence for either of these suggestions, it was necessary to examine more closely the manner in which the reaction progresses.

Two simple idealised models can be considered¹³. In the progressive-conversion reaction model, the reactant gas enters and reacts throughout the pellet at all times. The solid reactant is therefore converted continuously and progressively throughout the pellet. Reactions which proceed in this way are usually governed by the rate of the chemical process, since diffusion of the reactant gas through the pellet is relatively unhindered. On the other hand, the reaction may occur by the advance of a well-defined reactant-product interface through the solid. Since this reaction configuration results in an outer layer of converted solid and an inner core of unreacted material, this behaviour is said to follow the unreacted shrinking-core model. The rates of such reactions may be limited by either chemical or mass-transfer processes. These two models are depicted schematically in Figure 6.1.

The manner in which the oxidation of CrCl_3 occurs was

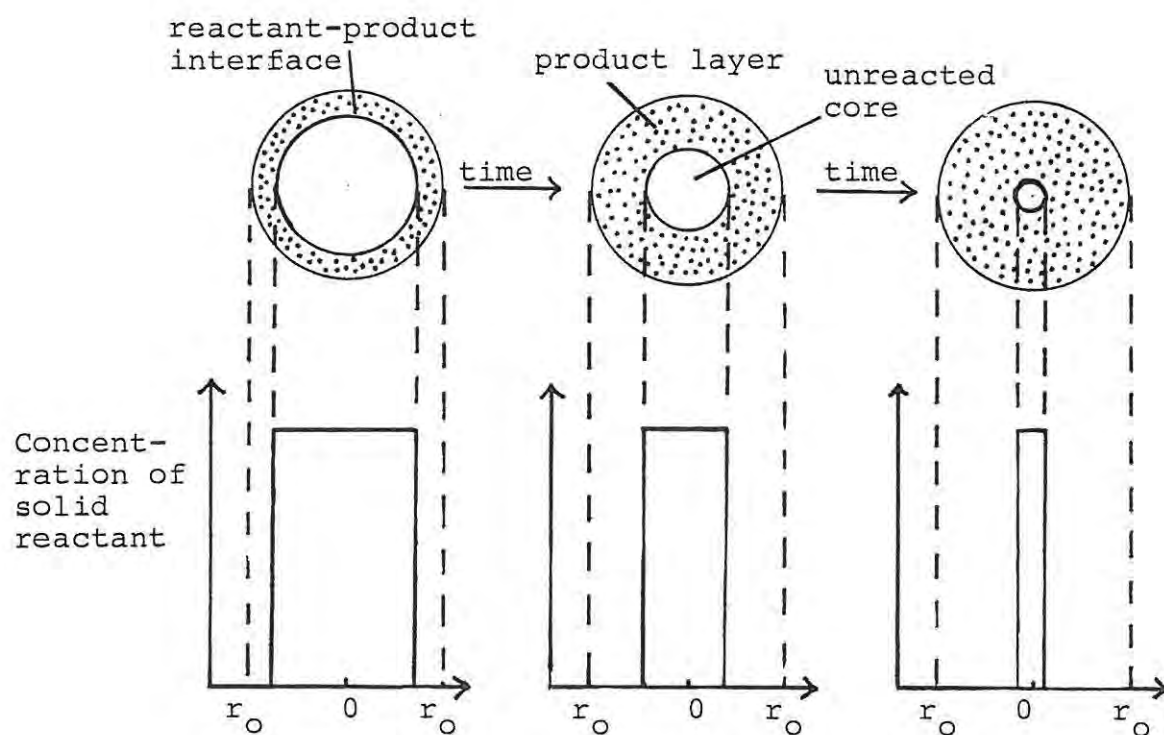
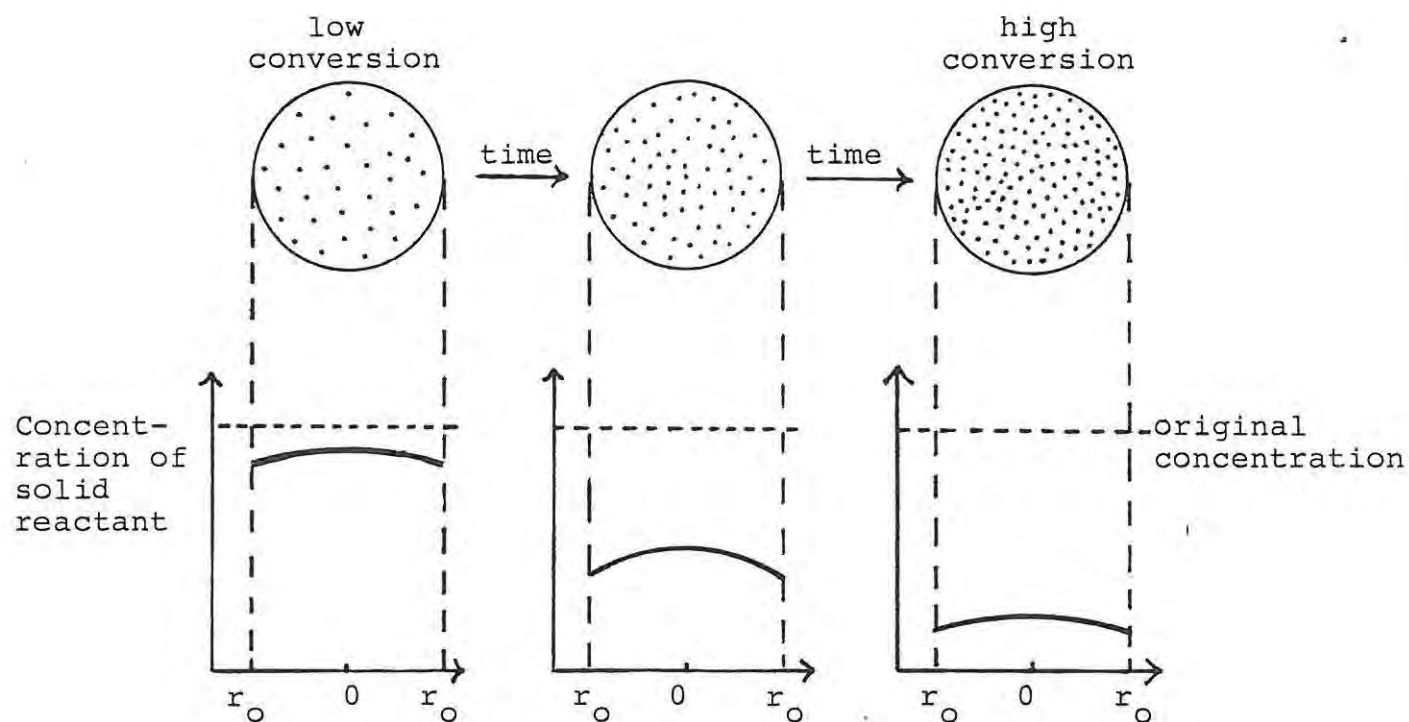


Figure 6.1 Models of solid-gas reactions
 (a) Progressive-conversion model
 (b) Unreacted shrinking core model
 (Adapted from Levenspiel¹³)

identified by sectioning and examining partially-reacted pellets by scanning electron microscopy (SEM). By operating the instrument in the back-scattered electron image mode, differences in atomic number, and hence chemical composition, can be detected. By comparing the volume of the product layer with the volume of the remaining unreacted core, the extent of reaction could be calculated for various values of α .

After preparing the samples as described in Section 4.4.1, each was examined for atomic-number contrast in the SEM. A magnification of 15 times was used. Because of the relatively large size of the cross-sections ($\sim 2.5 \times 13$ mm), three overlapping images were obtained for each sample. The α -time curve, constructed from the mass loss measurements at 600°C , is shown in Figure 6.2. In contrast to the isothermal TG curves of Chapter 5 where the mass of a reacting sample was monitored continuously, this graph is plotted from discrete points where the mass of the individual samples is measured after reaction for a specified time. The corresponding SEM photomicrographs of the partially-reacted pellet cross-sections are shown in Figures 6.3(a) to (g).

It is readily seen that this reaction is of the unreacted shrinking-core type, with the reaction occurring at a well-defined reactant-product interface. To measure the thickness of the product layer as accurately as possible, a hard copy ($\sim 8 \times 36$ cm) of each image was printed out using a dot-

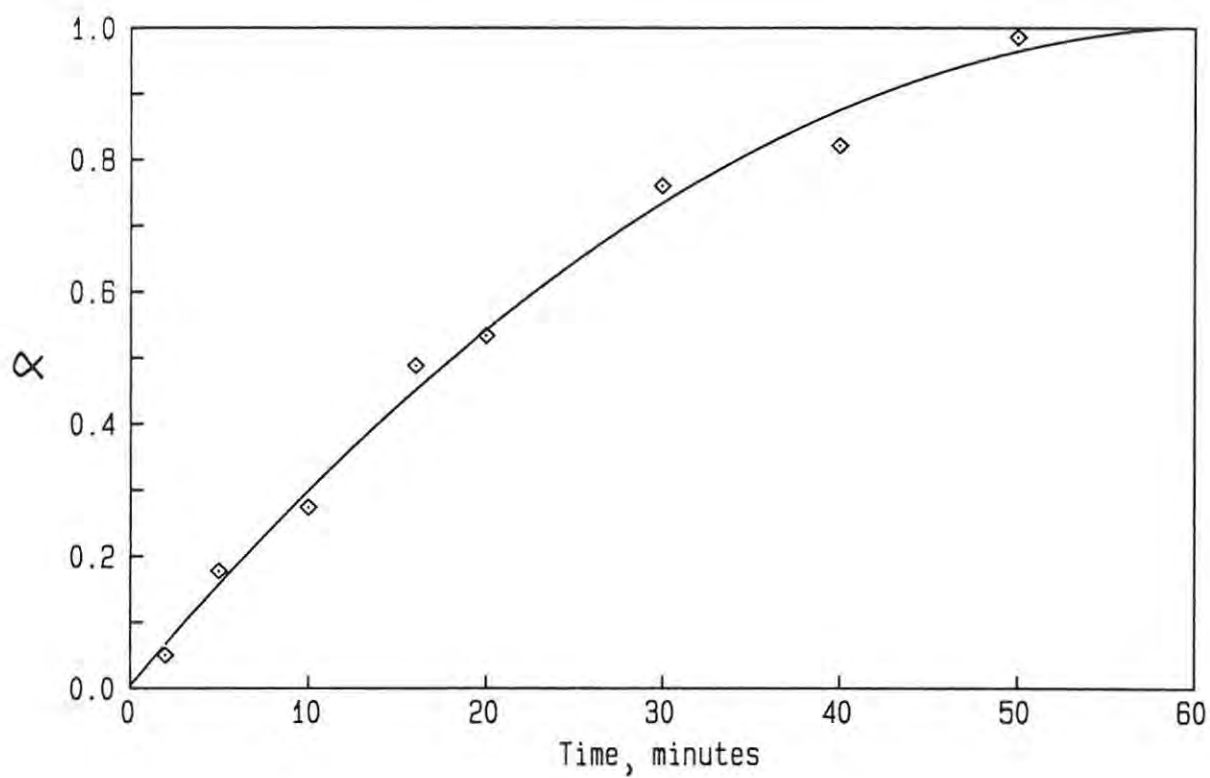


Figure 6.2 The fractional conversion of partially-reacted pellets used for SEM analysis
Conditions : Oxidation in tube furnace
1 g CrCl_3 pellet
static air
600°C

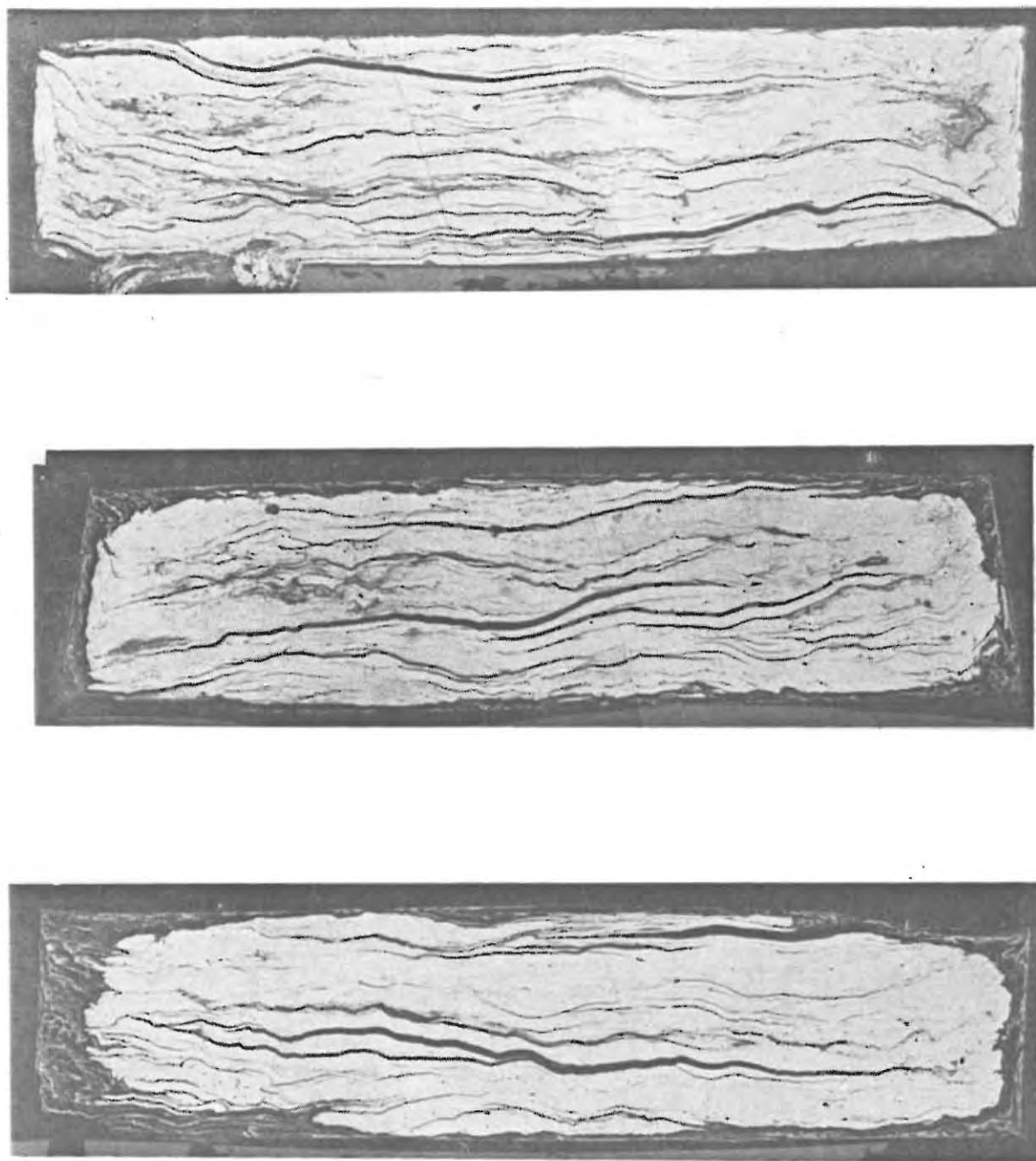


Figure 6.3 SEM photomicrographs of the cross-sections of partially-reacted pellets
(a) $t = 2 \text{ min}$; $\alpha = 0,050$
(b) $t = 5 \text{ min}$; $\alpha = 0,178$
(c) $t = 10 \text{ min}$; $\alpha = 0,274$

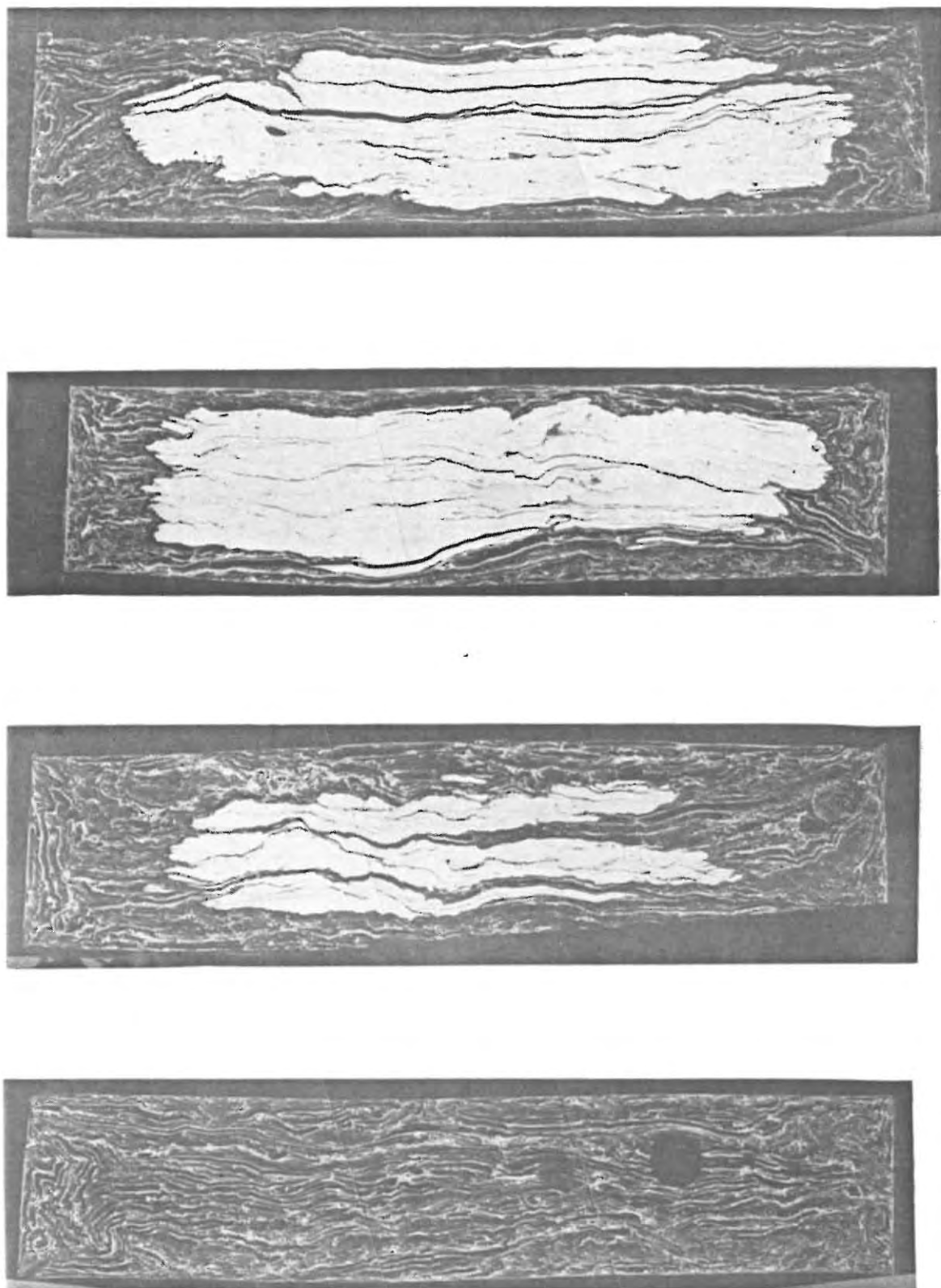


Figure 6.3 SEM photomicrographs of the cross-sections of partially-reacted pellets

(d)	$t = 16 \text{ min}$; $\alpha = 0,484$
(e)	$t = 20 \text{ min}$; $\alpha = 0,534$
(f)	$t = 30 \text{ min}$; $\alpha = 0,760$
(g)	$t = 50 \text{ min}$; $\alpha = 0,986$

matrix printer. Because of the uneven thickness of the product layer, about 20 measurements were made at equal intervals along the top and bottom of each pellet, and about 8 measurements along each side. The mean thickness of the product layer in each direction was then calculated. The fractional conversion of each pellet was calculated by comparing the relative bulk volumes of reactant and product. The validity of this technique was determined by comparing this value with the fractional conversion calculated from the mass lost during the reaction (Figure 6.1). A typical detailed analysis of an SEM cross-section is presented in Appendix C. The experimental conditions and SEM analyses are correlated in Table 6.1.

Table 6.1 SEM analyses of cross-sections of partially reacted CrCl_3 pellets
 Conditions : Oxidation in tube furnace
 1 g CrCl_3 pellet
 Static air atmosphere
 600°C

Time (min)	Mass loss (%)	α_m^*	α_s	r (mm)	h (mm)	r/h
2	2,6	0,050	0,057	0,070	0,052	1,33
5	9,2	0,178	0,203	0,386	0,158	2,43
10	14,3	0,274	0,287	0,657	0,186	3,54
16	25,4	0,488	0,625	1,457	0,475	3,07
20	27,8	0,534	0,622	1,732	0,414	4,18
30	39,5	0,760	0,834	2,572	0,627	4,10
40	42,7	0,821	0,896	3,881	0,713	5,44
50	51,3	0,986	~1,00	-	-	-
60	52,3	1,005	~1,00	-	-	-

* α_m = fractional conversion calculated from mass loss

α_s = fractional conversion calculated from SEM analysis

r = average thickness of Cr_2O_3 layer on sides of pellet

h = average thickness of Cr_2O_3 layer on top and bottom of pellet

Table 6.1 shows a comparison of the fractional conversions calculated from the measured mass loss (α_m) and from the SEM analyses (α_s). These two values generally agree to within 5%, thereby demonstrating that the technique used for measuring product layer thicknesses is valid.

By comparing the average product layer thickness on the sides of the pellet, r , with that on the top and bottom, h , it can be seen that the ratio r/h increases with increasing reaction time. This shows that although Cr_2O_3 is formed on all surfaces of the pellet, the rate of growth of the thickness of the product layer is considerably faster from the sides than from the flat ends of the pellet. This is confirmed by inspection of the photomicrographs in Figure 6.3.

This effect is depicted quantitatively in Figure 6.4, which shows plots of product-layer thicknesses as a function of reaction time for reaction in the two directions. The linearity of these plots indicates that the reactant-product interfaces advance at constant rates. For these particular experimental conditions, the average rate of interface advance in the x,y -direction is $\sim 93,7 \mu\text{m min}^{-1}$, while that in the z -direction it $\sim 19,1 \mu\text{m min}^{-1}$. Only at high fractional conversions, when the reaction is almost complete, does deviation from this linear behaviour occur.

Since the ratio of the rates of reaction from the sides and from the top and bottom of a pellet is $\sim 5:1$, the

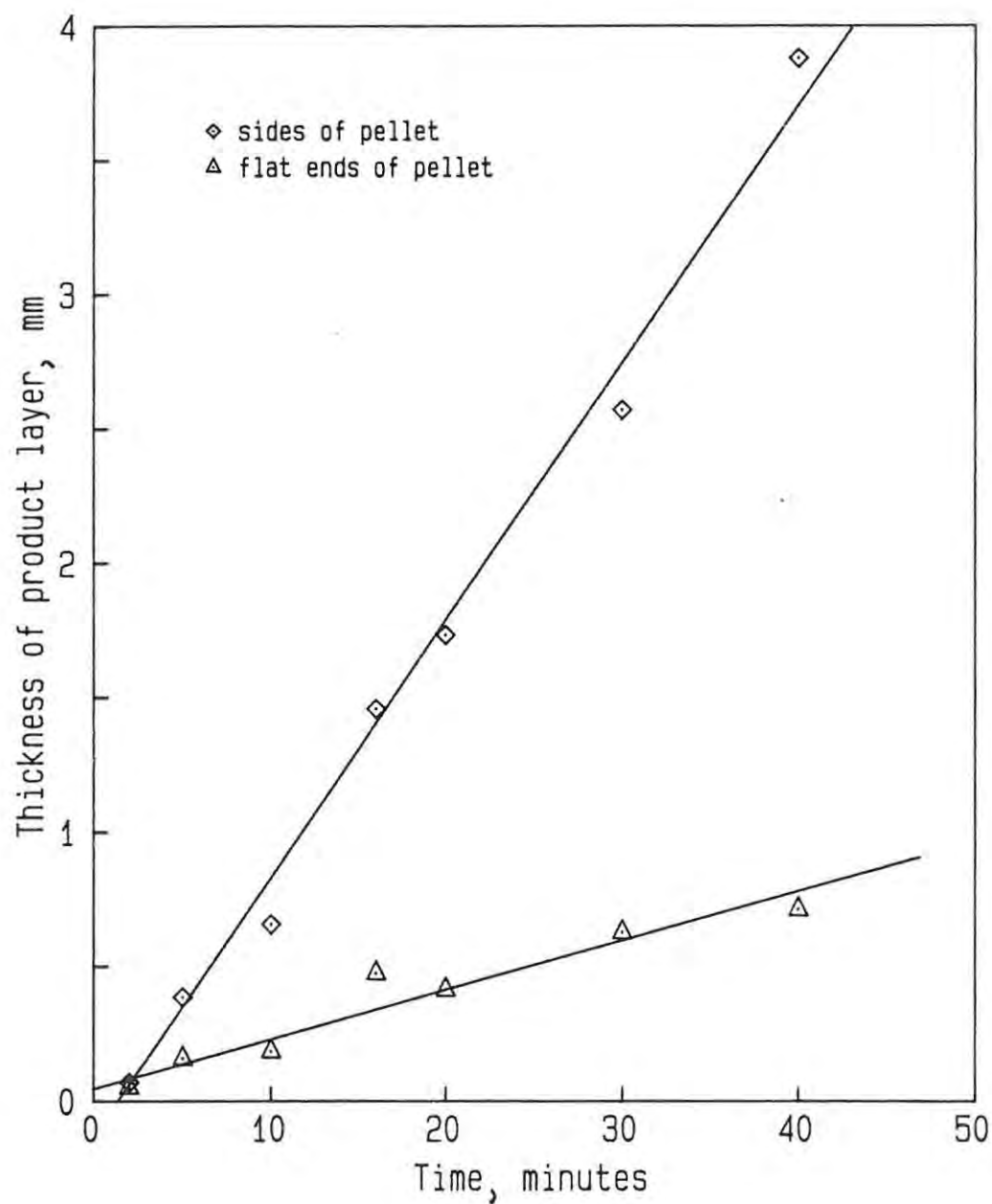


Figure 6.4 The rate of interface advance during the oxidation of CrCl_3 pellets
 Conditions : Oxidation in tube furnace
 1 g CrCl_3 pellets
 static air
 600°C

contribution from the top and bottom cannot be regarded as negligible. This means that the kinetic behaviour of the oxidation of a CrCl_3 pellet is expected to be described by deriving the rate expression from contracting-cylinder geometry, with two different rate constants for the two directions involved.

Observation of these linear rates of interface advance is also significant because this provides direct experimental evidence that the rate of the overall reaction is limited by the rate of the chemical reaction. This will be discussed further in Chapter 8.

7. DENSITY, POROSITY, PORE-SIZE AND SURFACE-AREA MEASUREMENTS

Experimental evidence discussed so far has indicated that the probable kinetic behaviour of the solid-state oxidation of CrCl_3 to Cr_2O_3 is that the reaction is under chemical control and that the rate expression is given by a contracting-geometry model. However, in Section 5.8.1, it was shown that when non-isothermal TG experiments are carried out in air at a fast heating rate ($20^\circ\text{C min}^{-1}$), diffusion of oxygen through the product layer certainly is the rate-determining step, and, if oxygen starvation occurs, a different product, CrOCl , is formed.

It can therefore be seen that under certain experimental conditions, gas diffusion through the product layer is the rate-limiting step. However, whether this is so for the majority of the isothermal TG experiments of this study is still uncertain. A quantitative examination of the differences in various physical properties between the solid reactant and solid product was therefore undertaken in order to assess how readily diffusion could be expected to occur. The measurements of absolute density, bulk density, and surface area, and the calculation of porosity for various samples are summarised in Table 7.1.

Table 7.1 Absolute density, bulk density, porosity and surface areas of reaction samples

Sample	ρ_o (g cm ⁻³)	ρ_b (g cm ⁻³)	Porosity (%)	Surface area (m ² g ⁻¹)
CrCl ₃ flakes	2,99	0,907	69,8	1,613
CrCl ₃ pellets	2,96	2,61	11,9	0,100
Cr ₂ O ₃ pellets*	5,05	1,26	75,2	2,475

* completely-oxidised CrCl₃ pellets

Table 7.1 shows that the oxide product layer is extremely porous when compared with the unreacted CrCl₃ core. This suggests that diffusion of oxygen through this layer should be relatively unhindered, and is unlikely to be the rate-limiting step of the oxidation reaction.

There is an approximately 25 times increase in surface area on converting a CrCl₃ pellet to Cr₂O₃, confirming that the porosity of the product layer is significantly greater than that of the CrCl₃ core.

Assuming that limited structural changes occur during the reaction, this increased porosity can be partially explained in terms of the ionic radii of the anions involved. For each chloride ion removed from the crystal lattice, only "half" an oxide ion replaces it. In addition, the ionic radius of the O²⁻ ion is ~25% smaller than that of the Cl⁻ ion. Ionic radii measured by various techniques have been tabulated by Cotton and Wilkinson¹⁵; the ionic radius of Cl⁻ is given as 18,1 ± 1,0 nm, while that of the O²⁻ ion is given as 13,2 ± 0,8 nm.

The total porosity may, however, be divided into three contributing components - porosity due to the existence of macropores (30 to 50 000 nm), of mesopores (1,8 to 30 nm) and of micropores (<1,8 nm). If a substantial fraction of the total porosity is derived from micropore volumes, then more restricted diffusion is to be expected than if the porosity is due mainly to macropores. Figures 7.1(a) and (b) show the pore-size distribution for a CrCl_3 pellet and for a pellet reacted completely to Cr_2O_3 . The relative contributions from these pore-size ranges are given in Table 7.2.

Table 7.2 Pore-size distribution in CrCl_3 and Cr_2O_3 pellets

Sample	Porosity (%)	Macropores (% of total pore volume)	Mesopores	Micropores
CrCl_3	5,58	90,7	9,3	~0
Cr_2O_3	75,20	92,5	7,5	~0

The porosity of the Cr_2O_3 product layer is derived mainly from macropores and cracks. The porosity of the CrCl_3 itself is also due to the existence of macropores. The relative porosities indicate that the rates of diffusion of reactant and product gases through the product layer are expected to be faster than through the CrCl_3 core. This observation, however, gives no indication of the importance of diffusion through the product layer in determining the rate-determining step of the reaction.

The following chapter discusses a comprehensive analysis of the isothermal TG results in an attempt to clarify the mechanism of the reaction and to identify the rate-determining step.

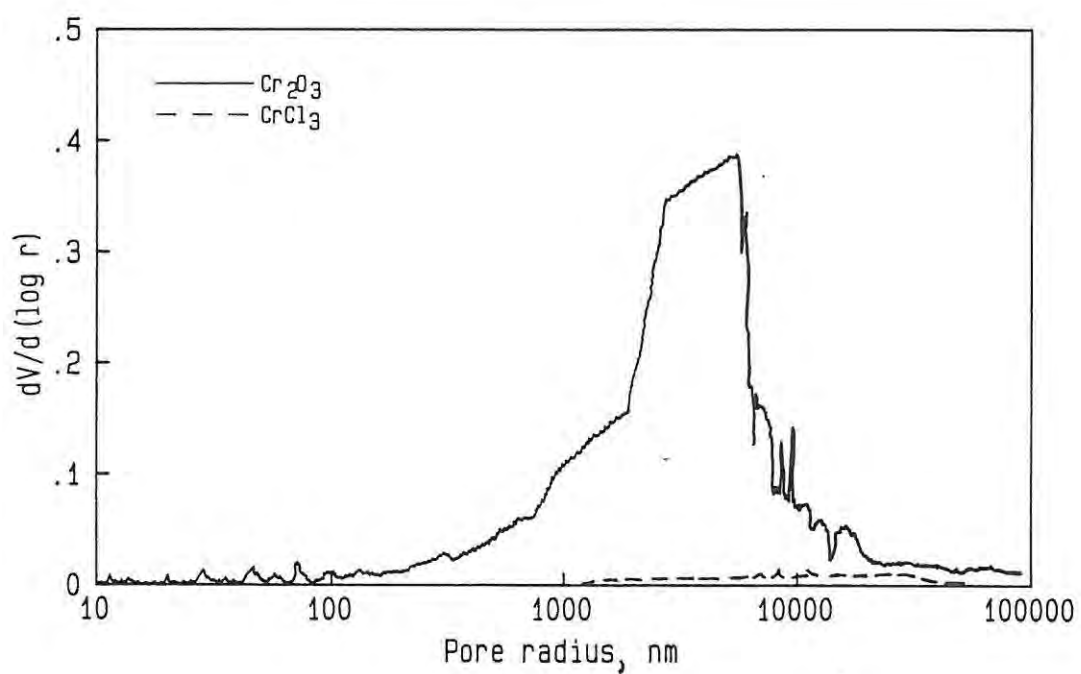
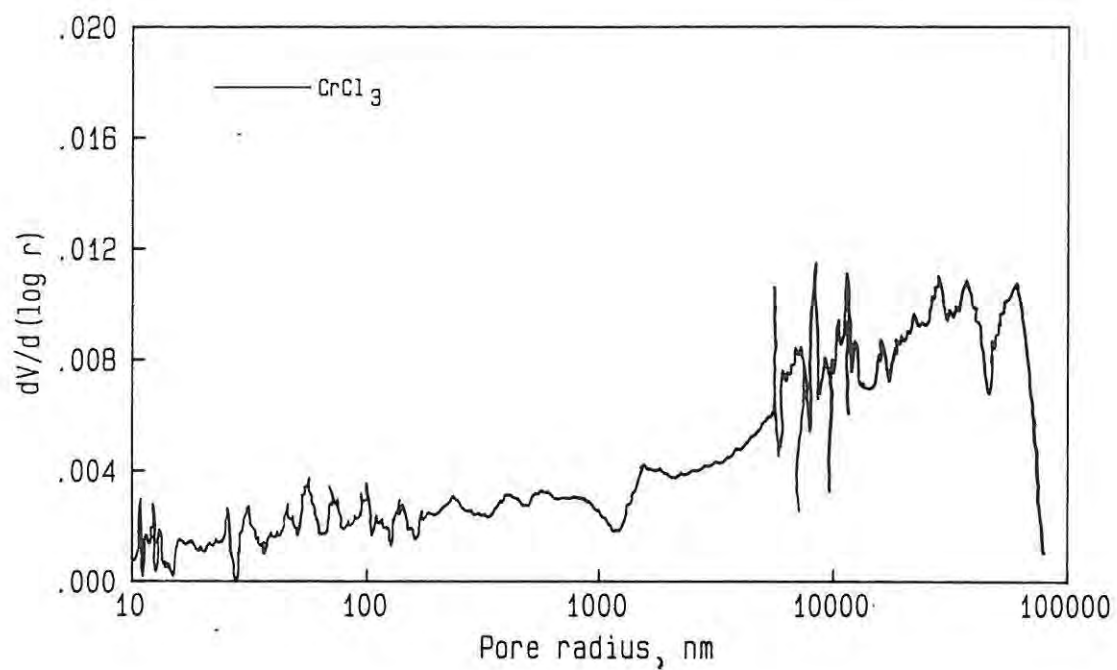


Figure 7.1 The pore-size distribution in CrCl_3 and Cr_2O_3 pellets
 (a) CrCl_3
 (b) CrCl_3 and Cr_2O_3

8. KINETIC ANALYSIS OF ISOTHERMAL THERMOGRAVIMETRIC DATA

8.1 Models of isothermal kinetic behaviour

Although thermal analysis experiments are usually carried out under dynamic heating conditions, and a number of techniques for non-isothermal kinetic analyses have been developed³⁵⁻⁴⁸, the validity and interpretation of results obtained using such techniques is questionable, and considerable controversy therefore exists over the use of non-isothermal methods⁴⁹⁻⁵¹. It is generally agreed that unless the mechanism of the reaction is known in advance, or the rate is controlled by an order-of-reaction mechanism, significant errors in the interpretation of non-isothermal kinetics can arise. It is usually preferable to carry out a number of isothermal experiments at different temperatures in order to obtain kinetic information about a particular system.

A number of models describing the kinetic behaviour of various solid-state reaction systems under isothermal conditions have been developed¹⁴. The kinetic behaviour is usually described by an equation of the form

$$f(\alpha) = kt \quad (8.1)$$

where α is the fractional conversion

k is the apparent rate constant (rate coefficient)

t is the time (corrected if necessary for any time interval, t_0 , before the model begins to apply).

Table 8.1 Classification of solid-gas isothermal rate expressions

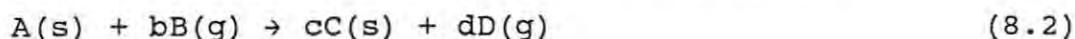
		$f(\alpha) = kt$
1.	Acceleratory α -time curves	
P1	power law	$\alpha^{1/n}$
E1	exponential law	$\ln \alpha$
2.	Sigmoid α -time curves	
A2	Avrami-Erofeev	$[-\ln(1-\alpha)]^{1/2}$
A3	Avrami-Erofeev	$[-\ln(1-\alpha)]^{1/3}$
A4	Avrami-Erofeev	$[-\ln(1-\alpha)]^{1/4}$
B1	Prout-Tompkins	$\ln[\alpha/(1-\alpha)]$
3.	Deceleratory α -time curves	
3.1	Based on geometric models	
R2	contracting-area	$1-(1-\alpha)^{1/2}$
R3	contracting-volume	$1-(1-\alpha)^{1/3}$
3.2	Based on diffusion mechanisms	
D1	one-dimensional	α^2
D2	two-dimensional	$(1-\alpha)\ln(1-\alpha)+\alpha$
D3'	three-dimensional	$1-3(1-\alpha)^{2/3}+2(1-\alpha)$
D3	Jander	$[1-(1-\alpha)^{1/3}]^2$
D4	Ginstling-Brounshtein	$(1-2\alpha/3)-(1-\alpha)^{2/3}$
3.3	Based on 'order of reaction'	
F1	first order	$-\ln(1-\alpha)$
F2	second order	$1/(1-\alpha)$
F3	third order	$[1/(1-\alpha)]^2$

Table 8.1 gives a broad classification of the better-known solid-gas rate expressions, labelled according to the system devised by Sharp *et al*⁴³, and subdivided according to the shape of the α -time curves as acceleratory, deceleratory or sigmoid. These models represent a simplified approach as they usually only take into account a single rate-limiting step (as discussed in Chapter 2), although both physical and chemical processes will always operate to a greater or lesser extent in any real system. This means that such models only account for the major resistance to reaction and will only be able to describe the kinetic behaviour over a limited range of the reaction. Nevertheless, these models have found wide application in describing the overall rates of solid-gas reactions, and they can provide useful information concerning kinetic behaviour, provided that their limitations are understood and appreciated.

8.2 Rate expressions for a disc-shaped pellet exhibiting contracting-geometry kinetic behaviour

Evidence from the analysis of SEM photomicrographs of the cross-sections of partially-reacted pellets (Chapter 6) showed that the oxidation of CrCl_3 pellets proceeds by the advance of a reactant-product interface according to an unreacted shrinking-core model. The rate expressions for the reaction of such disc-shaped pellets are now presented¹³.

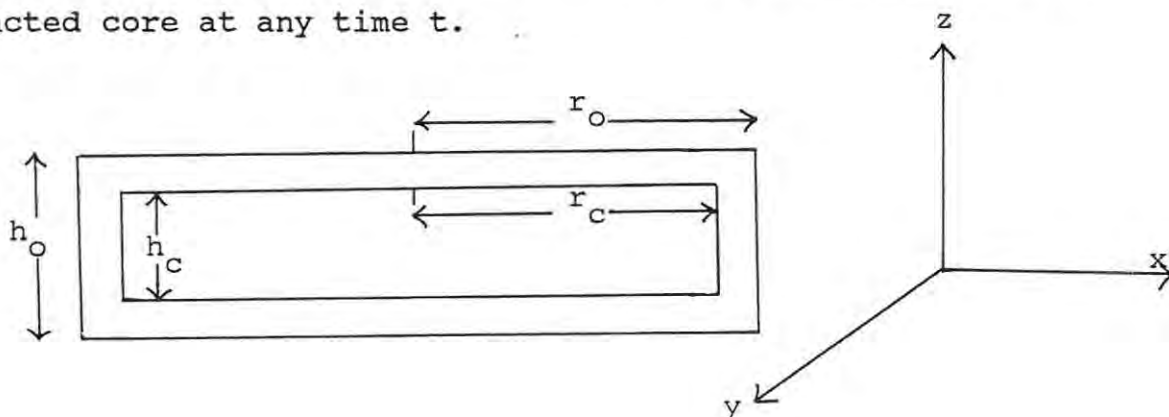
Consider a disc-shaped pellet of initial height, h_0 , and radius, r_0 , reacting according to the equation



It is assumed that

- (i) the reaction occurs at a well-defined reactant-product interface;
- (ii) the product layer is not removed from the unreacted core, and the dimensions of the final product are the same as those for the starting pellet;
- (iii) the unreacted core is considered to be essentially non-porous, while the product layer is considered to be porous.

The progress of such a reaction is depicted below, where r_c and h_c refer to the radius and height respectively of the unreacted core at any time t .



Although evidence in Chapter 6 showed that the interface advanced at different rates from the sides and from the ends of the pellet, for ease of calculation two simplified situations will be considered initially :

- (i) equal rates of interface advance in the x -, y - and z -directions;
- (ii) equal rates of interface advance in the x - and y -directions, assuming no reaction in the z -direction.

Full details of the derivations of all equations are given in Appendix D.

It is first assumed that the movement of the interface occurs at equal rates in the x-, y- and z-directions. It can then be shown that at any time t, the thickness of the product layer may be described by the relation

$$r_c = r_0(1 - \alpha)^{1/3} \quad (8.3)$$

The rate of the reaction is determined by the rate of interface advance, dr_c/dt ($= dh_c/dt$ for this particular situation). This may be governed either by the rate of diffusion of the reactant gas B through the product layer C, or by the rate of the chemical reaction itself at the reactant-product interface.

If the rate of reaction is limited by mass transfer of the reactant gas to the reaction site, then it can be shown¹³ that the rate expression is given by

$$1 - 3(1 - \alpha)^{2/3} + 2(1 - \alpha) = kt \quad (8.4)$$

with the apparent rate constant, k, given by

$$k = - \frac{6(1 + 2a)DC}{b\rho_A ar_0^2} \quad (8.5)$$

where $a = h_c/2r_c$

D = diffusion coefficient of gaseous reactant B

C = concentration (partial pressure) of gas B

ρ_A = absolute density of solid A.

It can further be shown that the rate of interface advance under these conditions is given by

$$\frac{dr_c}{dt} = - \frac{kr_0^3}{6(r_0r_c - r_c^2)} \quad (8.6)$$

The rate of advance of the reactant-product interface for a reaction under diffusion control is therefore not constant with time - it is dependent on the radius of the unreacted core at any time t . This is because the greater the diffusion length, or thickness of the product layer (related to the radius of the unreacted core), the longer the reactant gas takes to reach the unreacted core and the greater the resistance to reaction.

If the reaction is limited by the rate of the chemical reaction at the reactant-product interface, and it is assumed that the reaction is first order with respect to reactant gas B, then the rate expression for the reaction is given by

$$1 - (1 - \alpha)^{1/3} = kt \quad (8.7)$$

with the apparent rate constant, k , given by¹³

$$k = \frac{(2a + 1)k_g C}{3a\rho_A r_0} \quad (8.8)$$

where k_g is the first order rate constant.

In this case, the rate of interface advance is given by

$$\frac{dr_c}{dt} = \frac{(2a + 1)k_g C}{3a\rho_A} \quad (8.9)$$

demonstrating that the movement of the interface is constant with time.

The rate expressions can be similarly derived (Appendix D) for a pellet reacting only by radial movement of the reaction interface in the x,y-plane. The rate expression for a reaction of this nature under diffusion control is given by

$$\alpha + (1 - \alpha)\ln(1 - \alpha) = kt \quad (8.10)$$

with the apparent rate constant, k , given by

$$k = - \frac{8DC}{b\rho_A r_0^2} \quad (8.11)$$

and the rate of the 2-dimensional interface advance given by

$$\frac{dr_c}{dt} = \frac{8DC}{4r_c b\rho_A \ln(r_0/r_c)} \quad (8.12)$$

If the two-dimensional reaction is controlled by the rate of the chemical reaction then the rate expression is given by

$$1 - (1 - \alpha)^{1/2} = kt \quad (8.13)$$

with the apparent rate constant, k , given by

$$k = \frac{k_g C}{b\rho_A r_0} \quad (8.14)$$

and

$$\frac{dr_c}{dt} = \frac{r_0 k_g C}{b\rho_A} \quad (8.15)$$

Equations (8.12) and (8.15) confirm that a reaction controlled by the rate of diffusion of the reactant gas through the product layer shows a non-linear dependence of the rate of interface advance on time, while a constant rate of interface advance is observed for a reaction controlled by the rate of the chemical reaction. It can reasonably be

inferred, therefore, that in the actual situation where two linear rates are observed, similar considerations would apply. The development of a generalised equation describing this behaviour will be discussed in Section 10.2.

8.3 Methods of data treatment

A first step in kinetic analysis is usually the conversion of the experimental TG data from units of percentage mass loss to α , the fractional conversion or fractional extent of reaction, defined (for thermogravimetric experiments) by

$$\alpha_i = \frac{m_0 - m_i}{m_0 - m_f} \quad (8.16)$$

where m_0 is the initial mass of the sample

m_f is the final mass of the sample

m_i is the mass of the sample at time t_i .

Once the (α_i, t_i) values have been obtained, these are readily converted to $(f(\alpha)_i, t_i)$ values, with $f(\alpha)$ usually being given by one of the rate expressions listed in Table 8.1.

Comparison of experiments carried out at different heating rates or different isothermal temperatures is more readily achieved by using the concept of reduced-time. Reduced-time is usually defined as

$$t_{red} = \frac{t}{t_{0,5}} \quad (8.17)$$

where $t_{0,5}$ is the time at which $\alpha = 0,5$.

Since $f(\alpha) = kt$

$$f(0,5) = kt_{0,5}$$

Therefore

$$k = \frac{f(0,5)}{t_{0,5}}$$

$$\text{and so } f(\alpha) = f(0,5) \frac{t}{t_{0,5}} \quad (8.18)$$

The use of this mathematical manipulation eliminates different k values at different temperatures and enables data to be scaled along the abscissa. If the mechanism of the reaction does not change with temperature, plots of α against reduced-time at different temperatures should coincide. Changes in the shapes of curves (possibly corresponding to changes in the reaction mechanism) can then be easily detected.

In view of the large number of models which have been proposed for solid-gas reactions, and, in many cases, the close similarities between them, it is often difficult to identify which rate expression (if any) best fits the experimental data. A number of approaches have been mentioned in the literature¹⁴. These include comparison of the experimental and theoretically-calculated curves for α -time plots⁴³, α -reduced-time plots⁵², $(d\alpha/dt)$ -time plots⁵³, or $(d\alpha/dt)$ -reduced-time plots⁵⁴. However, the most commonly used method is to test the linearity of plots of $f(\alpha)$ against time for the different models (Table 8.1).

Various statistical analyses have been used to measure

quantitatively the goodness-of-fit of a least-squares line through the experimental points. The most commonly used parameter is the correlation coefficient, r . The correlation coefficient has, however, a number of shortcomings⁵⁵. In particular, the magnitude of r is influenced by the number of points included and by the slope of the least-squares fit. It has been shown^{55,56} that other statistical parameters such as the standard error of the slope of the regression line, s_b , or the standard error of the regression, $s_{y,x}$, are more reliable indicators of the goodness-of-fit. Since distinguishability of different kinetic models may be difficult, more than one statistical parameter should be evaluated in order to identify the kinetic model which best fits the experimental results⁵⁶.

Finally, the residual function, defined as

$$(f(\alpha)_{\text{exp}} - f(\alpha)_{\text{model}})_i \quad (8.19)$$

where $f(\alpha)_{\text{model}}$ are the theoretical values for each t_i and $f(\alpha)_{\text{exp}}$ are the values calculated from the experimental data for each t_i , may be plotted against α_i . The shapes of such residual plots will then give an indication of the extent of deviation of the experimental data from the chosen kinetic model, and so aid in distinguishing between two closely-related models⁵⁶.

8.4 Present method of data treatment

All isothermal TG data have been analysed as follows :

- (i) TG data in units of percentage mass loss were converted to units of fractional conversion, α ;
- (ii) α -data at the limits of the reaction were discarded, so that the data analysed fell in the range $0,05 \leq \alpha \leq 0,95$;
- (iii) α -time data were then converted to $f(\alpha)$ -time data, using various expressions for $f(\alpha)$ as tabulated in Table 8.1;
- (iv) the best straight line through the points $(f(\alpha)_i, t_i)$ was calculated from a least-squares linear regression;
- (v) the correlation coefficient, r , the standard error of the regression line, $s_{y,x}$, and the percentage standard error of the slope of the regression line, $\%s_b$, were calculated;
- (vi) plots of α against the residual function and α against reduced-time were drawn;
- (vii) by analysis of the statistical parameters, residual plots and reduced-time plots for different kinetic models, the model which best describes the experimental data was then selected.

The above data manipulations were carried out using the series of computer programs, STA429. Existing Applesoft Basic software (Section 4.3) enabled raw data from the thermal analyser to be captured and then processed. The kinetic programs designed for the present work were structured to be compatible with this existing software.

Program ALPHA was used to convert experimental data, in units of percentage mass loss, to α , the fractional conversion. The α -time or α -reduced-time data created by this program were then the input to program KINETICS. This program converts the data from α to $f(\alpha)$ values, where $f(\alpha)$ is calculated from any of the rate expressions listed in Table 8.1. The fit of the theoretical function to the experimental $f(\alpha)$ -time data thus obtained may then be judged from the following statistical parameters.

- (i) The best straight line through the $f(\alpha)$ -time data, as calculated by linear regression⁵⁶, is given by

$$y = a + bx \quad (8.20)$$

where

$$a = \frac{\sum y - b \sum x}{n} \quad \text{and} \quad b = \frac{n \sum xy - \sum x \sum y}{n \sum x^2 - (\sum x)^2} \quad (8.21)$$

and n is the number of points (typically 200 to 500).

The correlation coefficient is then given by

$$r = \frac{n \sum xy - \sum x \sum y}{\{[n \sum x^2 - (\sum x)^2][n \sum y^2 - (\sum y)^2]\}^{1/2}} \quad (8.22)$$

- (ii) The standard error of the regression is calculated according to⁵⁵

$$s_{y.x} = \left[\frac{\sum d_i^2}{n-2} \right]^{1/2} \quad (8.23)$$

where d_i is the vertical distance of each point

(x_i, y_i) from the regression line, given by

$$d_i = y_i - (bx_i + a) \quad (8.24)$$

- (iii) The standard error of the slope of the regression is given by⁵⁵

$$s_b = \frac{s_{y.x}}{(\sum x^2)^{1/2}} \quad (8.25)$$

where $x = x_i - \bar{x}$

and $\bar{x}$ is the mean of the x values = $\sum x_i/n$.

The standard errors of two slopes are compared more easily by converting s_b values to percentages of slopes, given by

$$\%s_b = \frac{100 \cdot s_b}{b} \quad (8.26)$$

The programs ALPHA and KINETICS are listed in Appendix E.

8.5 Kinetic analyses

The results of the kinetic analyses of the isothermal TG runs are listed in Tables 8.2(a) to (c). In each case, the model which best fits the experimental data has been marked with an asterisk.

Table 8.2(a) shows the analyses of experiments carried out at different temperatures in air. On the basis of the statistical parameters calculated, the contracting-volume (R3) model best describes the kinetic behaviour at temperatures up to 400°C, while above this temperature the contracting-area model (R2) shows better agreement. In an oxygen atmosphere (Table 8.2(b)), the reactions at the lower

Table 8.2(a) Kinetic analyses : Isothermal TG experiments
in air ($0,05 \leq \alpha \leq 0,95$)

Temp (°C)	Model	a	b ($\times 10^3$)	r	$s_{y \cdot x}$ ($\times 10^3$)	% s_b
350	R2	-0,0805	0,7745	0,9984	12,88	0,3493
	*R3	-0,0850	0,6237	0,9989	8,841	0,2978
	D1	-0,2081	1,020	0,9939	34,07	0,7016
	D2	-0,2138	0,8646	0,9888	38,80	0,9425
	D3	-0,1129	0,3831	0,9632	31,79	1,743
	D3'	-0,1383	0,4649	0,9298	68,52	2,210
	D4	-0,0637	0,2408	0,9827	13,52	1,179
375	R2	-0,0821	1,069	0,9988	11,84	0,5267
	*R3	-0,0888	0,865	0,9989	8,999	0,4942
	D1	-0,2083	1,402	0,9941	33,81	1,146
	D2	-0,2185	1,202	0,9885	40,75	1,611
	D3	-0,1186	0,544	0,9618	34,38	3,000
	D3'	-0,1524	0,6644	0,9773	49,52	1,828
	D4	-0,0658	0,3372	0,9818	14,42	2,033
400	R2	-0,0296	1,490	0,9992	8,715	0,279
	*R3	-0,0483	1,209	0,9997	4,271	0,169
	D1	-0,149	1,981	0,9969	23,59	0,569
	D2	-0,172	1,703	0,9918	32,99	0,925
	D3	-0,0990	0,768	0,9645	31,55	1,960
	D3'	-0,1512	1,021	0,9630	60,39	1,685
	D4	-0,0532	0,4773	0,9851	12,42	2,050
400	R2	-0,0143	1,817	0,9927	26,43	0,977
	*R3	-0,0163	1,489	0,9981	10,89	0,491
	D1	-0,0924	2,427	0,9930	34,50	0,954
	D2	-0,134	2,128	0,9983	14,90	0,470
	D3	-0,0885	0,984	0,9829	22,07	1,505
	D3'	-0,1315	1,238	0,9709	49,97	1,691
	D4	-0,0440	0,602	0,9960	6,432	0,718
400	R2	-0,0169	1,606	0,9985	12,01	0,405
	*R3	-0,0387	1,305	0,9999	1,561	0,0648
	D1	-0,1334	2,139	0,9969	23,21	0,587
	D2	-0,1606	1,844	0,9938	28,57	0,839
	D3	-0,0948	0,8337	0,9688	29,44	1,912
	D3'	-0,1445	1,092	0,9625	58,39	1,794
	D4	-0,0501	0,5173	0,9879	11,20	1,172
400	*R2	-0,0355	1,453	0,9999	1,798	0,0582
	R3	-0,0517	1,173	0,9986	9,267	0,371
	D1	-0,1580	1,933	0,9971	22,41	0,545
	D2	-0,1756	1,644	0,9881	38,76	1,109
	D3	-0,0976	0,730	0,9551	34,32	2,210
	D3'	-0,1528	0,999	0,9489	67,97	2,035
	D4	-0,0535	0,458	0,9795	14,27	1,464

Continued.

Table 8.2(a) Kinetic analyses : Isothermal TG experiments
Continued. in air ($0,05 \leq \alpha \leq 0,95$)

Temp (°C)	Model	a	b ($\times 10^3$)	r	$s_{y \cdot x}$ ($\times 10^3$)	% s_b
420	*R2	-0,0395	1,897	0,9997	4,956	0,143
	R3	-0,0531	1,523	0,9967	14,33	0,514
	D1	-0,1621	2,518	0,9956	27,16	0,590
	D2	-0,1739	2,117	0,9827	45,88	1,186
	D3	-0,0936	0,923	0,9446	36,92	2,184
	D3'	-0,1532	1,312	0,9203	81,65	2,365
	D4	-0,0532	0,587	0,9723	16,21	1,511
420	*R2	-0,0389	2,023	0,9996	6,002	0,170
	R3	-0,0522	1,620	0,9963	14,85	0,526
	D1	-0,1631	2,691	0,9954	27,59	0,5881
	D2	-0,1733	2,251	0,9818	46,14	1,176
	D3	-0,0920	0,974	0,9433	36,35	2,142
	D3'	-0,1289	1,258	0,9080	72,82	2,579
	D4	-0,0519	0,622	0,9713	16,17	1,491
450	*R2	-0,0707	2,983	0,9973	16,32	0,467
	R3	-0,0759	2,384	0,9920	22,64	0,811
	D1	-0,1981	3,929	0,9892	43,56	0,946
	D2	-0,1982	3,272	0,9720	58,98	1,534
	D3	-0,1009	1,415	0,9307	41,46	2,501
	D3'	-0,1910	2,097	0,9124	89,52	2,523
	D4	-0,0583	0,904	0,9602	19,59	1,850
450	*R2	-0,0226	2,705	0,9999	2,207	0,0625
	R3	-0,0409	2,179	0,9977	11,85	0,416
	D1	-0,1436	3,612	0,9966	24,06	0,510
	D2	-0,1615	3,055	0,9859	41,51	1,041
	D3	-0,0898	1,344	0,9509	35,01	1,995
	D3'	-0,1386	1,801	0,9195	74,24	2,385
	D4	-0,0492	0,849	0,9766	14,96	1,350
480	*R2	-0,1083	5,417	0,9961	19,51	0,712
	R3	-0,1035	4,301	0,9899	25,14	1,152
	D1	-0,2421	7,077	0,9862	48,70	1,357
	D2	-0,2284	5,823	0,9668	63,10	2,137
	D3	-0,1106	2,476	0,9222	42,56	3,389
	D3'	-0,1686	3,519	0,8995	87,64	3,506
	D4	-0,0659	1,599	0,9539	20,61	2,541
500	*R2	-0,0553	7,489	0,9998	3,999	0,128
	R3	-0,0668	6,041	0,9983	10,46	0,415
	D1	-0,1803	9,909	0,9957	27,72	0,671
	D2	-0,1923	8,415	0,9865	42,07	1,198
	D3	-0,1042	3,739	0,9541	35,32	2,265
	D4	-0,0579	2,346	0,9780	15,06	1,539

Continued.

Table 8.2(a) Kinetic analyses : Isothermal TG experiments
Continued. in air ($0,05 \leq \alpha \leq 0,95$)

Temp (°C)	Model	a	b ($\times 10^3$)	r	$s_{y \cdot \bar{x}}$ ($\times 10^3$)	% s_b
500	*R2	-0,1175	7,064	0,9974	16,12	0,514
	R3	-0,1124	5,634	0,9920	22,77	0,910
	D1	-0,2553	9,245	0,9889	44,13	1,075
	D2	-0,2436	7,678	0,9712	59,86	1,756
	D3	-0,1199	3,314	0,9283	42,20	2,868
	D4	-0,0707	2,119	0,9590	19,90	2,115
500	*R2	-0,1204	5,961	0,9978	14,63	0,428
	R3	-0,1139	4,741	0,9926	21,51	0,792
	D1	-0,2585	7,799	0,9896	42,08	0,942
	D2	-0,2443	6,442	0,9719	58,01	1,572
	D3	-0,1187	2,753	0,9286	40,92	2,595
	D3'	-0,1867	3,987	0,9063	87,93	2,683
530	*R2	-0,1608	10,33	0,9996	6,150	0,235
	R3	-0,1489	8,272	0,9966	14,83	0,707
	D1	-0,3159	13,60	0,9942	31,98	0,927
	D2	-0,2999	11,39	0,9811	48,76	1,687
	D3	-0,1471	4,960	0,9439	37,61	2,989
	D4	-0,0869	3,155	0,9709	16,87	2,109
530	*R2	-0,1074	8,632	0,9997	5,660	0,199
	R3	-0,1099	6,977	0,9993	6,517	0,283
	D1	-0,2522	11,47	0,9969	23,45	0,619
	D2	-0,2567	9,781	0,9899	36,07	1,117
	D3	-0,1343	4,359	0,9604	32,62	2,266
	D4	-0,0762	2,731	0,9820	13,37	1,483
530	*R2	-0,1308	9,046	0,9997	5,671	0,209
	R3	-0,1255	7,247	0,9966	14,57	0,669
	D1	-0,2811	11,98	0,9952	28,40	0,789
	D2	-0,2716	10,03	0,9821	46,57	1,546
	D3	-0,1349	4,354	0,9436	36,99	2,862
	D4	-0,0791	2,774	0,9716	16,36	1,962
570	*R2	-0,1437	12,79	0,9990	9,919	0,435
	R3	-0,1344	10,21	0,9947	18,14	0,995
	D1	-0,2957	16,87	0,9930	34,40	1,144
	D2	-0,2799	14,03	0,9772	52,34	2,090
	D3	-0,1363	6,042	0,9359	39,04	3,621
	D3'	-0,2024	8,428	0,9059	84,68	4,007
	D4	-0,0809	3,872	0,9657	17,88	2,588

Continued.

Table 8.2(a) Kinetic analyses : Isothermal TG experiments
Continued. in air $(0,05 \leq \alpha \leq 0,95)$

Temp (°C)	Model	a	b ($\times 10^3$)	r	$s_{y \cdot x}$ ($\times 10^3$)	% s_b
570	*R2	-0,1497	12,92	0,9991	9,806	0,414
	R3	-0,1402	10,36	0,9953	17,66	0,930
	D1	-0,3018	17,02	0,9926	36,38	1,166
	D2	-0,2881	14,28	0,9785	52,55	2,008
	D3	-0,1424	6,242	0,9403	39,50	3,451
	D3'	-0,2175	8,857	0,9129	88,81	3,752
	D4	-0,0837	3,958	0,9680	17,94	2,473
580	*R2	-0,1931	14,47	0,9996	6,016	0,286
	R3	-0,1760	11,60	0,9963	15,04	0,892
	D1	-0,3678	19,24	0,9954	27,85	0,995
	D2	-0,3452	16,11	0,9820	46,58	1,986
	D3	-0,1670	6,993	0,9433	36,94	3,630
	D4	-0,0995	4,458	0,9714	16,36	2,522
600	*R2	-0,1534	16,93	0,9994	7,562	0,381
	R3	-0,1439	13,57	0,9959	16,13	1,015
	D1	-0,3130	22,45	0,9942	31,56	1,200
	D2	-0,2987	18,82	0,9805	49,15	2,229
	D3	-0,1468	8,183	0,9424	37,81	3,944
	D3'	-0,2504	12,45	0,9127	93,31	4,370
	D4	-0,0866	5,210	0,9699	17,01	2,787
600	*R2	-0,1584	15,94	0,9989	10,44	0,5121
	R3	-0,1469	12,75	0,9945	18,44	1,131
	D1	-0,3182	21,10	0,9930	34,72	1,287
	D2	-0,3003	17,60	0,9775	52,38	2,328
	D3	-0,1459	7,609	0,9370	39,10	4,020
	D3'	-0,2290	11,01	0,9059	89,28	4,478
	D4	-0,0867	4,863	0,9662	17,89	2,878
600	*R2	-0,2028	17,42	0,9998	4,554	0,232
	R3	-0,1836	13,97	0,9970	13,69	0,868
	D1	-0,3774	23,09	0,9952	28,69	1,102
	D2	-0,3533	19,37	0,9830	45,97	2,104
	D3	-0,1709	8,249	0,9465	36,46	3,835
	D3'	-0,2538	11,83	0,9156	85,22	4,326
	D4	-0,1018	5,364	0,9731	16,13	2,665
600	*R2	-0,1234	13,04	0,9989	9,955	0,451
	R3	-0,1192	10,43	0,9946	17,99	1,019
	D1	-0,2747	17,33	0,9936	32,74	1,177
	D2	-0,2644	14,44	0,9781	50,93	2,085
	D3	-0,1302	6,225	0,9375	38,33	3,641
	D3'	-0,2181	9,334	0,8951	95,87	4,369
	D4	-0,0768	3,987	0,9668	17,48	2,592

Continued.

Table 8.2(a) Kinetic analyses : Isothermal TG experiments
Continued. in air ($0,05 \leq \alpha \leq 0,95$)

Temp (°C)	Model	a	b ($\times 10^3$)	r	$s_{y \cdot x}$ ($\times 10^3$)	% s_b
600	*R2	-0,1507	15,27	0,9996	6,076	0,287
	R3	-0,1409	12,23	0,9965	14,93	0,880
	D1	-0,3050	20,16	0,9946	30,59	1,093
	D2	-0,2905	16,87	0,9815	47,83	2,043
	D3	-0,1428	7,324	0,9431	37,57	3,697
	D3'	-0,1961	9,536	0,9141	73,96	4,229
	D4	-0,2842	4,666	0,9711	16,69	2,577
630	*R2	-0,1789	19,69	0,9995	7,009	0,339
	R3	-0,1641	15,76	0,9959	16,00	0,967
	D1	-0,3460	26,09	0,9949	29,55	1,079
	D2	-0,3258	21,84	0,9808	48,32	2,109
	D3	-0,1584	9,481	0,9408	38,01	3,820
	D3'	-0,1896	11,18	0,9197	61,18	4,206
	D4	-0,0941	6,042	0,9698	16,90	2,665

Table 8.2(b) Kinetic analyses : Isothermal TG experiments in oxygen ($0,05 \leq \alpha \leq 0,95$)

Temp (°C)	Model	a	b ($\times 10^3$)	r	$s_{y \cdot x}$ ($\times 10^3$)	% s_b
350	R2	0,1071	0,5527	0,9563	62,42	2,205
	R3	0,0536	0,4625	0,9730	40,58	1,713
	D1	0,0399	0,731	0,9550	83,83	2,241
	D2	-0,0369	0,6691	0,9843	44,40	1,300
	*D3	-0,0575	0,3305	0,9985	6,694	0,395
	D3'	-0,0678	0,3490	0,9968	16,65	0,452
	D4	-0,0193	0,1935	0,9929	8,575	0,865
375	R2	0,0440	1,308	0,9608	64,28	3,168
	R3	0,0045	1,089	0,9753	42,00	2,486
	D1	-0,0400	1,719	0,9569	88,78	3,331
	D2	-0,0995	1,559	0,9820	51,03	2,111
	*D3	-0,0831	0,764	0,9968	10,36	0,875
	D3'	-0,0492	0,6676	0,9961	18,84	0,705
	D4	-0,0362	0,4492	0,9902	10,80	1,550
400	*R2	-0,1153	4,329	0,9997	4,975	0,186
	R3	-0,1146	3,489	0,9984	10,27	0,475
	D1	-0,2561	5,705	0,9956	28,41	0,804
	D2	-0,2559	4,842	0,9866	42,29	1,410
	D3	-0,1324	2,153	0,9540	35,68	2,675
	D3'	-0,1871	2,851	0,9703	58,76	1,689
	D4	-0,0756	1,350	0,9781	15,16	1,812
400	R2	-0,1335	5,251	0,9993	8,697	0,508
	*R3	-0,1301	4,240	0,9993	6,819	0,494
	D1	-0,2808	6,932	0,9959	27,76	1,229
	D2	-0,2792	5,905	0,9898	37,40	1,944
	D3	-0,1440	2,636	0,9611	33,30	3,876
	D3'	-0,1862	3,272	0,9842	45,94	1,800
	D4	-0,0823	1,649	0,9826	13,67	2,545
450	*R2	-0,1212	9,331	0,9993	8,537	0,312
	R3	-0,1170	7,467	0,9957	16,51	0,755
	D1	-0,2656	12,31	0,9933	34,06	0,944
	D2	-0,2565	10,29	0,9797	50,25	1,667
	D3	-0,1275	4,463	0,9412	38,18	2,920
	D3'	-0,2113	6,668	0,9121	91,20	3,077
	D4	-0,0747	2,845	0,9691	17,26	2,070
480	*R2	-0,1485	12,54	0,9983	12,61	0,555
	R3	-0,1379	9,999	0,9934	20,04	1,106
	D1	-0,3039	16,57	0,9918	37,12	1,236
	D2	-0,2853	13,74	0,9748	54,57	2,192
	D3	-0,1375	5,885	0,9323	39,60	3,714
	D3'	-0,2326	9,055	0,9108	94,15	3,765
	D4	-0,0821	3,784	0,9628	18,43	2,688

Continued.

Table 8.2(b) Kinetic analyses : Isothermal TG experiments
Continued. in oxygen ($0,05 \leq \alpha \leq 0,95$)

Temp (°C)	Model	a	b ($\times 10^3$)	r	$s_{y,x}$ ($\times 10^3$)	% s_b
500	*R2	-0,2323	18,89	0,9956	21,46	1,088
	R3	-0,2020	15,01	0,9893	26,65	1,701
	D1	-0,4006	24,58	0,9851	51,66	2,013
	D2	-0,3592	20,28	0,9659	65,56	3,097
	D3	-0,1672	8,678	0,9221	44,22	4,881
	D3'	-0,2759	13,36	0,9110	96,27	4,528
	D4	-0,1020	5,580	0,9530	21,38	3,670
500	*R2	-0,1387	15,25	0,9999	3,510	0,168
	R3	-0,1358	12,33	0,9988	8,542	0,507
	D1	-0,3000	20,40	0,9969	23,33	0,836
	D2	-0,2977	17,38	0,9891	37,30	1,569
	D3	-0,1522	7,724	0,9586	33,10	3,133
	D3'	-0,2433	11,04	0,9435	76,39	3,154
	D4	-0,0876	4,848	0,9813	13,72	2,070
500	*R2	-0,1390	14,10	0,9997	5,154	0,232
	R3	-0,1332	11,33	0,9975	12,61	0,707
	D1	-0,2935	18,71	0,9950	29,59	1,005
	D2	-0,2849	15,77	0,9845	44,43	1,790
	D3	-0,1426	6,915	0,9507	35,67	3,278
	D3'	-0,2171	9,509	0,9447	68,16	3,049
	D4	-0,0832	4,378	0,9755	15,61	2,265
530	*R2	-0,2585	25,68	0,9991	9,941	0,582
	R3	-0,2258	20,53	0,9955	17,59	1,288
	D1	-0,4378	33,58	0,9925	37,01	1,657
	D2	-0,3989	28,05	0,9784	53,21	2,852
	D3	-0,1893	12,20	0,9390	40,08	4,938
	D3'	-0,2782	17,19	0,9315	81,97	4,478
	D4	-0,1140	7,762	0,9675	18,19	3,523
570	*R2	-0,2791	31,62	0,9995	7,036	0,477
	R3	-0,2446	25,36	0,9960	16,09	1,359
	D1	-0,4764	41,81	0,9944	31,53	1,616
	D2	-0,4360	35,08	0,9809	49,56	3,026
	D3	-0,2074	15,31	0,9421	38,82	5,431
	D3'	-0,2894	20,74	0,9097	84,86	6,155
	D4	-0,1248	9,723	0,9703	17,27	3,804
600	*R2	-0,3639	46,67	0,9995	7,333	0,619
	R3	-0,3153	37,56	0,9993	6,572	0,689
	D1	-0,5918	61,97	0,9981	18,28	1,162
	D2	-0,5419	52,46	0,9904	35,21	2,643
	D3	-0,2575	23,06	0,9592	32,32	5,571
	D3'	-0,4354	35,68	0,9431	83,63	5,572
	D4	-0,1551	14,58	0,9823	13,32	3,599

Continued.

Table 8.2(b) Kinetic analyses : Isothermal TG experiments
Continued. in oxygen ($0,05 \leq \alpha \leq 0,95$)

Temp (°C)	Model	a	b ($\times 10^3$)	r	$s_{y \cdot x}$ ($\times 10^3$)	% s_b
630	*R2	-0,4662	57,37	0,9999	2,016	0,193
	R3	-0,3930	45,83	0,9980	11,33	1,359
	D1	-0,7307	76,34	0,9964	25,24	1,819
	D2	-0,6448	53,58	0,9851	43,05	3,725
	D3	-0,2927	27,24	0,9508	34,39	6,944
	D3'	-0,5032	44,51	0,9106	109,5	8,023
	D4	-0,1816	17,52	0,9758	15,22	4,777

Table 8.2(c) Kinetic analyses : Isothermal TG experiments
under other experimental conditions
Conditions : Gas flowrate 200 ml min⁻¹ (air
unless otherwise stated)
500°C

Other Conditions	Model	a	b (x10 ³)	r	s _{y.x} (x10 ³)	%s _b
+ 5% Cr ₂ O ₃	*R2	-0,1251	8,990	0,9993	8,838	0,303
	R3	-0,1199	7,204	0,9966	15,15	0,648
	D1	-0,2652	11,79	0,9928	36,26	0,948
	D2	-0,2568	9,894	0,9810	49,84	1,552
	D3	-0,1287	4,329	0,9462	37,74	2,687
	D3'	-0,2076	6,258	0,9491	75,13	2,184
	D4	-0,0750	2,744	0,9716	17,03	1,913
+ 50% Cr ₂ O ₃	R2	-0,0674	8,786	0,9994	7,775	0,275
	*R3	-0,0785	7,120	0,9996	4,976	0,217
	D1	-0,1998	11,69	0,9968	23,71	0,630
	D2	-0,2144	10,01	0,9914	33,58	1,041
	D3	-0,1171	4,498	0,9634	31,79	2,194
	D3'	-0,1679	5,813	0,9672	54,33	1,743
	D4	-0,0648	2,803	0,9845	12,67	1,403
+ 5% Al ₂ O ₃	*R2	-0,1275	7,129	0,9976	15,58	0,485
	R3	-0,1201	5,685	0,9926	22,01	0,860
	D1	-0,2675	9,326	0,9890	44,12	1,052
	D2	-0,2534	7,744	0,9722	58,99	1,694
	D3	-0,1239	3,340	0,9308	41,51	2,763
	D3'	-0,1815	4,628	0,9107	84,67	2,823
	D4	-0,0733	2,137	0,9605	19,59	2,038
+ 50% Al ₂ O ₃	*R2	-0,1049	9,775	0,9997	5,756	0,208
	R3	-0,1065	7,883	0,9987	9,445	0,422
	D1	-0,2432	12,90	0,9955	28,50	0,779
	D2	-0,2455	10,96	0,9873	41,04	1,320
	D3	-0,1280	4,875	0,9560	34,88	2,522
	D3'	-0,2018	6,845	0,9468	74,68	2,373
	D4	-0,0728	3,056	0,9793	14,73	1,699
+ 5% Fe ₂ O ₃	*R2	-0,1581	9,480	0,9978	15,44	0,649
	R3	-0,1449	7,576	0,9936	21,08	1,109
	D1	-0,3047	12,37	0,9891	45,07	1,452
	D2	-0,2859	10,32	0,9744	58,31	2,251
	D3	-0,1394	4,494	0,9362	41,29	3,662
	D3'	-0,2259	6,652	0,9386	84,23	3,010
	D4	-0,0826	2,857	0,9638	19,36	2,700

Continued.

Table 8.2(c) Kinetic analyses : Isothermal TG experiments
Continued.
under other experimental conditions
Conditions : Gas flowrate 200 ml min⁻¹ (air
unless otherwise stated)
500°C

Other Conditions	Model	a	b (x10 ³)	r	s _y .x (x10 ³)	%s _b
+ 50% Fe ₂ O ₃	R2	-0,1492	15,06	0,9989	10,73	0,474
	*R3	-0,1443	12,21	0,9993	6,777	0,369
	D1	-0,3034	19,92	0,9950	30,53	1,020
	D2	-0,3024	17,10	0,9902	36,97	1,439
	D3	-0,1570	7,728	0,9644	32,48	2,796
	D3'	-0,2131	9,918	0,9677	59,23	2,163
	D4	-0,0894	4,795	0,9840	13,33	1,850
+ 5% SiO ₂	*R2	-0,0708	6,088	0,9995	7,114	0,230
	R3	-0,0767	4,875	0,9964	15,27	0,617
	D1	-0,1971	8,014	0,9939	32,72	0,805
	D2	-0,1999	6,710	0,9809	48,99	1,439
	D3	-0,1035	2,921	0,9434	37,82	2,551
	D3'	-0,1623	4,067	0,9291	75,89	2,552
	D4	-0,0592	1,858	0,9706	16,94	1,800
+ 50% SiO ₂	*R2	-0,1258	11,75	0,9993	8,346	0,328
	R3	-0,1223	9,463	0,9971	14,06	0,686
	D1	-0,2708	15,50	0,9936	34,48	1,027
	D2	-0,2658	13,11	0,9832	47,47	1,672
	D3	-0,1353	5,805	0,9502	37,16	2,957
	D3'	-0,2224	8,344	0,9593	69,20	2,198
	D4	-0,0780	3,651	0,9745	16,42	2,078
Pelletised at 5 tons for 5 mins	*R2	-0,0936	5,963	0,9995	7,327	0,253
	R3	-0,0949	4,775	0,9966	15,00	0,648
	D1	-0,2257	7,836	0,9938	33,27	0,876
	D2	-0,2236	6,563	0,9813	48,74	1,532
	D3	-0,1139	2,861	0,9441	37,81	2,726
	D3'	-0,1902	4,182	0,9299	82,12	2,691
	D4	-0,0657	1,818	0,9713	16,87	1,914
Pelletised at 5 tons for 10 mins	*R2	-0,0671	6,270	0,9998	4,465	0,262
	R3	-0,0749	5,034	0,9977	12,26	0,897
	D1	-0,1957	8,297	0,9953	29,15	1,294
	D2	-0,2016	6,981	0,9845	44,68	2,358
	D3	-0,1056	3,055	0,9504	35,95	4,335
	D3'	-0,1915	4,620	0,9406	82,92	4,035
	D4	-0,0599	1,937	0,9754	15,74	2,993

Continued.

Table 8.2(c) Kinetic analyses : Isothermal TG experiments
Continued.

Conditions : Gas flowrate 200 ml min⁻¹ (air
unless otherwise stated)
500°C

Other Conditions	Model	a	b (x10 ³)	r	s _{y,x} (x10 ³)	%s _b
Pelletised at 10 tons for 5 mins	*R2	-0,0871	6,549	0,9993	8,719	0,485
	R3	-0,0894	5,240	0,9956	17,02	1,183
	D1	-0,2177	8,607	0,9931	35,17	1,488
	D2	-0,2162	7,195	0,9789	51,89	2,626
	D3	-0,1101	3,128	0,9399	39,31	4,576
	D3'	-0,2073	4,944	0,9338	89,40	4,108
	D4	-0,0636	1,991	0,9682	17,80	3,255
Pelletised at 10 tons for 10 mins	*R2	-0,0998	6,071	0,9977	15,24	0,753
	R3	-0,0984	4,844	0,9928	21,71	1,345
	D1	-0,2337	7,965	0,9894	43,46	1,637
	D2	-0,2261	6,621	0,9731	58,40	2,647
	D3	-0,1124	2,857	0,9323	41,28	4,336
	D3'	-0,1788	4,131	0,9159	86,97	4,298
	D4	-0,0659	1,828	0,9616	19,43	3,190
nO ₂ = 0,1	*R2	-0,0850	3,899	0,9996	6,267	0,180
	R3	-0,0881	3,120	0,9965	14,84	0,531
	D1	-0,2169	5,140	0,9944	31,08	0,675
	D2	-0,2164	4,297	0,9813	47,94	1,246
	D3	-0,1104	1,865	0,9432	37,34	2,237
	D3'	-0,1692	2,610	0,9153	83,00	2,476
	D4	-0,0637	1,189	0,9709	16,66	1,566
nO ₂ = 0,5	*R2	-0,0690	6,738	0,9999	0,831	0,032
	R3	-0,0784	5,433	0,9982	10,58	0,508
	D1	-0,2037	8,976	0,9971	22,23	0,646
	D2	-0,2133	7,608	0,9871	40,03	1,372
	D3	-0,1134	3,360	0,9525	34,82	2,702
	D3'	-0,1782	4,664	0,9302	75,50	2,957
	D4	-0,0638	2,117	0,9780	14,65	1,803
nO ₂ = 0,75	*R2	-0,1236	8,400	0,9995	7,323	0,276
	R3	-0,1195	6,737	0,9968	14,58	0,684
	D1	-0,2671	11,07	0,9939	33,14	0,947
	D2	-0,2597	9,295	0,9821	48,04	1,633
	D3	-0,1305	4,068	0,9464	37,40	2,906
	D3'	-0,2018	5,720	0,9286	79,46	2,987
	D4	-0,0759	2,578	0,9725	16,64	2,040

temperatures best fit the approximate Jander diffusion model, while above 400°C the kinetic behaviour is again consistently described by the contracting-area model. It therefore appears that for slow reaction kinetics (lower temperatures), the pellet reacts by means of an interface moving towards its centre in a 3-dimensional manner, while with increasing reaction rate (higher temperatures), a preferred orientation of interface advance exists and the predominant reaction occurs radially in 2-dimensions.

Table 8.2(c) shows the effect of other experimental conditions on kinetic behaviour. The additions of 50% Cr_2O_3 and of Fe_2O_3 to CrCl_3 give rise to contracting-volume kinetic behaviour, while all other oxide additions show contracting-area behaviour. These results can be correlated with those of Section 5.6, if it is recalled that the rate of reaction of the pellets containing 50% Fe_2O_3 and 50% Cr_2O_3 was markedly increased, apparently as a result of the catalytic behaviour of the oxide additives (Table 5.6). As shown in Section 5.4, different pelletising conditions have little effect on the kinetics of the oxidation, and under all conditions studied, the R2 model best described the experimental results. Similarly, changes in oxygen partial pressure did not influence the kinetic behaviour and the contracting-area model best fits the TG data.

Table 8.2 shows that in most cases, the goodness-of-fit of the best model to the experimental data is described by a correlation coefficient of greater than 0,999, with a standard error of the regression of less than 0,01

(depending on the magnitude of a and b) and the standard error of the slope of less than 0,5%. Except at low temperatures, where 3-dimensional models are preferred, the contracting-area model best describes the experimentally-observed kinetic behaviour in the range $0,05 \leq \alpha \leq 0,95$.

Figures 8.1(a) to (c) and 8.2(a) to (c) show the effect of temperature on the fit of the $f(\alpha)$ -time plots for the R2 model in air and in oxygen. These curves can be compared with their corresponding TG curves in Figures 5.5 and 5.8. For most experiments carried out in air, the lower limit of the straight line fit occurs at $f(\alpha) = 0,05$ to $0,1$, corresponding to $\alpha = 0,15$ to $0,2$, while the upper limit of the fit occurs from $f(\alpha) = 0,7$ to $0,85$, corresponding to $\alpha = 0,91$ to $0,98$. For experiments carried out in oxygen, the lower limit of the fit of the experimental data with the theoretical curves occurs at $f(\alpha) = 0,05$ to $0,15$ ($\alpha = 0,15$ to $0,30$) and the upper limit occurs at $f(\alpha) = 0,6$ to $0,8$ ($\alpha = 0,84$ to $0,96$). The best fits of the experimental data to the theoretical model occur at temperatures from 400 to 600°C ; outside this range significant deviations occur, particularly at temperatures below 400°C . It is therefore apparent that the contracting-area rate expression describes the kinetic behaviour of the oxidation of CrCl_3 pellets in the range $0,15 \leq \alpha \leq 0,90$ in the temperature range 400 to 600°C . Below 400°C , nucleation of Cr_2O_3 on the surface of the CrCl_3 pellet probably becomes a significant factor in the total resistance to reaction at low α -values; at temperatures above 600°C , the rate of the chemical reaction

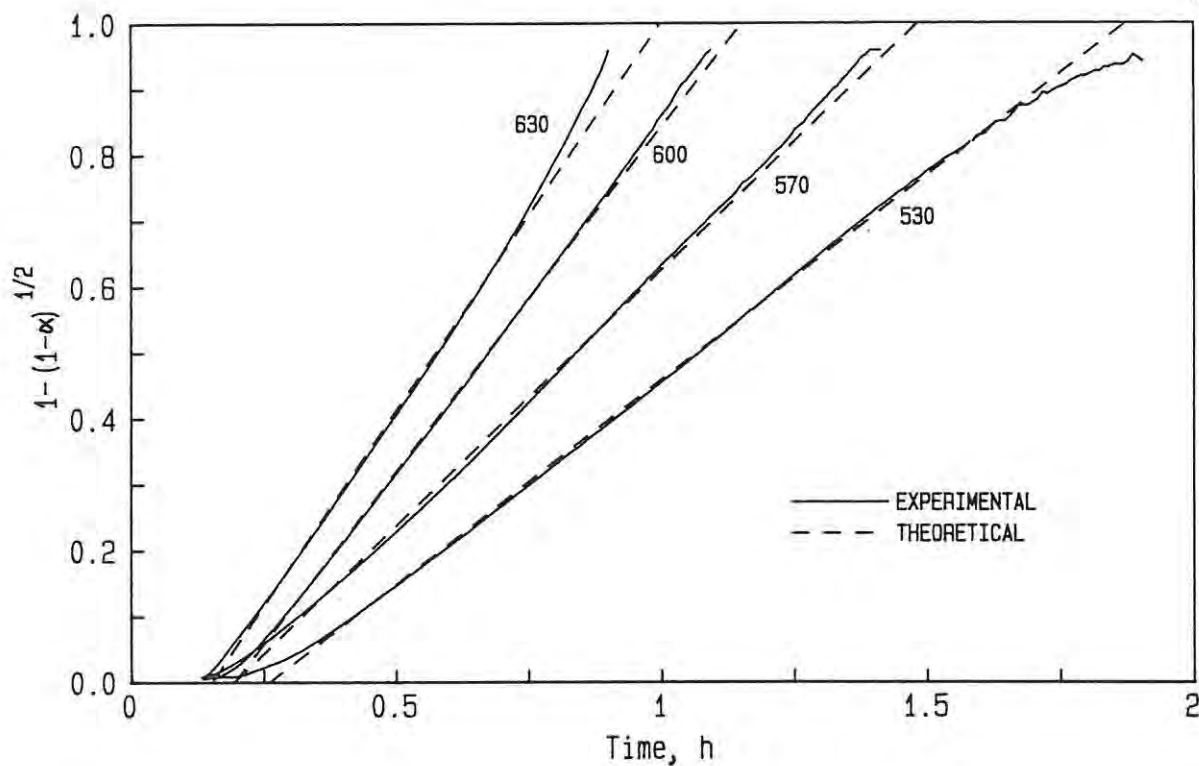


Figure 8.1(a) The effect of temperature on the goodness-of-fit of the $f(\alpha)$ -time plots for the R2 model (air atmosphere)
530 - 630°C

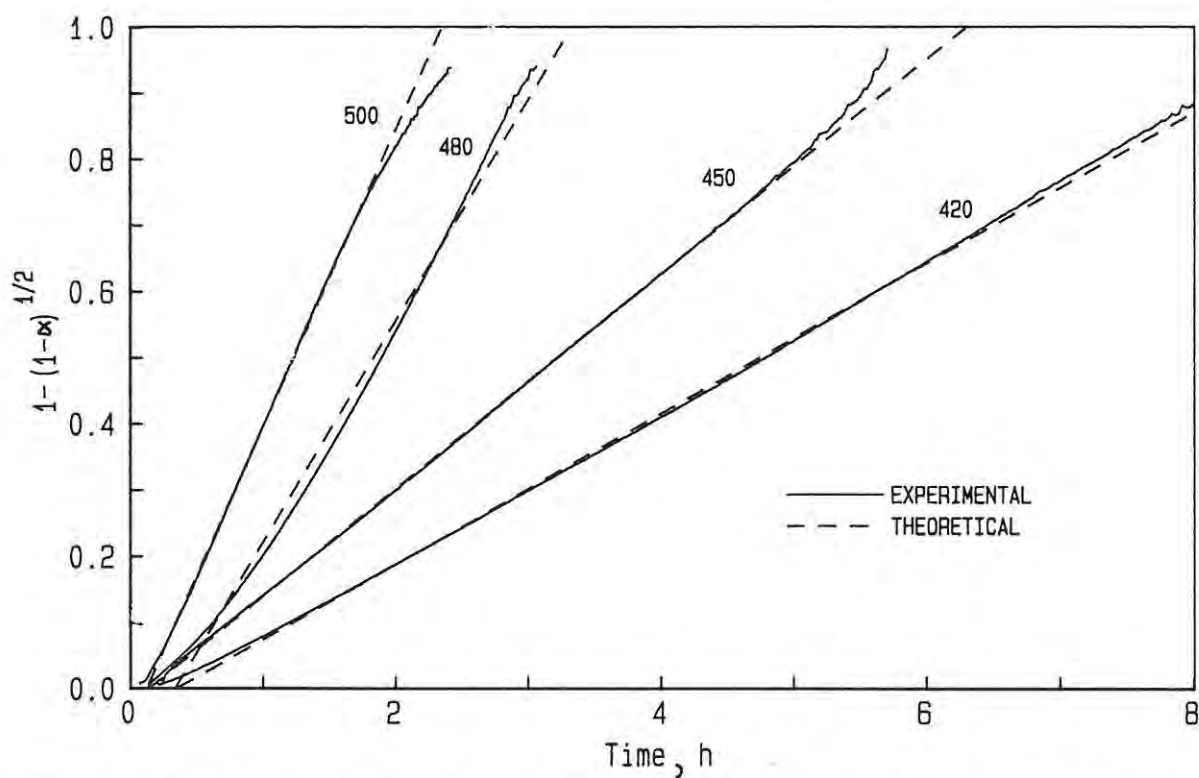


Figure 8.1(b) The effect of temperature on the goodness-of-fit of the $f(\alpha)$ -time plots for the R2 model (air atmosphere)
420 - 500°C

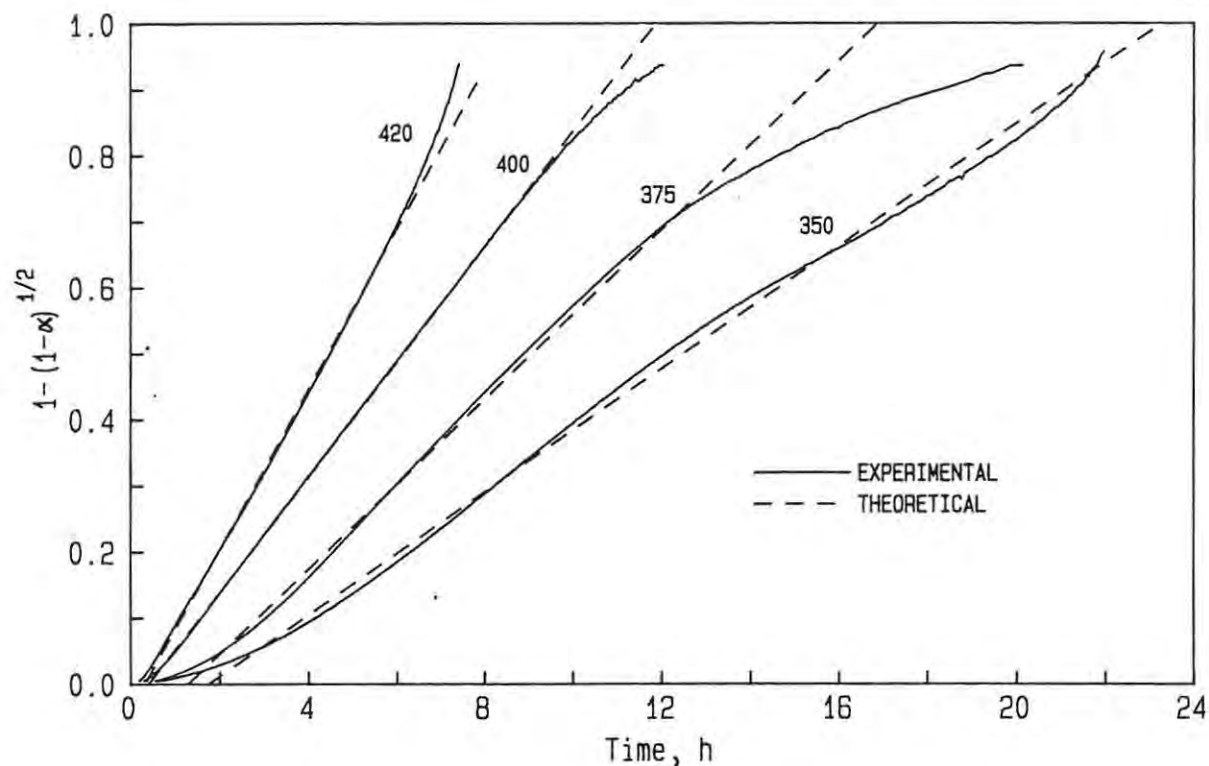


Figure 8.1(c) The effect of temperature on the goodness-of-fit of the $f(\alpha)$ -time plots for the R2 model (air atmosphere) 350 - 420°C

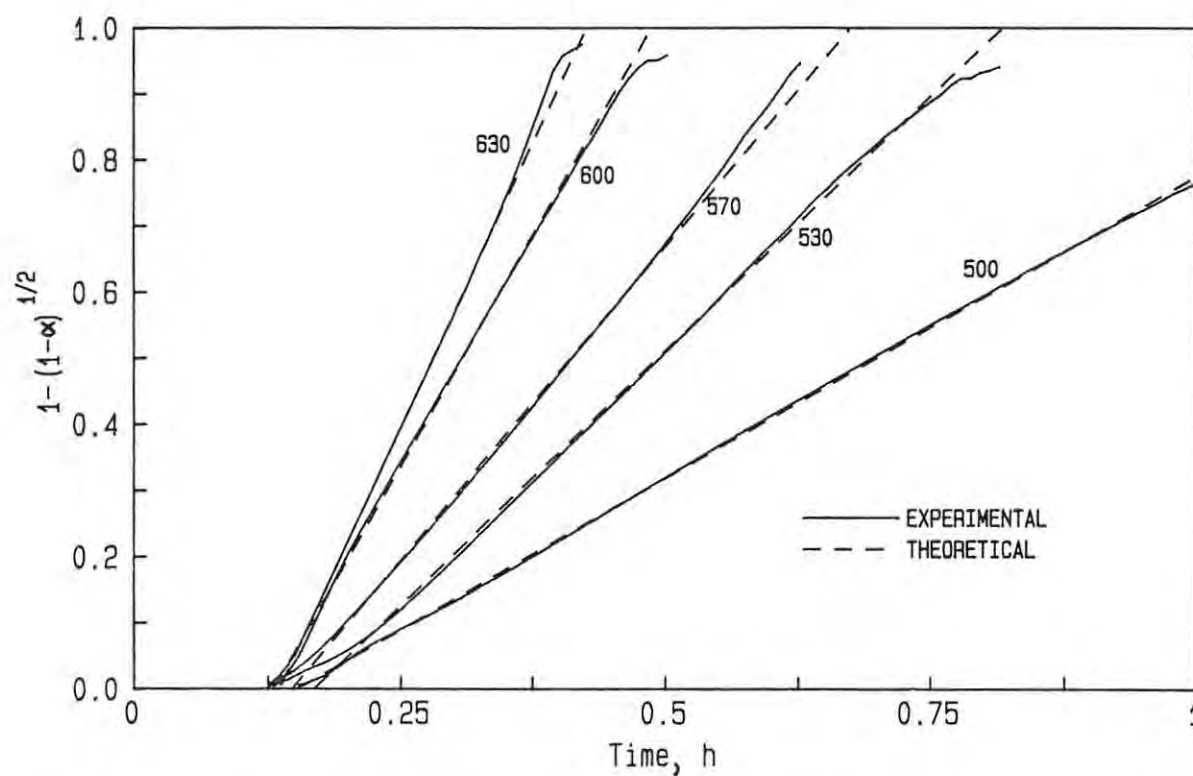


Figure 8.2(a) The effect of temperature on the goodness-of-fit of the $f(\alpha)$ -time plots for the R2 model (oxygen atmosphere) 500 - 630°C

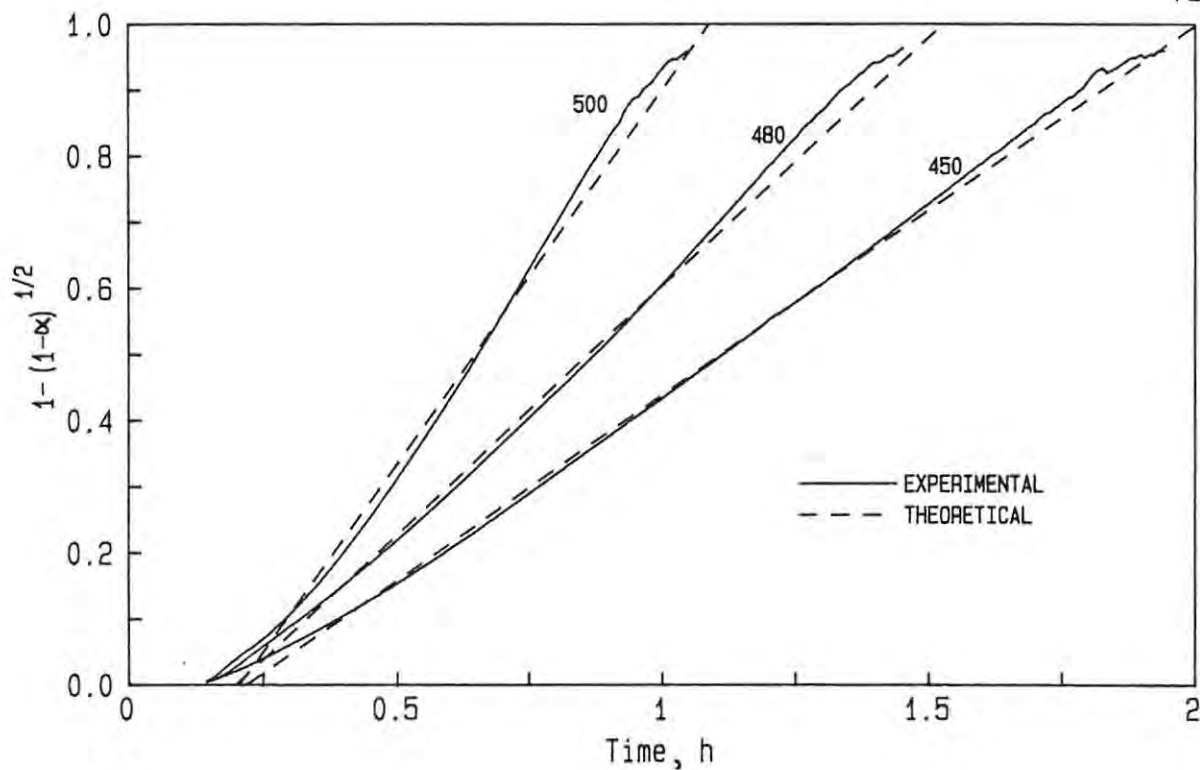


Figure 8.2(b) The effect of temperature on the goodness-of-fit of the $f(\alpha)$ -time plots for the R2 model (oxygen atmosphere) 450 - 500°C

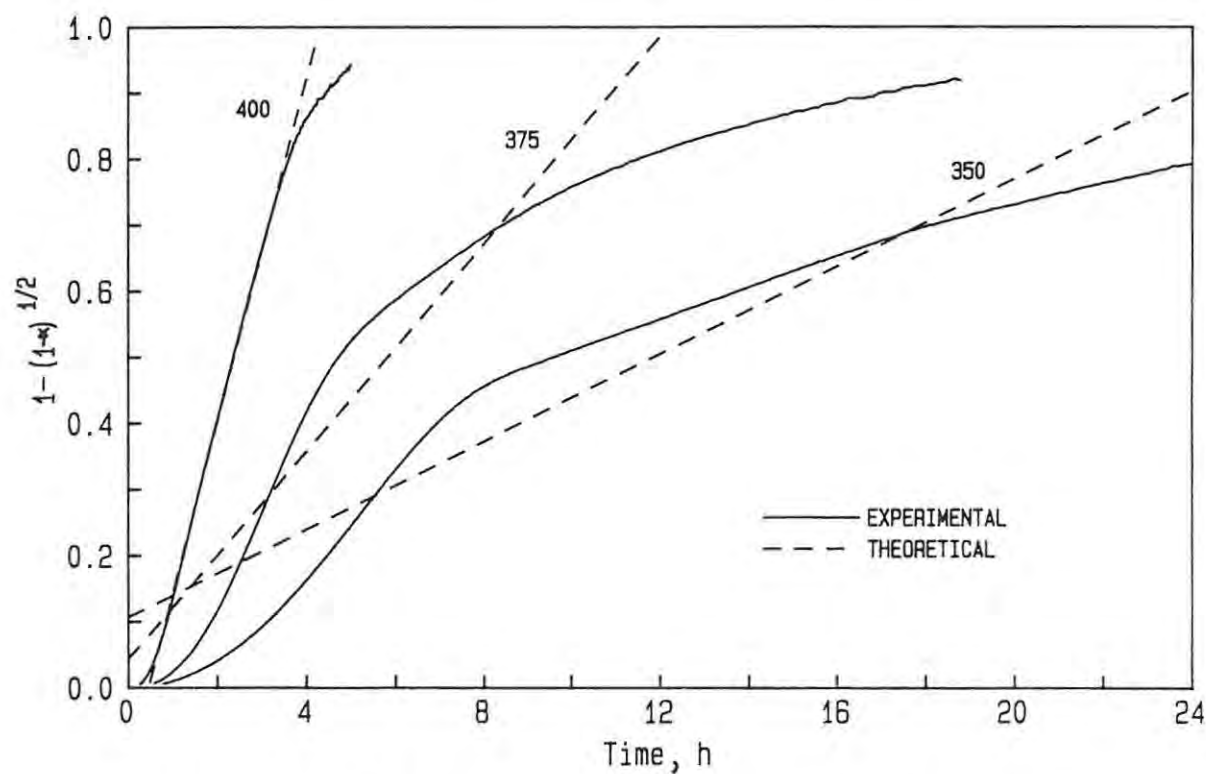


Figure 8.2(c) The effect of temperature on the goodness-of-fit of the $f(\alpha)$ -time plots for the R2 model (oxygen atmosphere) 350 - 400°C

is high and deviations from the (chemical control) R2 model result because mass-transfer resistance to the reaction becomes significant at high conversions.

8.6 Distinguishability of the rate expressions

To determine whether the distinction between the closely-related R2 and R3 models is valid, a technique proposed by Brown and Galwey⁵⁶ has been adopted. They found that the introduction of simulated experimental errors decreased the distinguishability between models, and hence determined acceptable levels for the statistical parameters which would ensure reliable distinction. They showed that $s_{y,x}$ and $\%s_b$ are comparable as reliable indicators of the goodness-of-fit of the model with the experimental data, but that interpretations based on the correlation coefficient could not be made with confidence. The ratios $\%s_{bA}/\%s_{bB}$ and $s_{y,xA}/s_{y,xB}$ were calculated from simulated data for models A and B and the larger the ratios, the more reliably the models could be distinguished. Models R2 and R3 were found to be closely comparable, but even with random errors in α introduced up to a level of 10%, these models could be distinguished using either of the above ratios. The results of the application of this technique to the present study are shown in Tables 8.3(a) to (c).

Results of this analysis confirm that for the experimental conditions and α -range studied, the contracting-area (R2)

Table 8.3(a) Distinguishability of the R2 and R3 models for isothermal TG experiments in air (see Table 8.2(a))

Temp (°C)	$s_{y,x}$ ($\times 10^3$)		$\%s_b$		$s_{y,xR3}/s_{y,xR2}$	$\%s_{bR3}/\%s_{bR2}$	Best Model
	R2	R3	R2	R3			
350	12,88	8,841	0,349	0,298	0,686	0,854	R3
375	11,84	8,999	0,527	0,494	0,760	0,937	?
400	8,715	4,271	0,279	0,169	0,490	0,605	R3
400	1,798	9,267	0,0582	0,371	5,15	6,37	R2
400	26,43	10,89	0,977	0,491	0,412	0,503	R3
400	12,01	1,561	0,405	0,0648	0,130	0,160	R3
420	4,956	14,33	0,143	0,514	2,89	3,59	R2
420	6,002	14,85	0,170	0,526	2,48	3,09	R2
450	2,207	11,85	0,0625	0,416	5,37	6,66	R2
500	3,999	10,46	0,128	0,415	2,62	3,24	R2
500	16,12	22,77	0,514	0,910	1,412	1,77	R2
500	14,63	21,51	0,428	0,792	1,47	1,85	R2
530	6,150	14,83	0,235	0,707	2,41	3,01	R2
530	5,660	6,517	0,199	0,283	1,15	1,42	R2
530	5,671	14,57	0,209	0,669	2,57	3,20	R2
570	9,919	18,14	0,435	0,995	1,83	2,29	R2
570	9,806	17,66	0,414	0,930	1,80	2,25	R2
580	6,016	15,04	0,286	0,892	2,50	3,12	R2
600	7,562	16,13	0,381	1,015	2,13	2,66	R2
600	10,44	18,44	0,512	0,131	1,77	0,256	?
600	4,554	13,69	0,232	0,868	3,01	3,74	R2
600	9,955	17,99	0,451	1,019	1,81	2,26	R2
600	6,076	14,93	0,287	0,880	2,46	3,07	R2
630	7,009	16,00	0,339	0,967	2,28	2,85	R2

model best describes the reaction rate in most cases. Deviations from this behaviour usually occur at temperatures less than 400°C, where the R3 model appears to fit better. A possible explanation of this observation is that rate constants for reaction in different directions through the pellet have different temperature dependences (i.e. different A and E_a values for reaction in different directions). The relative rates in different directions thus change with temperature.

Table 8.3(b) Distinguishability of the R2 and R3 models for isothermal TG experiments in oxygen (see Table 8.2(b))

Temp (°C)	$s_{y,x}$ ($\times 10^3$)		$\%s_b$		$s_{y,xR3}/s_{y,xR2}$	$\%s_{bR3}/\%s_{bR2}$	Best Model
	R2	R3	R2	R3			
400	4,975	10,27	0,186	0,475	2,064	2,554	R2
400	8,697	6,819	0,508	0,494	0,784	0,972	?
450	8,537	16,51	0,312	0,755	1,934	2,420	R2
480	12,61	20,04	0,555	1,106	1,589	1,993	R2
500	21,46	26,65	1,088	1,701	1,240	1,563	R2
500	3,510	8,542	0,168	0,507	2,434	3,018	R2
500	5,154	12,61	0,232	0,707	2,447	3,047	R2
530	9,941	17,59	0,582	1,288	1,769	2,213	R2
570	7,036	16,09	0,477	1,359	2,287	2,849	R2
600	7,333	6,572	0,619	0,689	0,896	1,113	?
630	2,016	11,33	0,193	1,359	5,620	7,041	R2

Table 8.3(c) Distinguishability of the R2 and R3 models for isothermal TG experiments carried out under other experimental conditions (see Table 8.2(c))

Condi- tions	$s_{y,x}$ ($\times 10^3$)		$\%s_b$		$s_{y,xR3}/s_{y,xR2}$	$\%s_{bR3}/\%s_{bR2}$	Best Model
	R2	R3	R2	R3			
5% Cr ₂ O ₃	8,838	15,15	0,303	0,648	1,714	2,139	R2
50% Cr ₂ O ₃	7,775	4,976	0,275	0,217	0,640	0,789	R3
5% Al ₂ O ₃	15,58	22,01	0,486	0,860	1,413	1,769	R2
50% Al ₂ O ₃	5,756	9,445	0,208	0,422	1,641	2,029	R2
5% Fe ₂ O ₃	15,44	21,08	0,649	1,109	1,365	1,709	R2
50% Fe ₂ O ₃	10,73	6,777	0,474	0,369	0,632	0,778	R3
5% SiO ₂	7,114	15,27	0,230	0,617	2,146	2,683	R2
50% SiO ₂	8,346	14,06	0,328	0,686	1,685	2,091	R2
5 t 5 min	7,327	15,00	0,253	0,648	2,047	2,561	R2
5 t 10 min	4,465	12,26	0,262	0,897	2,746	3,424	R2
10 t 5 min	8,719	17,02	0,485	1,183	1,952	2,439	R2
10 t 10 min	15,24	21,71	0,753	1,345	1,425	1,786	R2
nO ₂ = 0,1	6,267	14,84	0,180	0,531	2,368	2,950	R2
nO ₂ = 0,5	7,323	14,58	0,276	0,684	1,991	2,478	R2
nO ₂ = 0,75	0,831	10,58	0,032	0,508	12,73	15,88	R2

An attempt was made to divide the low temperature curves into two sections and then to analyse each separately. The division was made where the slope of the curve changed from acceleratory to deceleratory. This procedure did not prove successful and the models tried showed less agreement with the experimental data than did the R2 and R3 models already discussed.

At lower temperatures the acceleratory period of the reaction contributes to a substantial fraction of the total reaction time and deviation from the contracting-geometry models is larger than for experiments at higher temperatures. Attempts to fit the Avrami-Erofeev and the Prout-Tompkins equations to these data were thus also made. Experimental data deviated substantially from any of the theoretical sigmoid models. Thus although a particular model may accurately describe a reaction system under certain conditions, it may not be able to account for the rate behaviour of the system under all conditions.

8.7 Determination of the Arrhenius parameters

Once the best rate expression

$$f(\alpha) = kt \tag{8.1}$$

for a series of experiments has been identified, and it has been shown that the model does not change as the temperature is changed, other kinetic parameters can be calculated.

The apparent rate constant, k , is given by the slope of the best straight line through the plot of $(f(\alpha)_i, t_i)$ values. The dependence of the rate constant on the reaction temperature (other experimental conditions being kept constant) is usually considered to be adequately described by the simplest form of the Arrhenius relation

$$k = A \exp (-E_A/RT) \quad (8.27)$$

where E_A is the apparent activation energy for the reaction

R is the universal gas constant

T is the absolute temperature at which k has been measured

A is the pre-exponential or frequency factor.

The constants E_A and A are usually determined from a plot of $\ln k$ against reciprocal temperature $(1/T)$, which should yield a straight line with slope $-E_A/R$ and y-intercept $\ln A$. The apparent activation energy for the reaction can then be determined.

The definition and interpretation of the kinetic parameters k , E_A and A for solid-gas reactions is, however, a contentious issue^{46,58,59}. Kinetic theory was originally developed from studies of homogeneous reaction systems. In such systems, the rate constant, k , is readily interpreted by relating the overall rate of the reaction to the concentrations of the reacting species. The activation energy, E_A , is the minimum energy needed to raise the energy of the reactants from their existing state to an "activated" state, from which they can either go on to the product state, or back to the reactant state. The pre-exponential

factor, A , is interpreted in terms of the frequency of occurrence of the reaction configuration; reactant species must have a particular physical orientation in space for the reaction to occur (other factors being suitable). Kinetic theory, as classically defined, assumes that the reacting species have an energy distribution described by the Boltzmann function, and that the rate constant has an exponential dependence on temperature as given by the Arrhenius relation.

In solid-gas reactions, the concepts of concentration and order of reaction have little significance. The reaction rate is measured in terms of the change with time of, for example, the thickness of the product layer or the moles of product formed. Factors which have no counterpart in homogeneous systems now become important. Thermal gradients will generally exist in a heated solid and crystal imperfections will give rise to marked energy changes within a single crystal. Grain boundaries, lattice vacancies, crystal dislocations and other defects result in certain localised regions of a crystal, such as surfaces and edges, being higher in energy, and therefore more reactive, than other regions. The concept of a collision between reactant species also needs rethinking when considering heterogeneous reactions.

It has been suggested^{58,60} that a physical interpretation for E_a and A can only be given when an adequate model for the reaction mechanism is known. In general, E_a and A are

usually thought of as empirical parameters which both need to be evaluated in order to define the temperature dependence of the rate constant, k , rather than as parameters which describe physical concepts at the molecular level. Although considerable debate on the use of the Arrhenius parameters still takes place, it is acknowledged that under certain conditions and for specific reaction systems, determination and interpretation of the kinetic parameters can be justified, and that provided that analogies with homogeneous systems are made with care, useful information may be obtained.

Figure 8.3 shows the Arrhenius plots for isothermal TG experiments carried out in air and in oxygen, while Table 8.4 summarises these results. The values of k have been obtained by fitting the experimental data to the R2 (contracting-area) rate equation. Arrhenius plots were also carried out using k values determined from other models, but, as has been reported^{61,62}, changing the model did not significantly affect the value of the activation energy calculated.

The calculated values of the "apparent activation energy" are the same for reactions carried out both in pure oxygen and in air above 400°C. Assuming the conventional interpretation of the activation energy, this suggests that (in the range of oxygen partial pressures examined) the rate of provision of oxygen at the reaction site does not influence the nature of the reaction occurring. The values of the

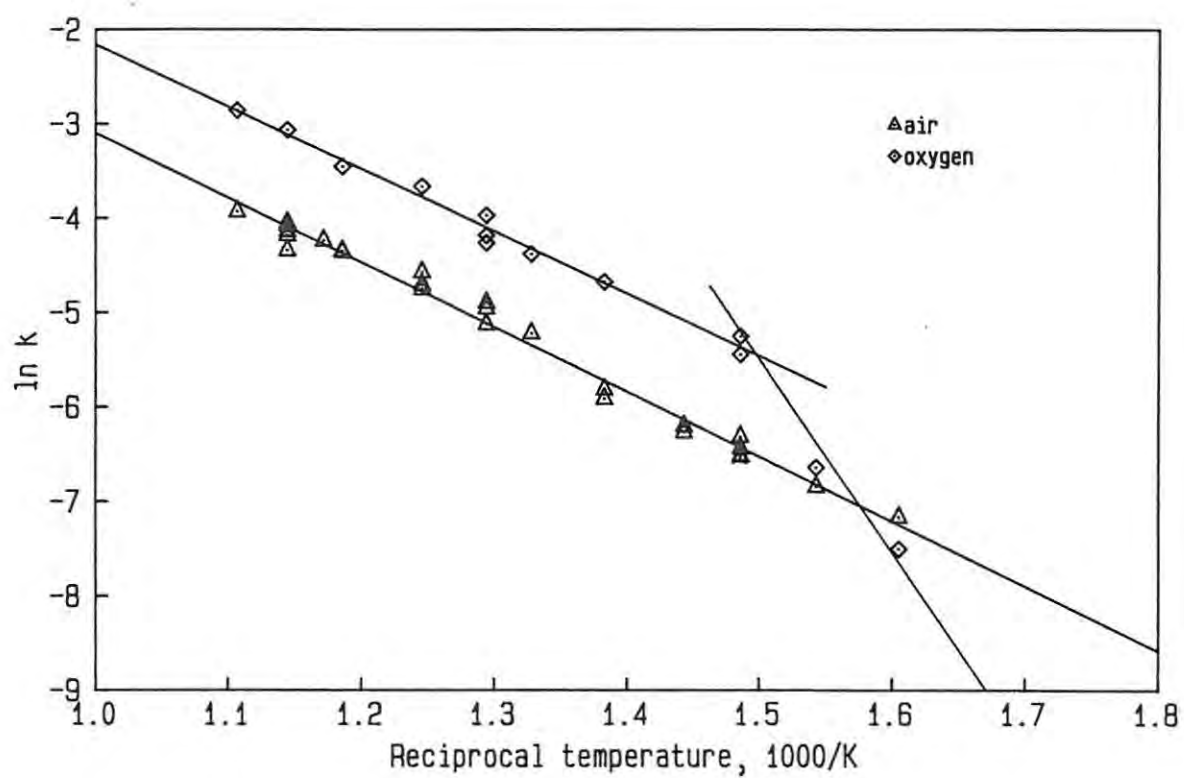


Figure 8.3 Arrhenius plots calculated for the oxidation of CrCl_3 from the R2 rate expression

Table 8.4 Analyses of the Arrhenius parameters for isothermal TG experiments in air and in oxygen, modelled according to the R2 and R3 models

Atm.	Model	Temp range (°C)	E_A (kJ mol ⁻¹)	A (min ⁻¹)
Air	R2	350-630	59,0 ± 1,3	43 ± 5
	R3	350-630	56,8 ± 1,3	33 ± 5
Oxygen	R2	350-400	160 ± 27	1 ± 0,2 × 10 ¹⁰
	R3	350-400	158 ± 28	1 ± 0,2 × 10 ¹⁰
	R2	400-630	54,9 ± 2,2	85 ± 8
	R3	400-630	54,8 ± 2,1	67 ± 7

pre-exponential (frequency) factor, A, are much higher for reactions carried out in oxygen, consistent with the observation of increasing reaction rates with increasing oxygen partial pressures (Figure 5.14).

At temperatures below 400°C there is a sharp and distinct change in the slope of the Arrhenius plot for reactions in oxygen. This probably corresponds to a change in the rate-determining mechanism from one type of chemical control to another, i.e. the chemical reaction occurring must itself be changing. Similarly, Figure 8.2(c) clearly demonstrated that the contracting-area (R2) model proposed for most reactions studied, does not account satisfactorily for the rate behaviour under these extreme conditions. In Section 5.3.2 it was observed that under conditions of low temperatures and high oxygen partial pressures, chromyl chloride was formed as a result of a competing side-reaction, and it is therefore likely that these effects may be due to the occurrence of this reaction. This has not been studied further in this investigation.

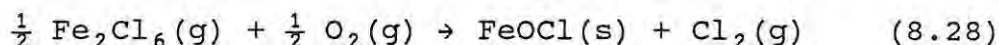
The magnitudes of apparent activation energies obtained from conventional Arrhenius plots have often been used as indicators of the reaction mechanisms which apply⁶³. Low values of the activation energy ($E_A < 20 \text{ kJ mol}^{-1}$) have been taken to imply diffusion control, and high values ($E_A \approx 40$ to 400 kJ mol^{-1}) to imply chemical control, while intermediate values are typical for reactions under mixed control. The value of the apparent activation energy obtained for the oxidation reaction in this study falls within the typical range for reactions under chemical control, although the value is still relatively low.

In Section 3.3, it was shown that the enthalpy change for the reaction, at a typical reaction temperature of 500°C , is $\sim 20 \text{ kJ mol}^{-1}$. This low value means that a low activation energy would not be unexpected.

In the present system, CrCl_3 is converted to Cr_2O_3 by a solid-gas reaction, and therefore the chromium atoms are unlikely to undergo any change in their lattice positions so that the solid product is pseudomorphic with the starting material. The relatively small structural changes occurring during the oxidation are further evidence that the low activation energy measured and attributed to chemical reaction rate control is not unreasonable.

Other researchers have also reported low E_A values for reactions under chemical control. Eckhardt and Flanagan⁶⁴ studied the dehydration of manganese formate, the kinetics

of which were described by a contracting-geometry model. They obtained an activation energy of $73,6 \text{ kJ mol}^{-1}$, which is close to the value for the enthalpy of dehydration, $57,7 \text{ kJ (mol H}_2\text{O)}^{-1}$. Basu and Roy⁶⁵ studied the oxidation of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ in the temperature range 195 to 535°C . They concluded that the chemical reaction proceeds in parallel with the sublimation of ferric chloride, and measured an activation energy of $18,6 \text{ kJ mol}^{-1}$. In a similar study, Gurov and Orlov⁶⁶ reported that the rate-controlling step of the reaction of anhydrous FeCl_3 with oxygen was the chemical reaction



and that the activation energy of the overall reaction was $72,0 \text{ kJ mol}^{-1}$. In contrast, Hills⁶⁷ has quoted examples of reactions in which it has been shown that mass-transfer effects provide the major resistance to the reaction, and yet such reactions have apparent activation energies typical of reactions limited by the rate of the chemical reaction.

It is therefore suggested that the numerical value of the activation energy may not always be a reliable indicator of the nature of the rate-determining step. In the present system, however, it has been shown that there is sufficient evidence to justify a claim of chemical control as the rate-limiting step, where the chemical reaction has an apparent activation energy of $\sim 60 \text{ kJ mol}^{-1}$.

8.8 An alternate method of kinetic analysis

As mentioned in Section 5.3.1, the shapes of the isothermal TG curves in Chapter 5 show that these comprise an initial acceleratory period corresponding to nucleation and the development of the interface, followed by a linear region during which the rate of reaction is approximately constant, before the deceleratory portion of the curve starts. In Section 8.5 it has been shown that the shapes of these curves are best described mathematically by the contracting-area model

$$1 - (1 - \alpha)^{1/2} = kt \quad (8.13)$$

in the α -range 0,15 to 0,90 and the temperature range 400 to 600°C.

Eckhardt and Flanagan⁶⁵ have shown that this rate equation can be rewritten using a series expansion :

$$\begin{aligned} \alpha &= 1 - (1 - kt)^2 \\ &= 1 - (1 - 2kt + k^2t^2) \\ &= 2kt - k^2t^2 \end{aligned} \quad (8.29)$$

Thus in the early stages of applicability of the R2 model (short reaction times - low t), there should be an approximately linear region of the α -time curves, where only the first term of equation (8.29) contributes significantly to the value of α . As the reaction progresses and the time increases, both the linear and quadratic terms contribute to describing the overall rate behaviour. As the temperature increases and hence k increases, this linear region would also become less noticeable.

Some of the α -time curves of this study were thus divided into "linear" and "deceleratory" portions, following which the apparent rate constants for these regions were calculated. Comparisons of these results with those obtained in Section 8.5 are presented in Tables 8.5(a) and (b). The linear portion has been defined as the interval $0,2 \leq \alpha \leq 0,5$ and the deceleratory portion as $0,5 \leq \alpha \leq 0,9$. The rate constants determined from these analyses have then been used in Arrhenius plots to determine the apparent activation energy of the reaction (Figures 8.4(a) and (b)).

By choosing more restricted α -ranges for analysis, the magnitude of the errors ($s_{y,x}$ and $\%s_b$) is reduced considerably, thus showing that although this method of analysis is an approximation only, useful results can be obtained. This approximation also provides mathematical support for the shape of the α -time curves and explains why the deceleratory nature of the plot is not obvious during the early stages of the reaction. The apparent activation energies of the reaction in air and oxygen (Table 8.6) are within the experimental error of the values determined in Section 8.7. A quick-and-easy approximation for the activation energy of a reaction can therefore be obtained from the slopes of the linear portion of the α -time curves, without resort to curve-fitting procedures.

Table 8.5(a) Comparison of data obtained from analysis of the deceleratory and linear portions of α -time curves (air atmosphere)

Temp (°C)	α_{min}	α_{max}	a	b ($\times 10^3$)	r	$s_{y \cdot \bar{x}}$ ($\times 10^3$)	% s_b
350	0,05	0,95	-0,0805	0,7745	0,9984	12,88	0,349
	0,20	0,50	-0,1396	1,321	0,9999	0,675	0,0981
	0,50	0,90	-0,0635	0,7642	0,9974	8,25	0,634
375	0,05	0,95	-0,0821	1,069	0,9988	11,84	0,5267
	0,20	0,50	-0,1474	1,853	0,9999	1,289	0,327
	0,50	0,90	-0,0829	1,087	0,9996	3,110	0,4112
400	0,05	0,95	-0,0296	1,490	0,9992	8,715	0,279
	0,20	0,50	-0,-426	2,581	0,9990	4,082	0,692
	0,50	0,90	-0,0181	1,476	0,9997	2,532	0,217
450	0,05	0,95	-0,707	2,982	0,9973	16,32	0,467
	0,20	0,50	-0,0300	4,121	0,9999	0,5891	0,080
	0,50	0,90	-0,1416	3,325	0,9998	2,280	0,184
480	0,05	0,95	-0,1083	5,417	0,9961	19,51	0,712
	0,20	0,50	-0,0982	7,663	0,9999	0,961	0,169
	0,50	0,90	-0,1875	6,068	0,9997	3,012	0,316
530	0,05	0,95	-0,1608	10,33	0,9996	6,150	0,235
	0,20	0,50	-0,2094	16,06	0,9997	2,187	0,425
	0,50	0,90	-0,1851	10,68	0,9999	1,314	0,139
570	0,05	0,95	-0,1437	12,92	0,9991	9,806	0,435
	0,20	0,50	-0,1703	19,15	0,9999	0,814	0,167
	0,50	0,90	-0,1935	13,74	0,9999	1,168	0,139
600	0,05	0,95	-0,1534	16,93	0,9994	7,562	0,381
	0,20	0,50	-0,1697	25,05	0,9999	1,361	0,340
	0,50	0,90	-0,1854	17,67	0,9999	1,424	0,191
630	0,05	0,95	-0,1789	19,69	0,9995	7,009	0,339
	0,20	0,50	-0,2255	30,14	0,9998	1,584	0,370
	0,50	0,90	-0,1968	20,10	0,9999	1,952	0,258

Table 8.5(b) Comparison of data obtained from analysis of the deceleratory and linear portions of α -time curves (oxygen atmosphere)

Temp (°C)	α_{min}	α_{max}	a	b ($\times 10^3$)	r	$S_{y \cdot x}$ ($\times 10^3$)	% S_b
400	0,05	0,95	-0,1153	4,329	0,9997	4,975	0,186
	0,20	0,50	-0,1779	7,238	0,9998	1,713	0,350
	0,50	0,90	-0,1152	4,348	0,9999	1,001	0,105
450	0,05	0,95	-0,1212	9,331	0,9993	8,537	0,312
	0,20	0,50	-0,1403	14,16	0,9999	0,7005	0,131
	0,50	0,90	-0,1464	9,672	0,9999	0,6738	0,0707
480	0,05	0,95	-0,1485	12,54	0,9983	12,61	0,555
	0,20	0,50	-0,1589	18,30	0,9999	0,7184	0,154
	0,50	0,90	-0,1940	13,30	0,9995	3,673	0,462
500	0,05	0,95	-0,2323	18,89	0,9956	21,46	1,088
	0,20	0,50	-0,2946	27,35	0,9999	1,154	0,306
	0,50	0,90	-0,3270	21,18	0,9997	2,690	0,397
530	0,05	0,95	-0,2585	25,68	0,9991	9,941	0,582
	0,20	0,50	-0,3883	41,06	0,9999	1,245	0,420
	0,50	0,90	-0,2878	26,59	0,9999	1,590	0,292
570	0,05	0,95	-0,2791	31,62	0,9995	7,036	0,477
	0,20	0,50	-0,3775	48,20	0,9998	1,814	0,669
	0,50	0,90	-0,3065	32,60	0,9999	1,167	0,210
600	0,05	0,95	-0,3639	46,67	0,9995	7,333	0,619
	0,20	0,50	-0,6120	80,60	0,9971	8,716	3,116
	0,50	0,90	-0,3330	45,13	0,9999	0,471	0,0965
630	0,05	0,95	-0,4662	57,37	0,9999	2,016	0,193
	0,20	0,50	-0,7119	92,00	0,9995	3,165	1,534
	0,50	0,90	-0,4663	57,32	0,9999	1,000	0,241

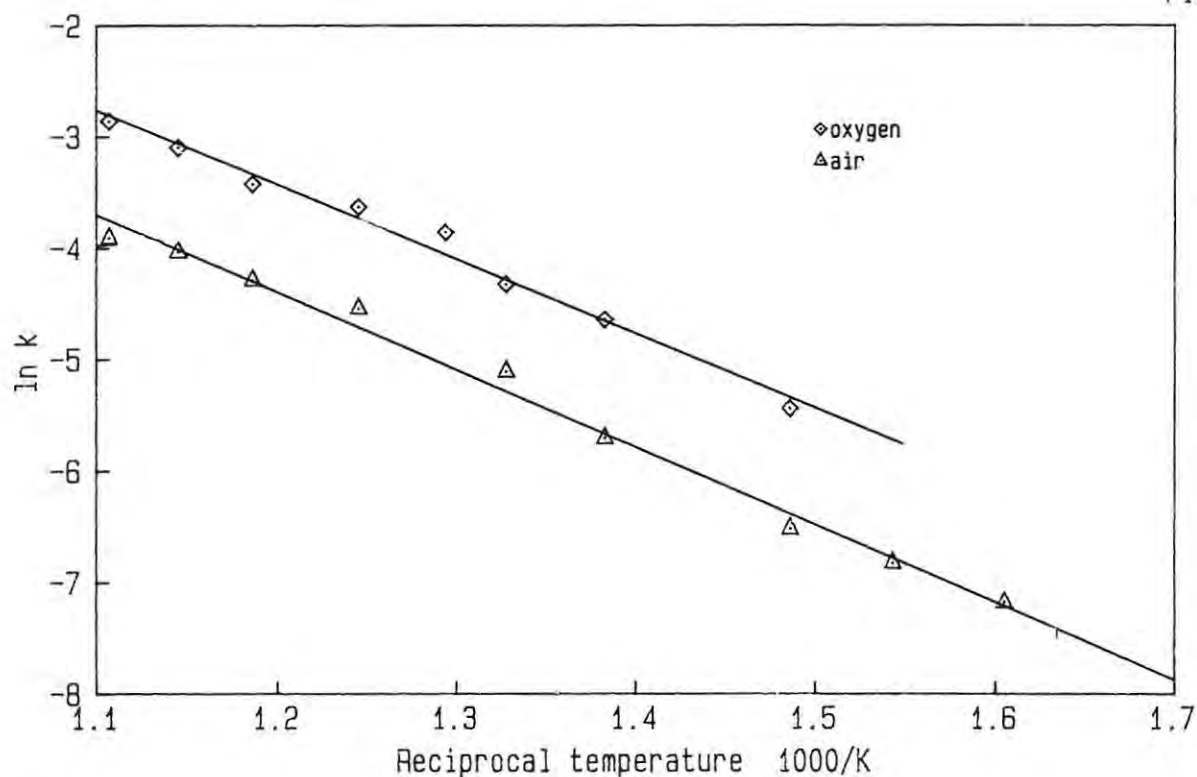


Figure 8.4(a) Arrhenius plots for the oxidation of CrCl_3 calculated from kinetic analysis of the deceleratory portion of the α -time curves

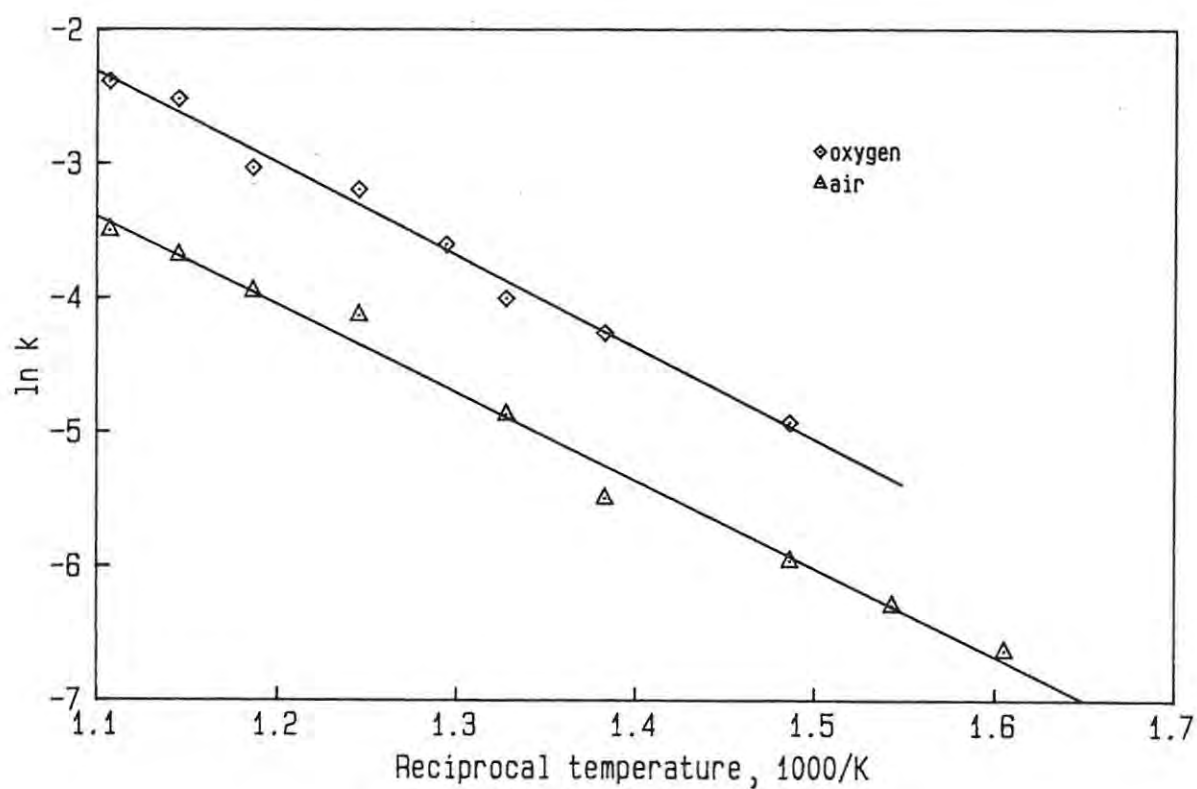


Figure 8.4(b) Arrhenius plots for the oxidation of CrCl_3 calculated from kinetic analysis of the linear portion of the α -time curves

Table 8.6 Arrhenius parameters calculated from kinetic analysis of the linear and deceleratory portions of α -time curves

Atmosphere	Temp range (°C)	α -range	E_a (kJ mol ⁻¹)
Air	350 - 630	0,05 - 0,95	59,0 ± 1,3
		0,20 - 0,50	54,5 ± 2,1
		0,50 - 0,90	57,8 ± 2,0
Oxygen	400 - 630	0,05 - 0,95	54,9 ± 2,2
		0,20 - 0,50	57,1 ± 2,5
		0,50 - 0,90	55,5 ± 2,8

8.9 Summary

Isothermal thermogravimetric data have been analysed using the rate expressions derived for the solid-gas reaction of a disc-shaped pellet according to the unreacted shrinking-core model. Under the experimental conditions used, it has been shown that over the range of reaction $0,15 \leq \alpha \leq 0,90$ the kinetic behaviour is best described by a contracting-geometry rate expression - either the R2 or the R3 model.

Arrhenius plots, obtained using rate constants from these models, are linear over the temperature range 400 to 600°C. The apparent activation energy of the reaction has been measured to be ~59 kJ mol⁻¹.

9. COMMERCIALY-IMPORTANT PROPERTIES OF Cr_2O_3 PRODUCED BY THE OXIDATION OF CrCl_3

In previous chapters it has been shown that Cr_2O_3 can be produced from CrCl_3 very readily, at relatively low temperatures, and without resort to sophisticated procedures. It is therefore probable that the engineering design of a reactor to carry out this reaction on a large scale should be straightforward and uncomplicated. As discussed in Chapter 1, both chemical and physical properties of the oxide are of considerable importance in determining its value to the end user. Commercially-important properties of this oxide are now briefly considered in order to identify suitable markets for the product.

9.1 Chemical analysis of Cr_2O_3 produced by the oxidation of CrCl_3

The oxide produced in the present study was derived from CrCl_3 manufactured from electrolytic chromium, so the only impurity of interest at this stage is the residual chloride content.

Cr_2O_3 pellets produced under various experimental conditions were analysed for residual chloride content. The values were all found to be <150 ppm, with some as low as 60 ppm. These values confirm the thermodynamic prediction (Section 3.1) that there is no difficulty in achieving completeness of reaction.

9.2 Physical properties

As discussed in Chapter 1, if the oxide is to be used as a pigment, physical properties such as colour, particle size, particle size distribution and shape become important. Some of these aspects are discussed below.

9.2.1 Colour

Three dimensions are used to describe colour quantitatively⁶⁷. The hue of a colour fixes its position in the spectrum and describes its relationship to other colours. The saturation, or "colourfulness", of a colour describes its strength or richness, e.g. a highly-saturated red comprises light reflected only from the red part of the spectrum and not diluted by any other colour. The brightness, or "lightness", may be described as the position of a colour in relation to a black to white scale.

A typical CIE chromaticity diagram is shown in Figure 9.1. Such a diagram is defined as a diagram in which distances along suitable axes represent chromaticity coordinates i.e. the colour of any sample may be plotted using x,y coordinates. The region of the plot where each of the primary colours predominates is illustrated, while the centre achromatic point, or "white point", (coordinates 0,3086;0,3154) has equal proportions of all three colours. The CIE diagram is two dimensional, dealing only with hue and colour saturation; it does not take into account

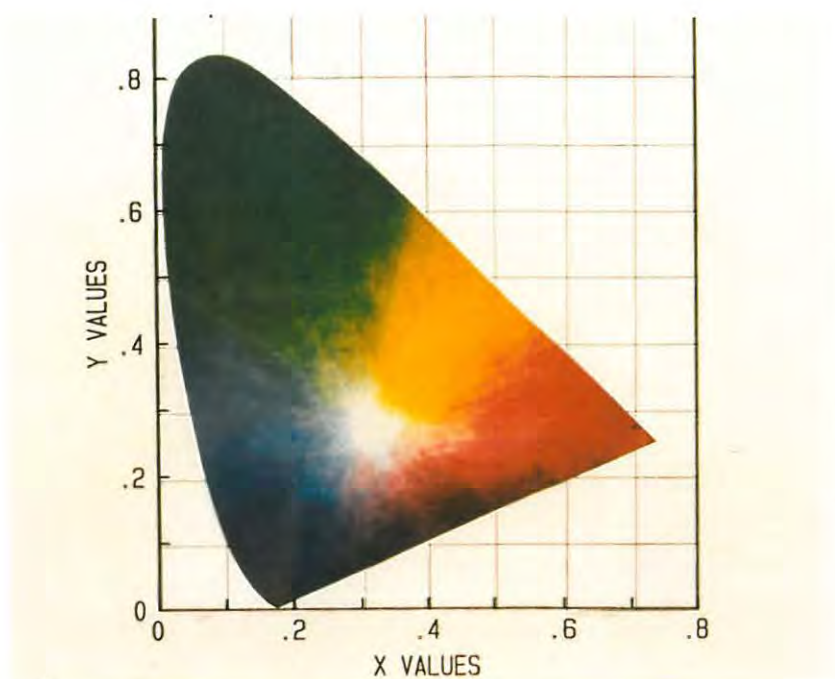


Figure 9.1 The CIE chromaticity diagram

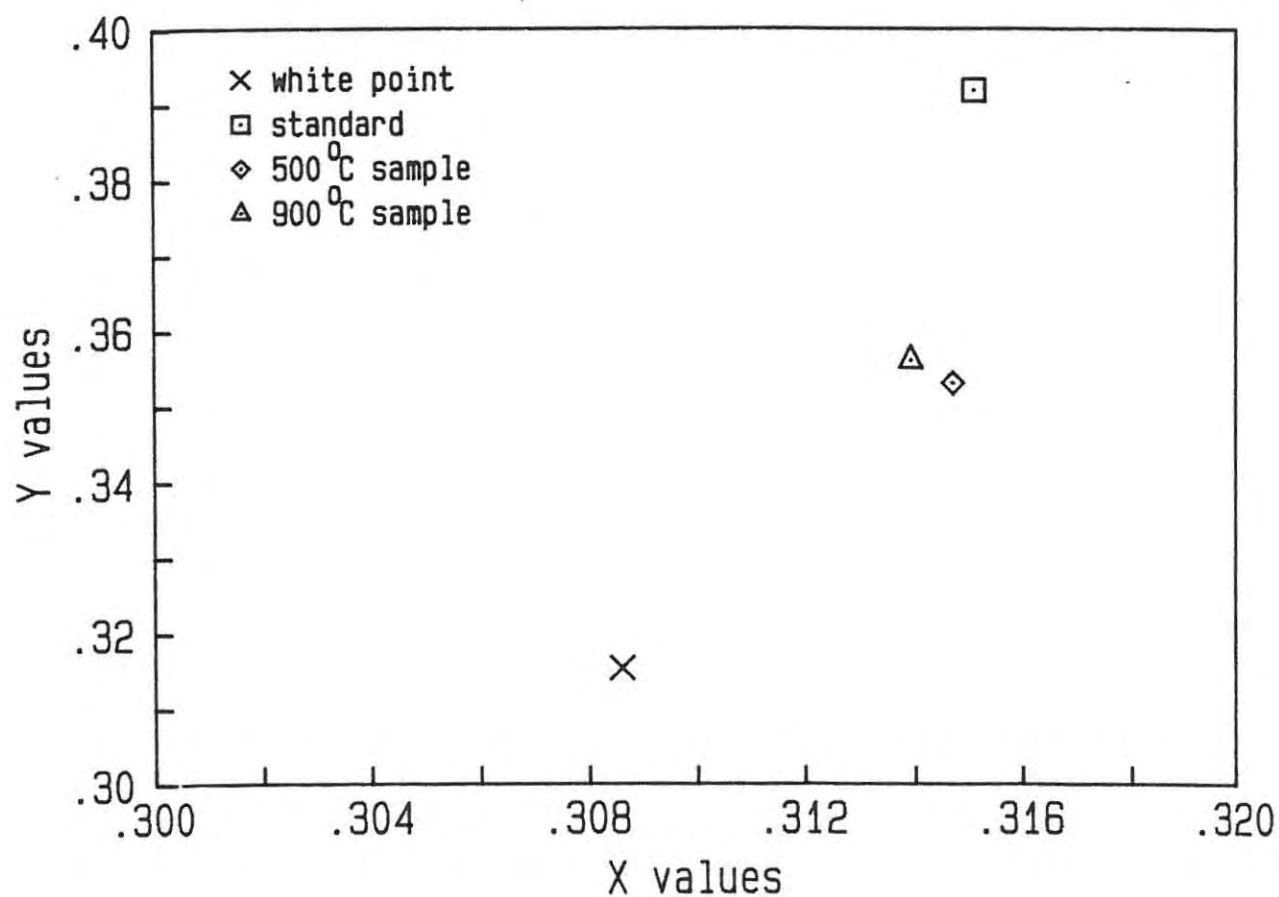


Figure 9.2 Chromaticity diagram showing a comparison of the colours of Cr_2O_3 samples

brightness value, so that any single point represents every possible brightness value. In order to define the brightness of a colour, the relative intensity of light reflected by the colour, compared to white under the same illumination, is measured; the higher the brightness, the more "alive" and clear the colour appears.

The colours of Cr_2O_3 samples produced by oxidation of CrCl_3 in air at 500 and 900°C were compared with that of commercially-available pigment-grade Cr_2O_3 . The chromaticity diagram showing the colours of the samples is shown in Figure 9.2, and their reflectance spectra are shown in Figures 9.3(a) and (b). The chromaticity diagram shows that there is little difference in colour between the Cr_2O_3 samples produced at different temperatures; that produced at 500°C has a slightly more reddish component. There is, however, a significant difference between the colour of commercial Cr_2O_3 pigment (standard) and the Cr_2O_3 produced in the present study. Moving along any line drawn from the white point to the colour locus (limits of colour saturation), the colour quantity represented is of constant hue, but has increasing saturation. The commercial oxide is therefore a more fully-saturated green and has much smaller red and blue components.

The reflectance spectra comparing the intensity of reflected light from a sample and the standard (Figure 9.3(a) and (b)) show that the oxide samples produced at 500 and 900°C have very similar brightness characteristics. The height of the

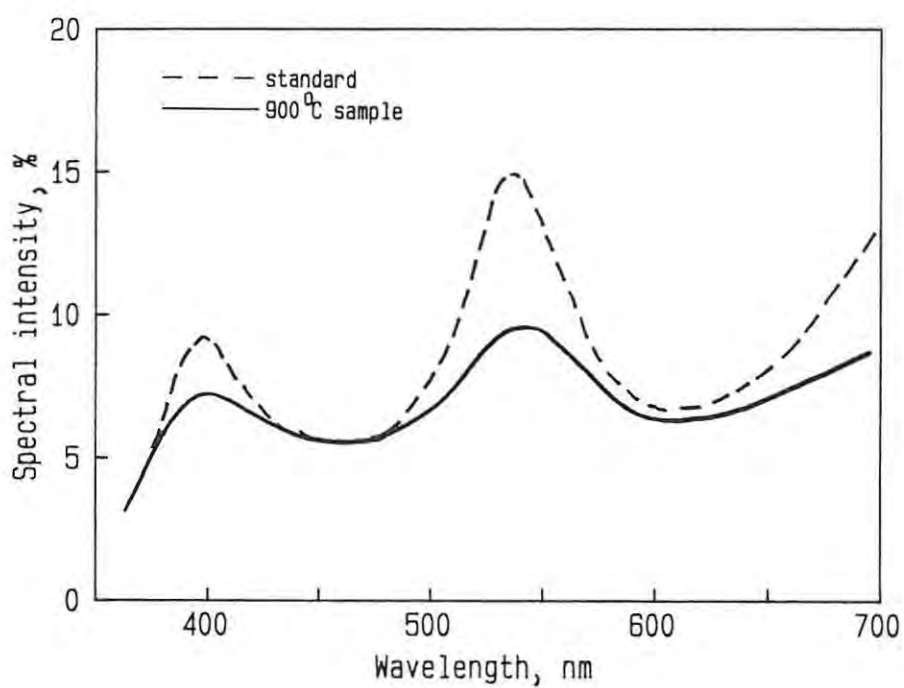
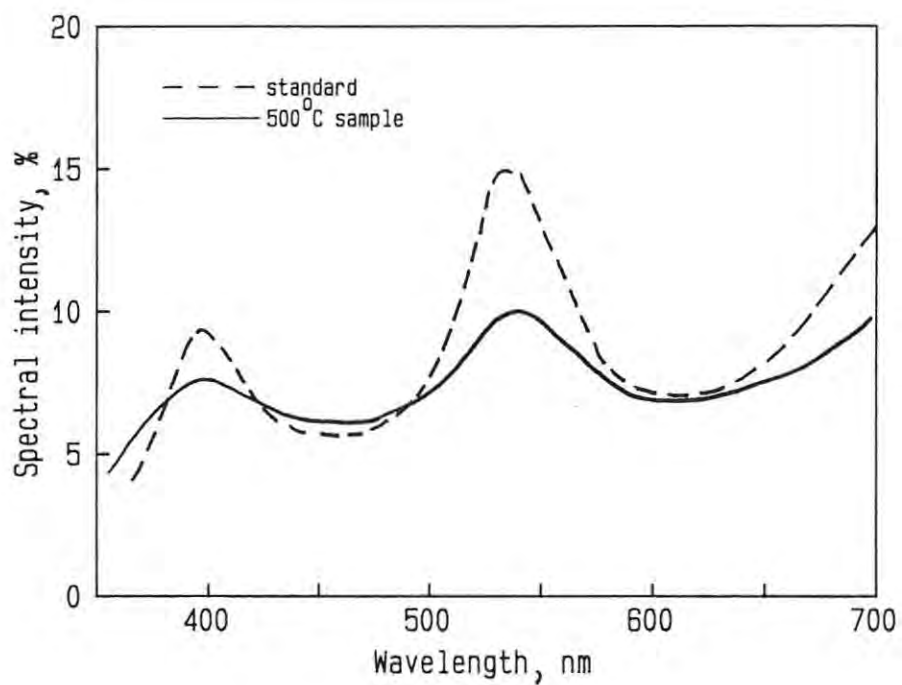


Figure 9.3 The reflectance spectra of Cr_2O_3 samples
(a) 500°C sample
(b) 900°C sample

reflectance peaks compared with the standard are, however, much lower. This means that the commercial oxide appears as a much brighter green, while that produced from CrCl_3 has a dull shade.

In order to match the colour of the commercial pigment, the Cr_2O_3 produced from CrCl_3 requires increased green saturation and increased brightness. As mentioned in Chapter 1, the colour shade of a pigment often depends on its particle size and size distribution.

9.2.2 Particle size and shape

Figures 9.4 to 9.8 show SEM secondary-electron images of Cr_2O_3 particles produced by the oxidation of CrCl_3 under various experimental conditions. It can be seen that the Cr_2O_3 crystals have a flat plate-like hexagonal shape. The crystals may be distorted or intergrown with other crystals to a greater or lesser extent, depending on the particular conditions under which the crystals were formed.

Figures 9.4(a) and (b) show Cr_2O_3 particles produced from CrCl_3 flakes at a temperature of 600°C in oxygen flowing at $10 \text{ cm}^3 \text{ min}^{-1}$. All particles are of very similar size, $\sim 1 \mu\text{m}$, and appear to be regularly-shaped hexagons. There is little intergrowth between particles. Figure 9.5 shows Cr_2O_3 produced from CrCl_3 flakes at 700°C in a rapidly flowing oxygen atmosphere. Under these conditions, a much

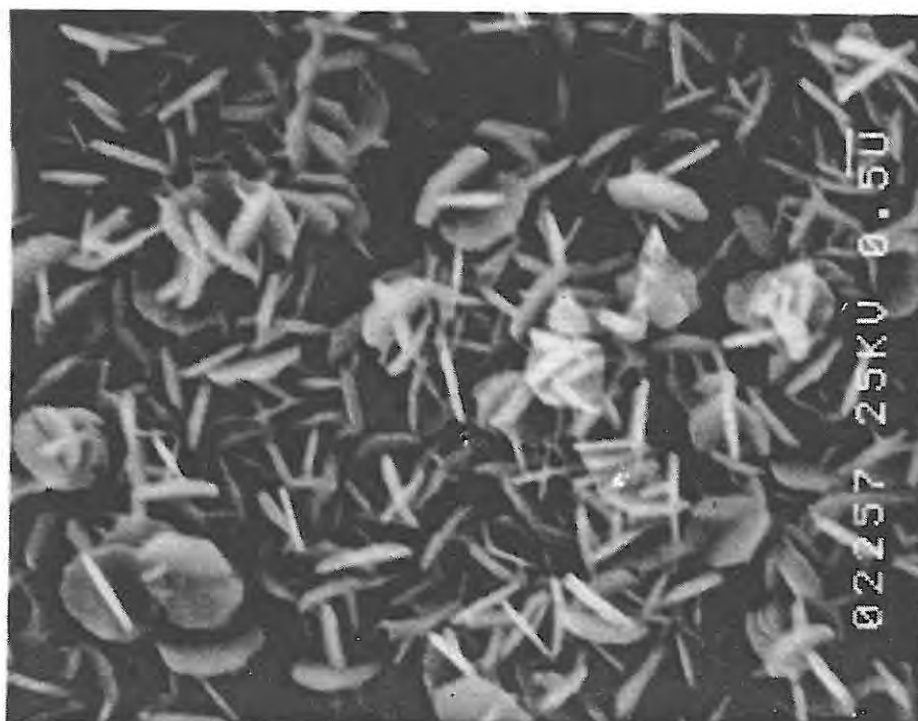


Figure 9.4 Crystal morphology of Cr_2O_3 produced from CrCl_3 flakes at 600°C in $10\text{ cm}^3\text{ min}^{-1}$ oxygen
(a) 2 500 x magnification
(b) 10 000 x magnification

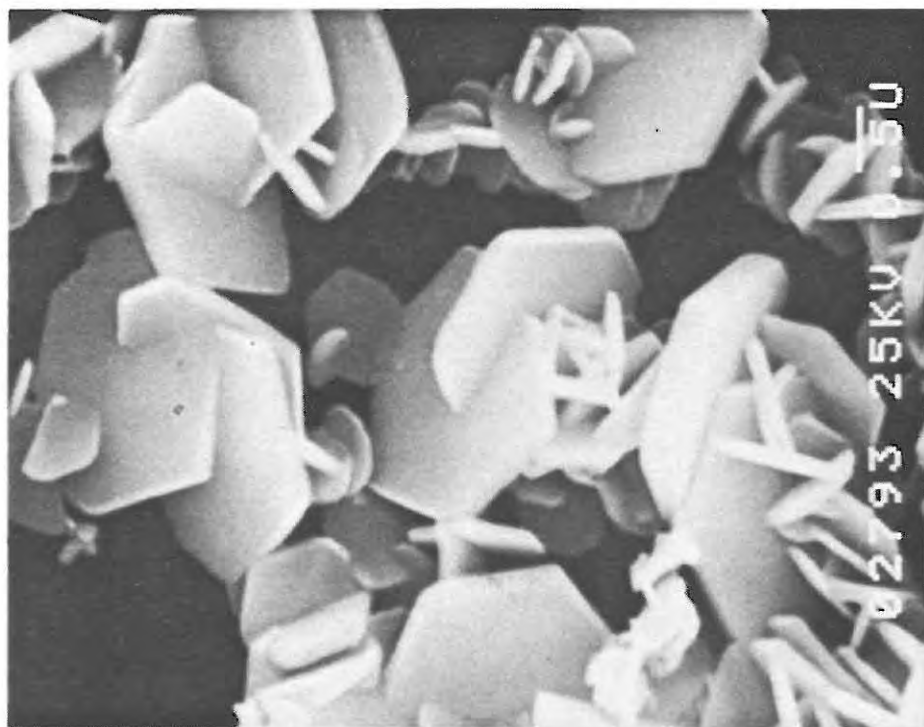


Figure 9.5 Crystal morphology of Cr_2O_3 produced from CrCl_3 flakes at 700°C in $200\text{ cm}^3\text{ min}^{-1}$ oxygen
10 000 x magnification

wider particle-size distribution is found, with crystals from $\sim 0,5$ to $2,5 \mu\text{m}$. Again, the crystals have a well-defined shape, although evidence of growth of the crystals into one another is found. This is probably due to the much faster rate of oxidation which occurred at the higher temperature.

Figures 9.6 to 9.8 show chromium oxide crystals produced on oxidation of CrCl_3 pellets under a range of experimental conditions. In all cases, most particles lie in the size range $\sim 0,3$ to $1,5 \mu\text{m}$, although occasionally larger crystals are found. These photographs show the tendency for these oxide crystals to grow in clusters, rather than as individual particles. The clusters range in size up to $\sim 25 \mu\text{m}$, and have angular shapes. The most densely intergrown crystal clusters occur as a result of oxidation at 900°C . It therefore appears that the size and density of the clusters may be determined by the rate at which the oxide was produced. The higher density of the CrCl_3 pellets, compared with CrCl_3 flakes, may also influence the likelihood of cluster formation.

During an examination of a number of samples produced under a wide range of experimental conditions, an attempt was made to correlate the crystal structure with the temperature or the oxygen partial pressure under which the oxidation was carried out. Although no definitive trends could be identified, it is thought that since the reaction has been shown to be limited by the rate of the chemical reaction,

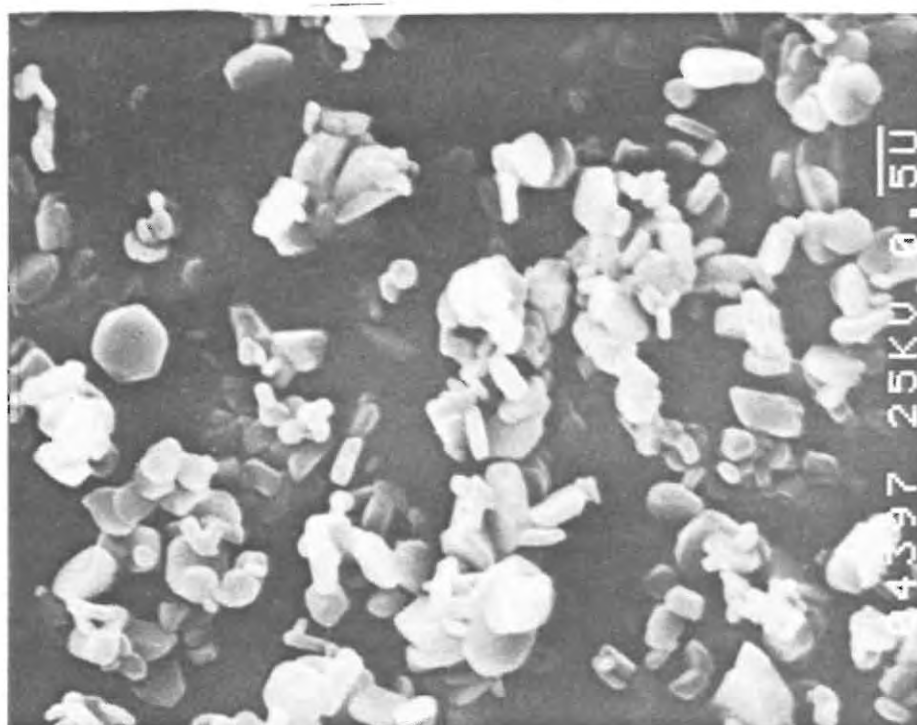
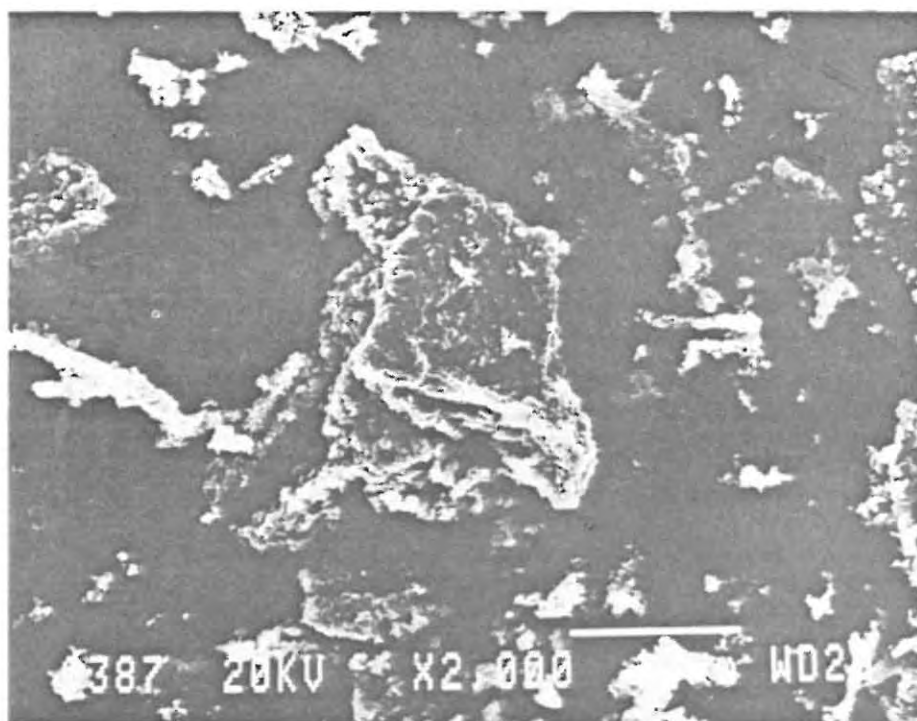


Figure 9.6 Crystal morphology of Cr_2O_3 produced from CrCl_3 pellet at 900°C in $200\text{ cm}^3\text{ min}^{-1}$ oxygen
(a) 2 000 x magnification
(b) 15 000 x magnification

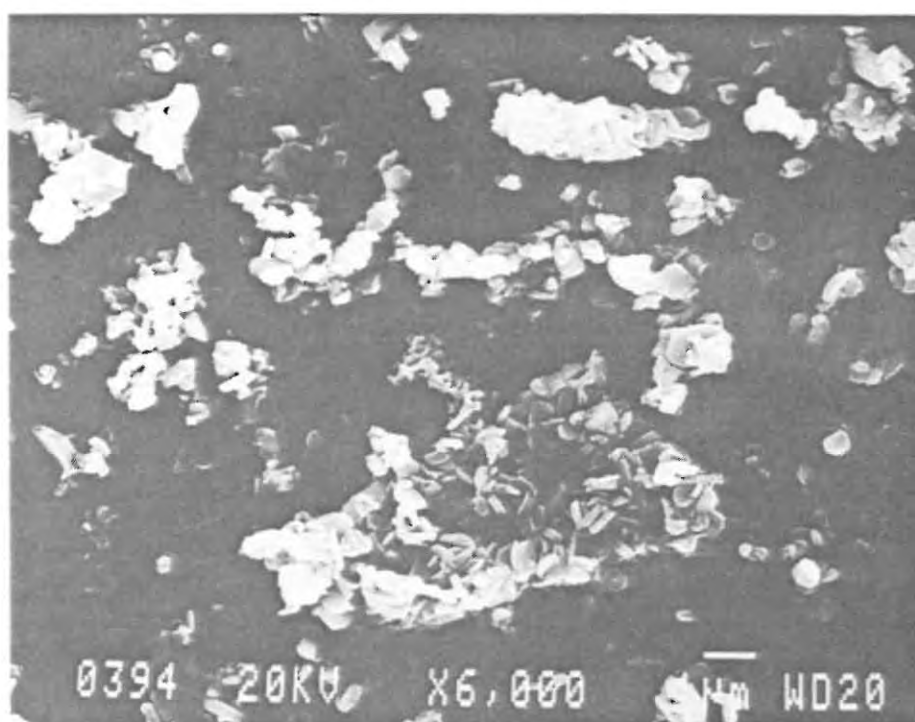
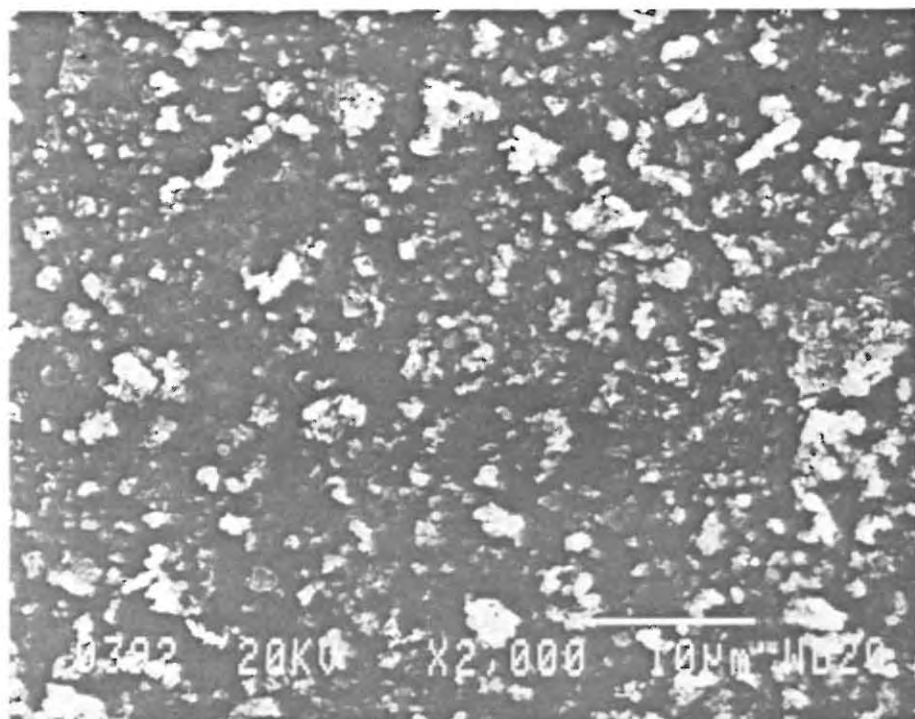


Figure 9.7 Crystal morphology of Cr_2O_3 produced from CrCl_3 pellet at 500°C in $50\text{ cm}^3\text{ min}^{-1}$ air
(a) 2 000 x magnification
(b) 6 000 x magnification

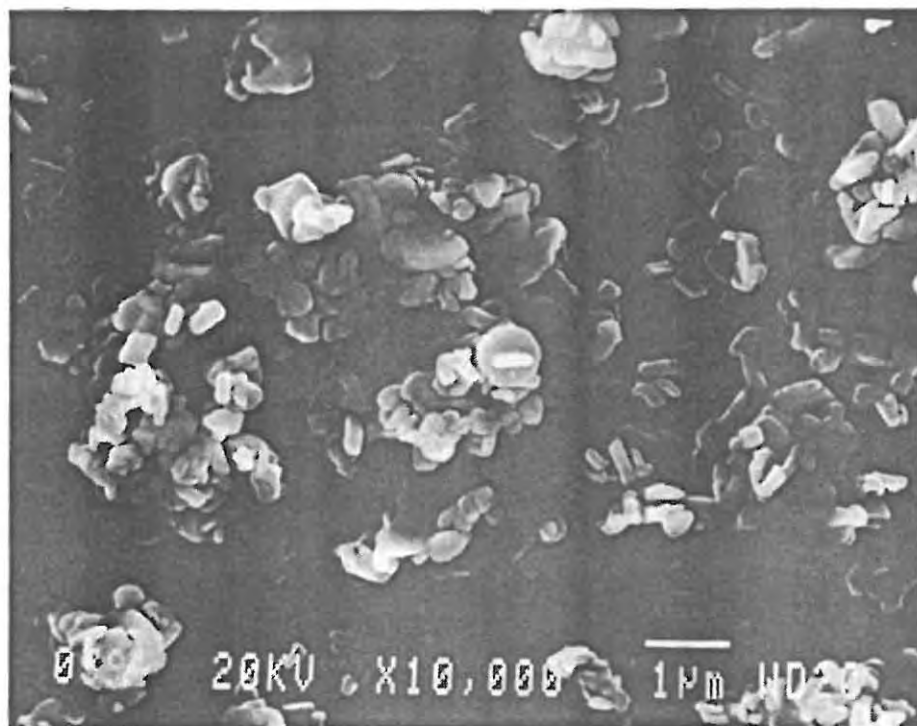


Figure 9.7 Crystal morphology of Cr_2O_3 produced from CrCl_3 pellet at 500°C in $50 \text{ cm}^3 \text{ min}^{-1}$ air
(c) 10 000 x magnification

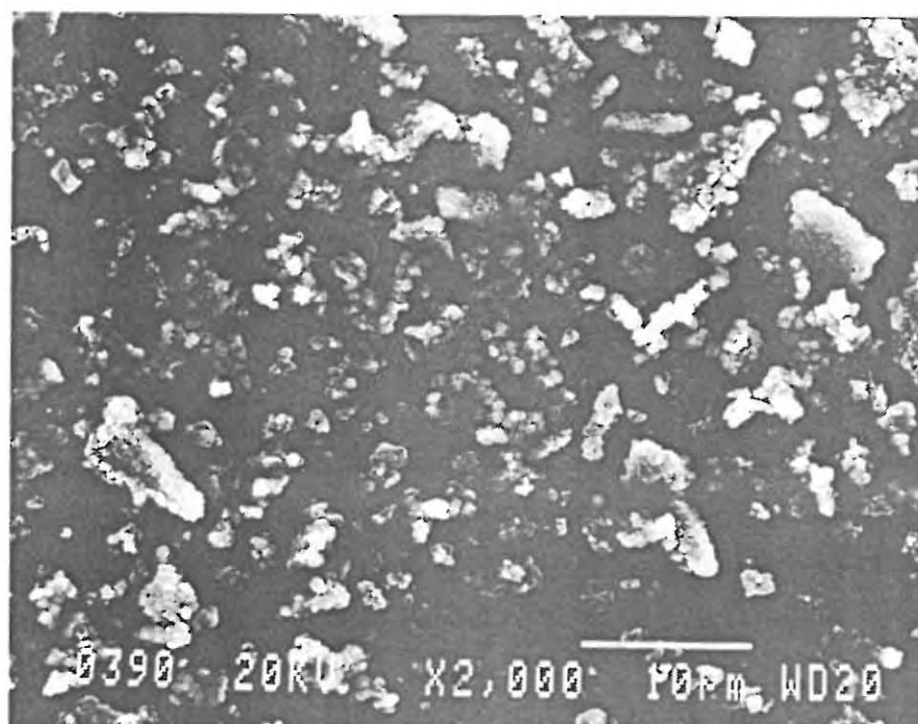


Figure 9.8 Crystal morphology of Cr_2O_3 produced from CrCl_3 pellet at 400°C in $200 \text{ cm}^3 \text{ min}^{-1}$ oxygen
(a) 2 000 x magnification

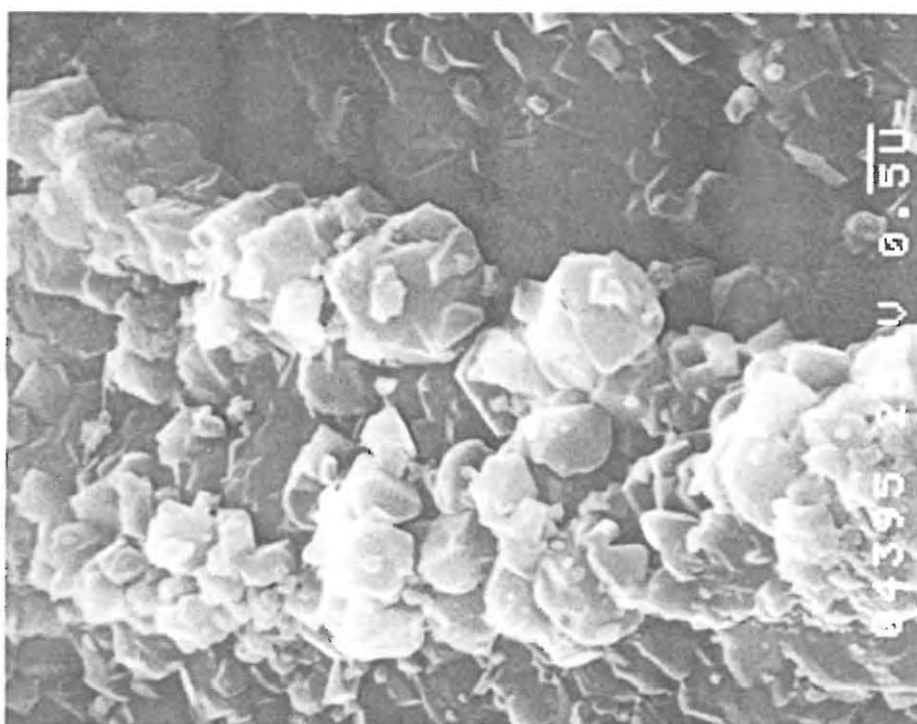
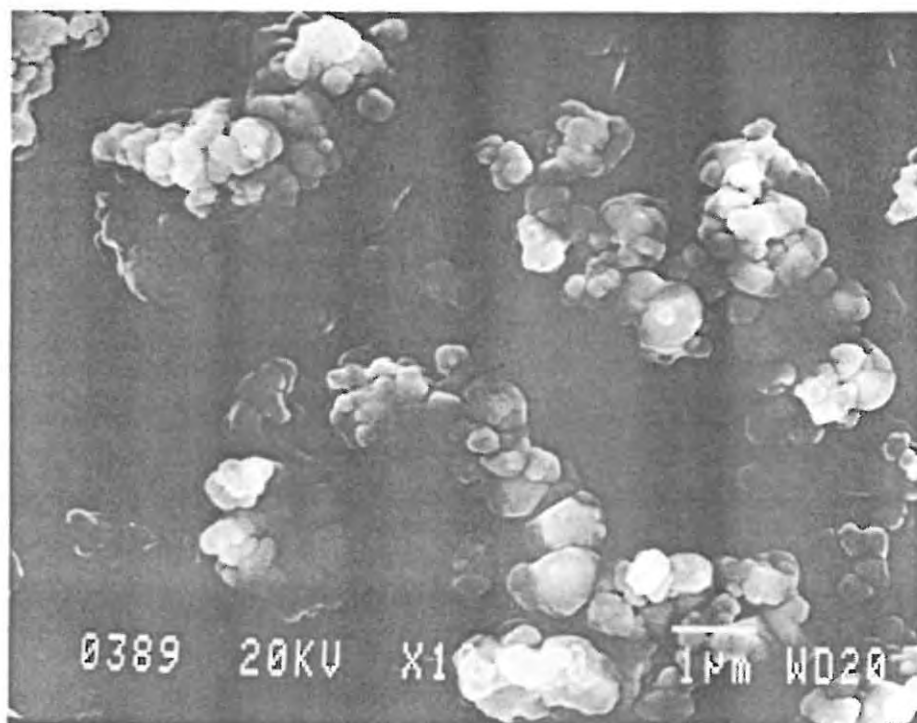


Figure 9.8 Crystal morphology of Cr_2O_3 produced from CrCl_3 pellet at 400°C in $200\text{ cm}^3\text{ min}^{-1}$ oxygen
 (b) 10 000 x magnification
 (c) 15 000 x magnification (showing intergrowth and cluster formation)

the effect of temperature probably plays the major role in determining the particle size and size distribution. The effect of the particle size of the CrCl_3 starting material on the product morphology is also uncertain.

Figures 9.9(a) to (h) show the sizes and shapes of commercial pigment-grade Cr_2O_3 crystals which have been produced wet-chemically (Section 1.3). There is a much wider range of particle sizes, $\sim 0,5$ to $7\ \mu\text{m}$, and although most particles fall in the range $0,5$ to $1\ \mu\text{m}$, there is a much higher proportion of larger crystals than has been observed in previous photographs. Several crystal aggregates are present, and crystal intergrowth occurs to a considerable extent. It also appears that the crystals formed by the wet-chemical process have a poorly-defined structure, and although an approximate hexagonal shape can be detected, the edges of the crystals are rounded. In many of the larger crystals, the hexagon shape has disappeared completely, although the 2-dimensional nature of the particles is retained.

This evidence gives little indication, however, of a physical reason for the difference in colour between the commercial pigment and the oxide produced from CrCl_3 . Since the colour of a pigment is very sensitive to particle size, it is suggested that the fraction of larger crystals present in the commercial oxide effect the range of wave-lengths of light reflected from the sample, and hence the colour of the sample.

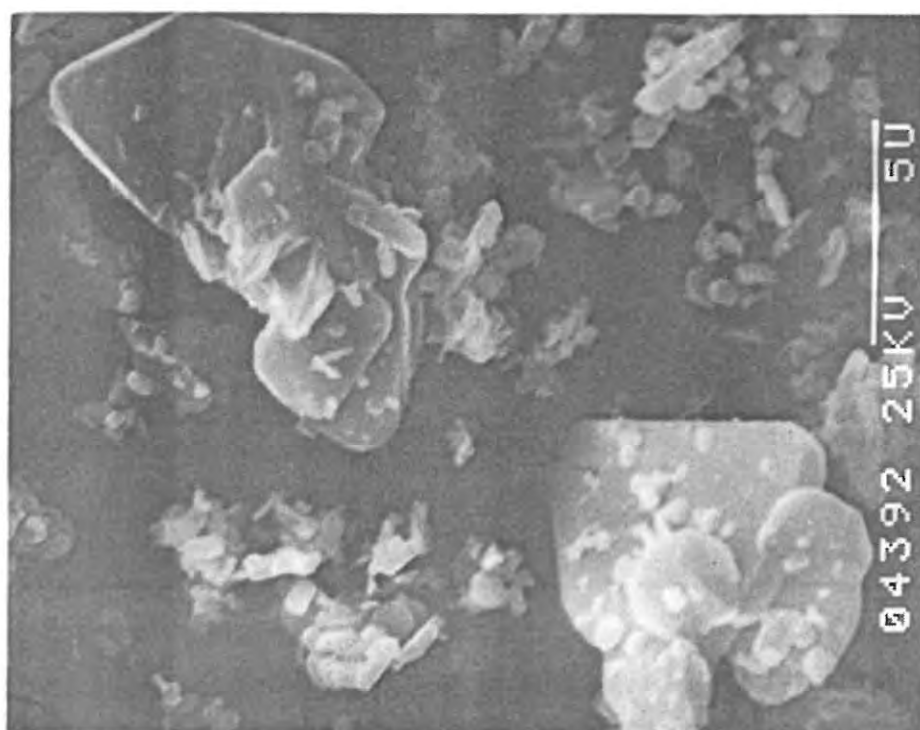
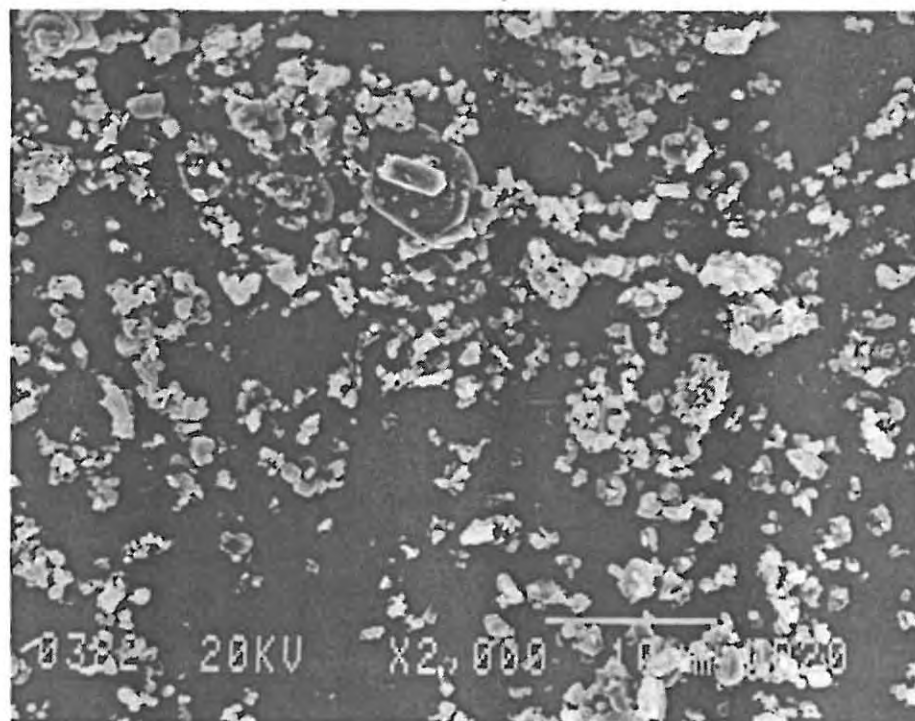


Figure 9.9 Crystal morphology of commercial pigment-grade Cr_2O_3
Delta Chrome Oxide Green D1110
(a) 2 000 x magnification
(b) 5 000 x magnification

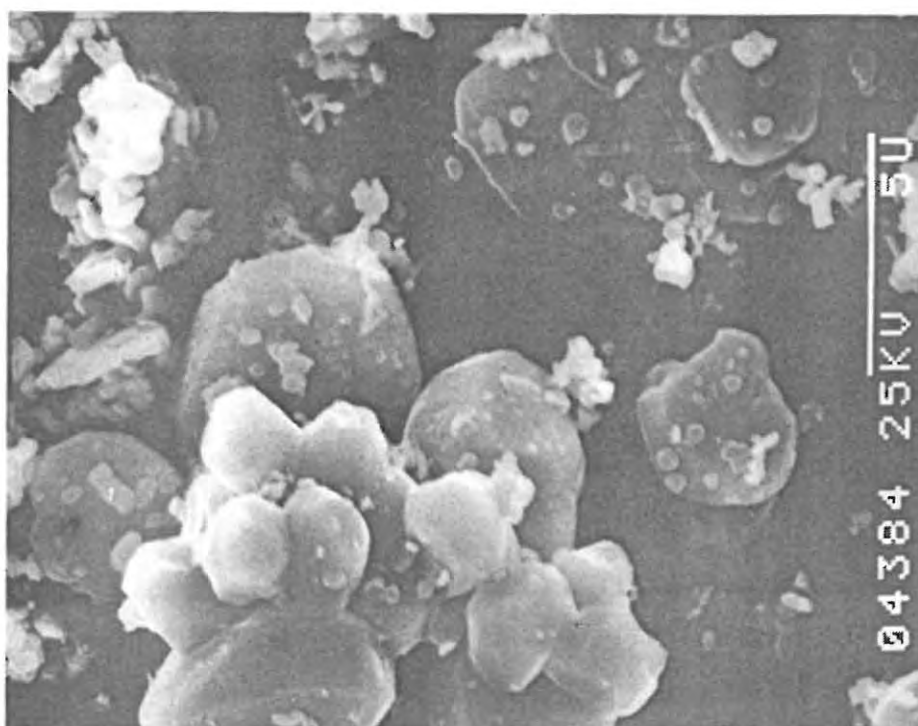
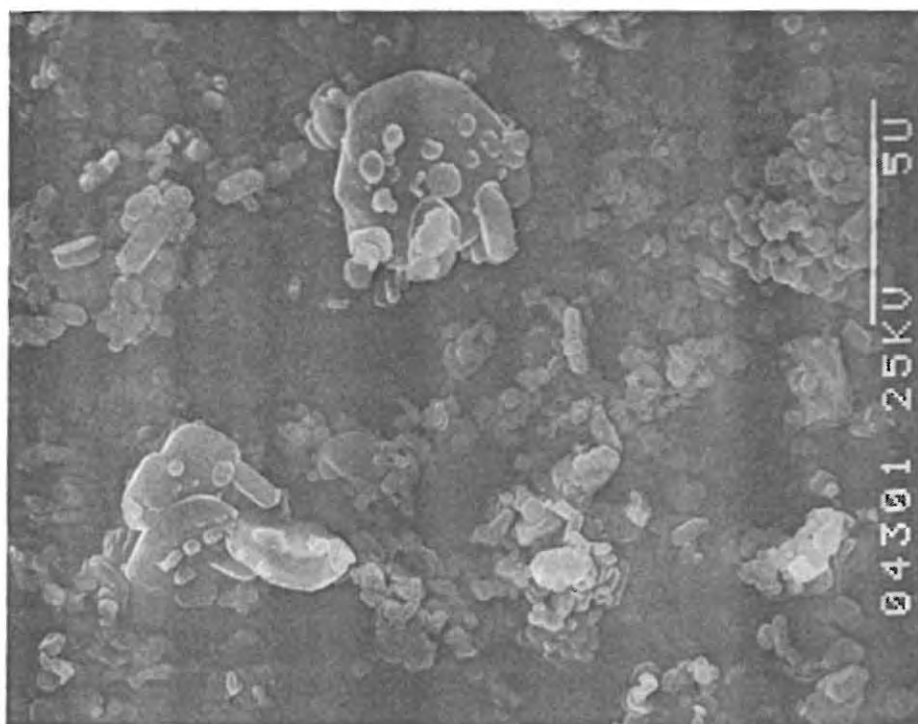


Figure 9.9 Crystal morphology of commercial pigment-grade Cr_2O_3
Delta Chrome Oxide Green D1110
(c) 5 000 x magnification - small crystals
(d) 5 000 x magnification - large crystals

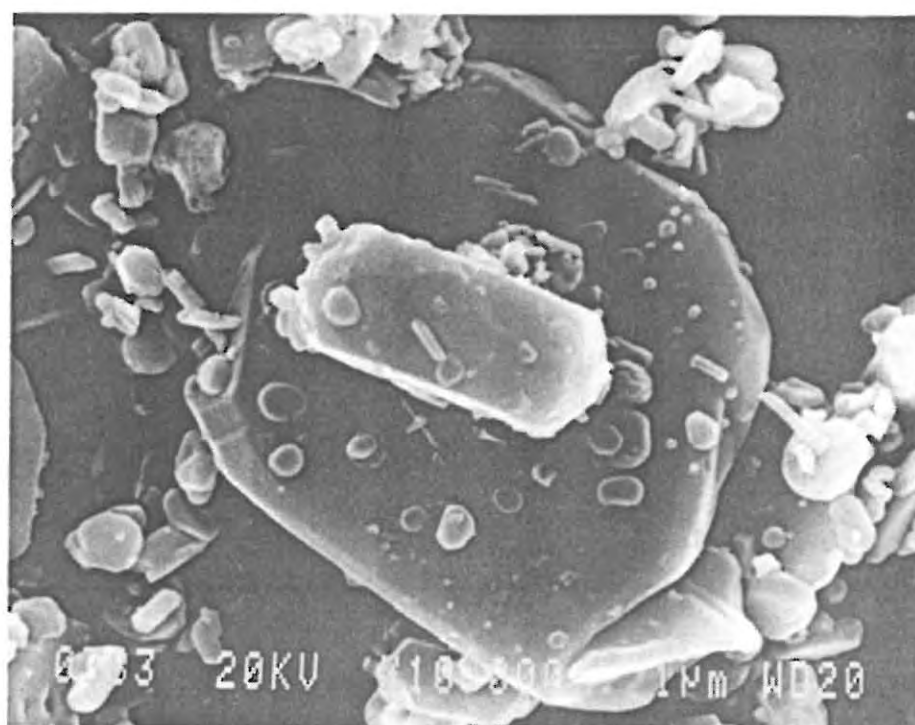
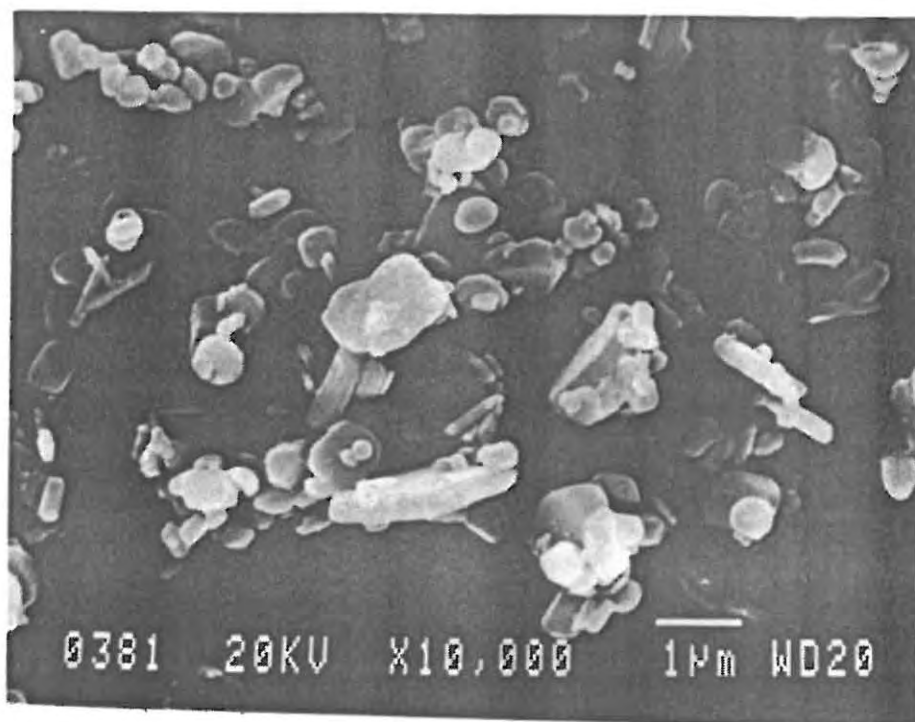


Figure 9.9 Crystal morphology of commercial pigment-grade Cr_2O_3
Delta Chrome Oxide Green D1110
(e) 10 000 x magnification - small crystals
(f) 10 000 x magnification - large crystals

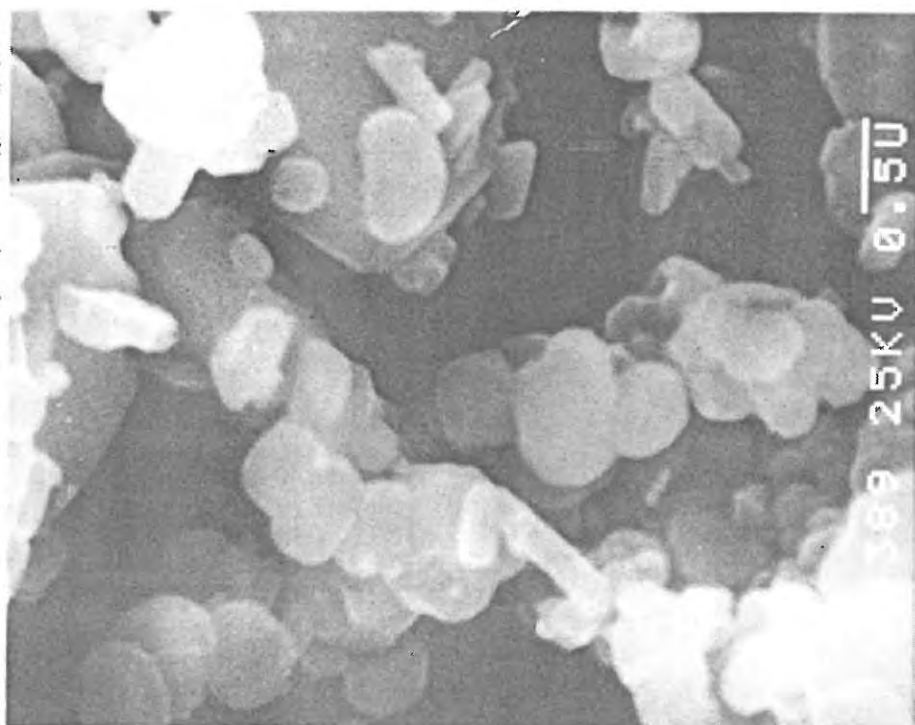
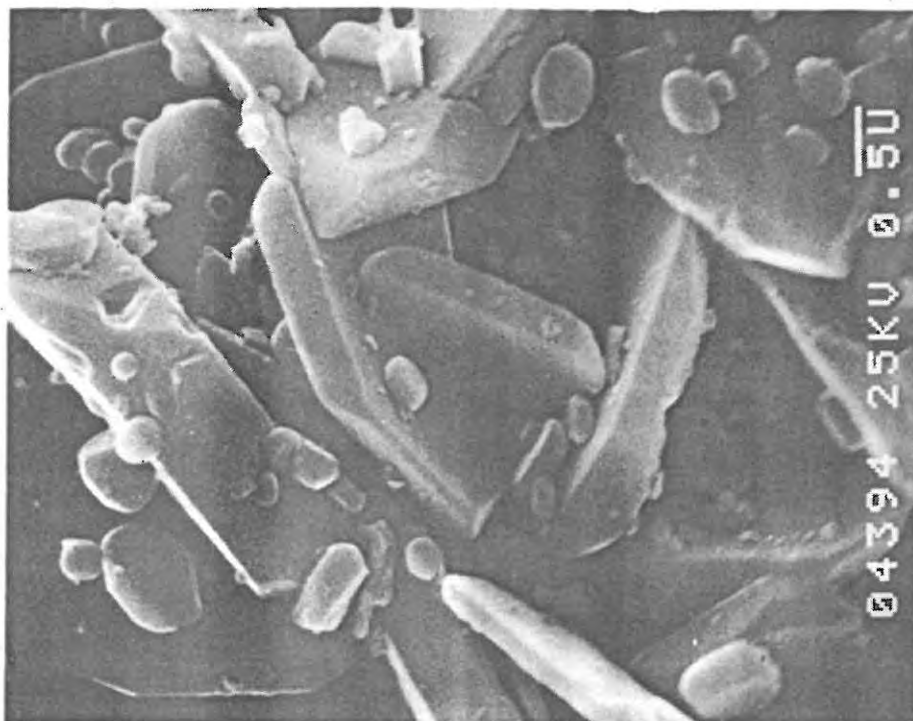


Figure 9.9 Crystal morphology of commercial pigment-grade Cr_2O_3
Delta Chrome Oxide Green D1110
(g) 15 000 x magnification - crystal intergrowth
(h) 20 000 x magnification - small crystals

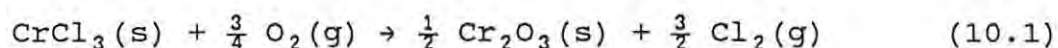
Although no direct correlations can be identified at present, it is apparent that the conditions under which CrCl_3 is oxidised to Cr_2O_3 influence the size, size distribution and shape of the oxide particles produced. Considerable scope exists for a more quantitative examination of these relationships.

~~X~~ →

10. DISCUSSION

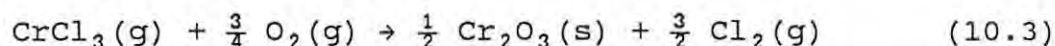
10.1 The oxidation reaction

The reaction



has been found to go readily to completion at temperatures as low as 400°C both in air and in oxygen. The rate of the reaction increases with increasing temperature and increasing oxygen partial pressure. As is typical for heterogeneous reactions, the greater the degree of subdivision of the solid reactant, the faster the reaction. The reaction rate has been found to be independent of the flowrate of the oxidising gas and of the pellet porosity. This suggests that the chemical reaction provides the greatest resistance to the rate of the overall reaction.

The most significant side-reaction occurring is the volatilisation of CrCl_3 , coupled with its subsequent oxidation



In this study an attempt was made to keep the CrCl_3 in the solid phase to simplify the reaction system and to prevent this side-reaction. In a practical situation, however, it may be desirable to enhance the gas-gas reaction, thus promoting contact between reactants and increasing the rate of reaction. A possible disadvantage of such a system would be the difficulty of controlling the site of deposition of

the Cr_2O_3 particles within a reactor. The Cr_2O_3 product of such a homogeneous process is also likely to have a much smaller particle size - this may or may not be advantageous, depending on the ultimate use of the product. The shape of the oxide particles may also change, as the hexagonal shape of the oxide particles produced under the experimental conditions used in this work, may arise directly as a topotactic consequence of the plate-like structure of the CrCl_3 crystals.

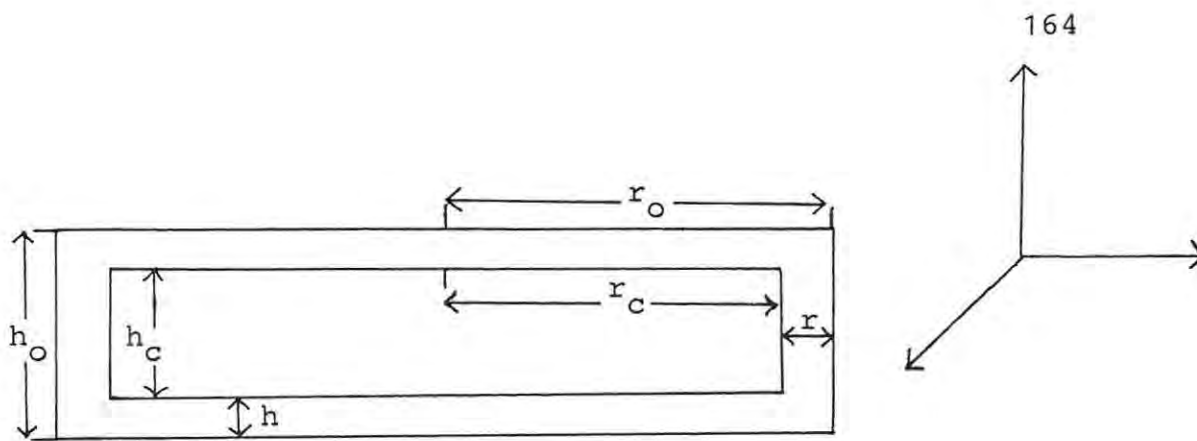
Also of importance in practical situations are the conditions under which by-products form. It has been shown that the formation of chromyl chloride, CrO_2Cl_2 , is favoured for oxidations carried out at low temperatures (low reaction rates) and in pure oxygen. This product exists in the liquid state at ambient temperature, and its presence would contaminate the major product, and could lead to accretions building up in a reactor.

The other by-product identified in this study is CrOCl , which forms when the reaction is subjected to conditions of oxygen starvation. Such conditions correspond to diffusion control, i.e. if the rate of chemical reaction is faster than the rate at which the gaseous reactant can be made available at the reaction site, then CrOCl is the favoured product. This compound appears to be relatively impervious and inhibits further gas diffusion through the product layer to the reaction interface; chromium chloride is thereby prevented from reacting to completion. Conditions under which this compound forms should thus be avoided.

10.2 Interpretation of the kinetic analyses

Kinetic analyses of the isothermal thermogravimetric data (Chapter 8) indicate that the rate of oxidation of CrCl_3 pellets, under the experimental conditions described, is limited mainly by the rate of chemical reaction which proceeds according to the contracting-area model, except at low temperatures where the contracting-volume model provides a better description of the observed data. However, SEM studies (Chapter 6) have shown that reaction occurs in three dimensions from the outer surface of the pellet, with the reaction interface advancing linearly with time. Two different rate constants appear to control the reaction; at 600°C the rate of interface advance from the circumferential sides of the pellet is ~ 5 times faster than the rate of interface advance from the flat base and top surfaces (Figure 6.4). The slower process cannot therefore be regarded as negligible in comparison with the faster, so that neither the contracting-area model nor the contracting-volume model can adequately describe the present system. An intermediate model, allowing for different rates of interface advance in different directions is thus required.

Again a pellet of initial radius r_0 and height h_0 is considered, where similar assumptions to those outlined in Section 8.2 apply.



If it is now assumed that the rate of interface advance in the x,y -plane (r -direction) is p times the rate of interface advance in the z -direction (h -direction), then

$$h = \frac{h_o - h_c}{2} = \frac{r_o - r_c}{p} \quad (10.4)$$

and the fractional conversion

$$\begin{aligned} \alpha &= \frac{\pi r_o^2 h_o - \pi r_c^2 (h_o - 2h)}{\pi r_o^2 h_o} \\ &= \frac{r_o^2 h_o - r_c^2 (h_o - 2(r_o - r_c)/p)}{r_o^2 h_o} \end{aligned} \quad (10.5)$$

Since the rate of interface migration in the r -direction is constant,

$$r_c = r_o - k_r t \quad (10.6)$$

where k_r is the rate constant for the reaction in the r -direction.

Therefore

$$\begin{aligned} \alpha &= \frac{r_o^2 h_o - r_c^2 h_o + 2r_c^2 k_r t/p}{r_o^2 h_o} \\ &= 1 - \frac{r_c^2}{r_o^2} + \frac{2r_c^2 k_r t}{r_o^2 h_o p} \\ &= 1 - \frac{r_c^2}{r_o^2} \left[1 - \frac{2k_r t}{h_o p} \right] \end{aligned}$$

$$\begin{aligned}
&= 1 - \left[\frac{r_0 - k_r t}{r_0} \right]^2 \left[1 - \frac{2k_r t}{h_0 p} \right] \\
&= 1 - \left[1 - \frac{k_r t}{r_0} \right] \left[1 - \frac{k_r t}{r_0} \right] \left[1 - \frac{2k_r t}{h_0 p} \right]
\end{aligned}$$

Therefore

$$1 - \alpha = \left[1 - \frac{k_r t}{r_0} \right] \left[1 - \frac{k_r t}{r_0} \right] \left[1 - \frac{k_r t}{h_0 p/2} \right] \quad (10.7)$$

Solving this equation for different values of $r_0 a p$ ($= h_0 p/2$ since $a = h/2r$) will give rise to different exponents in the general equation

$$1 - (1 - \alpha)^{1/x} = kt \quad (10.8)$$

where $k = k_r/r_0 a$.

Three particular cases are of special interest :

- (i) If the ratio of the rate of interface advance in the r -direction to the rate of interface advance in the h -direction is exactly equal to the ratio of the diameter to the height of the cylindrical pellet (which is unlikely to be easily achieved in practice, except when the two rates are equal and the diameter and height of the pellet are equal), then

$$p = 2r_0/h_0$$

and equation (10.7) may be simplified to

$$1 - \alpha = (1 - k_r t/r_0)^3$$

which may be written as

$$1 - (1 - \alpha)^{1/3} = kt \quad (10.9)$$

This is the rate equation for the contracting-volume ($R3$) model. Figure 10.1(a) depicts the contributions

made by reactions in the various directions to the overall reaction for this special case. It can be seen that reaction in both the r- and h-directions occurs in such a way that the unreacted core always has the proportions of the original pellet and the volume decreases uniformly until $\alpha = 1,0$.

- (ii) If $p \gg 2r_0/h_0$, i.e. the rate of interface advance in the r-direction is much faster than in the h-direction, then the way in which the volume of the unreacted core changes with time is more complex, with the contributions from reaction in the two directions being as shown in Figure 10.1(b). The major contribution to the reaction arises from interface migration inwards from the sides of the pellet. In the limiting case of no reaction from the flat ends of the pellet, the contracting-area (R2) model will apply, i.e. equation (10.7) can be simplified to

$$1 - \alpha = (1 - k_r t / r_0)^2$$

or

$$1 - (1 - \alpha)^{1/2} = k_t \quad (10.10)$$

- (iii) If the rate of interface advance from the top and bottom of the pellet is much faster than from the sides, then

$$p \ll 2r_0/h_0$$

Therefore, k_r is very small, and equation (10.7) simplifies to

$$1 - \alpha = (1 - k_r t / r_0 a p)$$

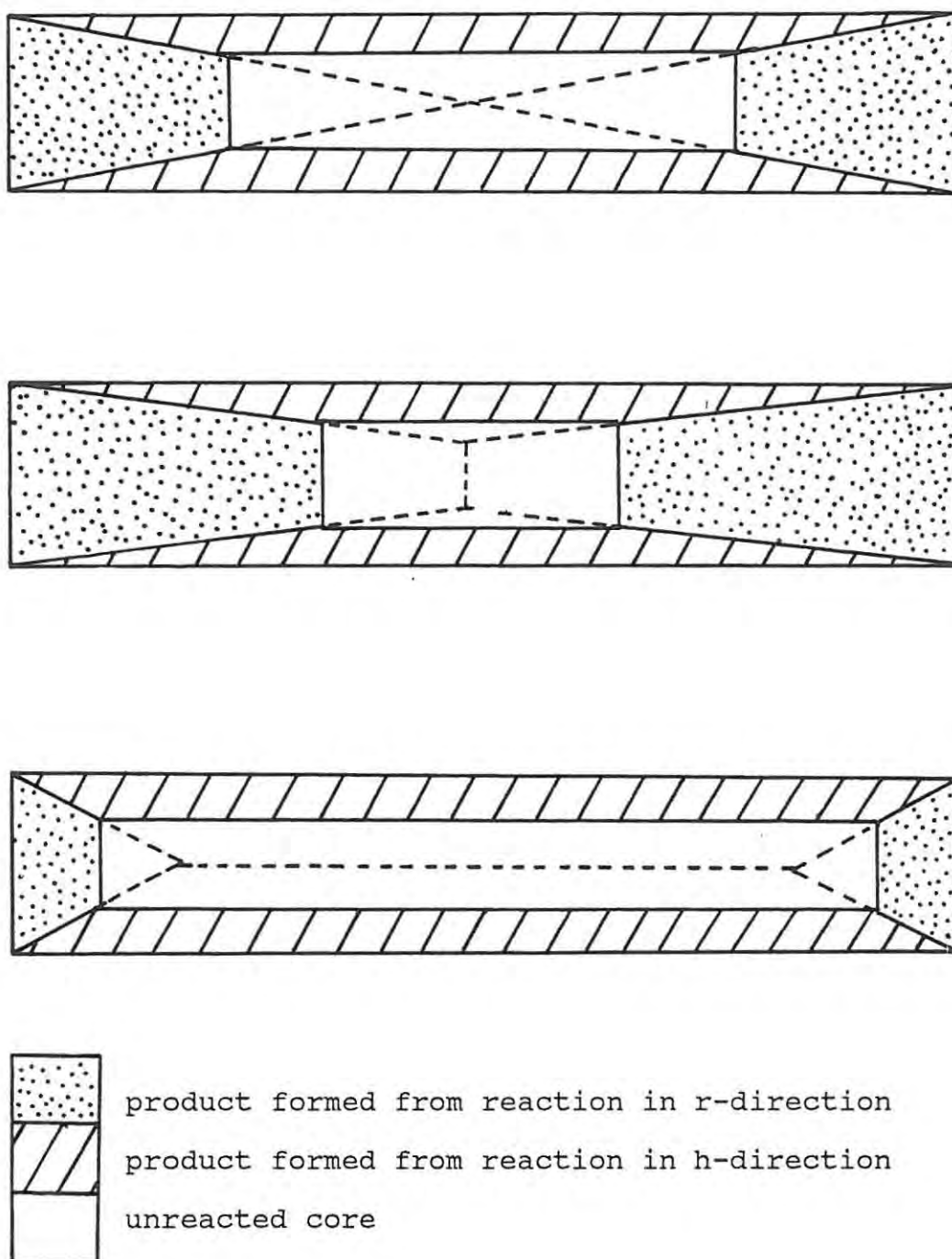


Figure 10.1 Representation of the contributions to the reaction by interface advance at different rates in different directions

(a) $p = 2r_0/h_0$
 (b) $p > 2r_0/h_0$
 (c) $p < 2r_0/h_0$

Figure 10.1(c) illustrates this situation. In the limiting case, no reaction from the sides occurs, and the rate expression may be written

$$1 - (1 - \alpha)^{1/1} = k't$$

or

$$\alpha = k't \quad (10.11)$$

where $k' = k_r/h_0a$.

This is the equation for linear advance of the reactant-product interface in a single direction.

These three special situations show that a physical explanation for various non-integer values of x can be provided.

A computer program, GEOMODEL, was developed to determine the value of x which best describes the experimental data. A copy of this program may be found in Appendix E. The program converts α -time data to $f(\alpha)$ -time data, where $f(\alpha)$ is given by equation (10.8) and x has values from 1,5 to 3,0, incremented in steps of 0,1. For each increment, the statistical parameters r , $s_{y,x}$ and $\%s_b$ are calculated. The best value of x is then obtained by maximising r and minimising $s_{y,x}$ and $\%s_b$.

Plots of these optimised values of x against temperature are shown in Figures 10.2(a) and (b) for air and for oxygen atmospheres. Although no direct correlations are immediately apparent, a trend can be discerned. The lower the temperature, the higher the value of x in equation (10.10),

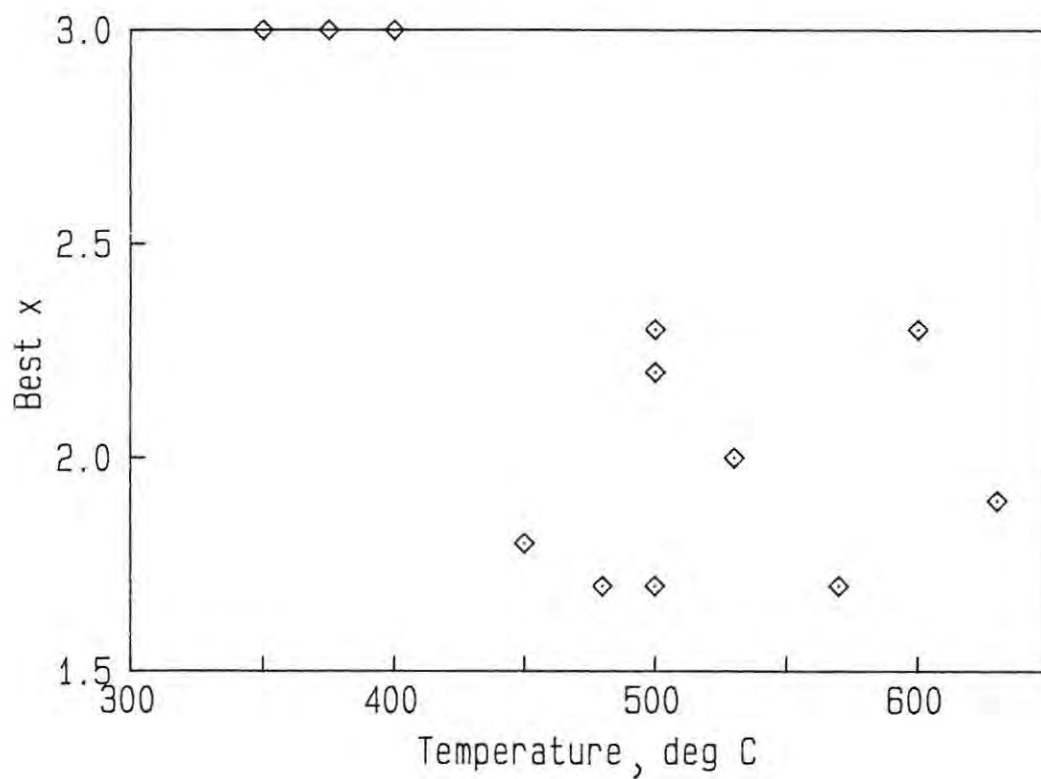
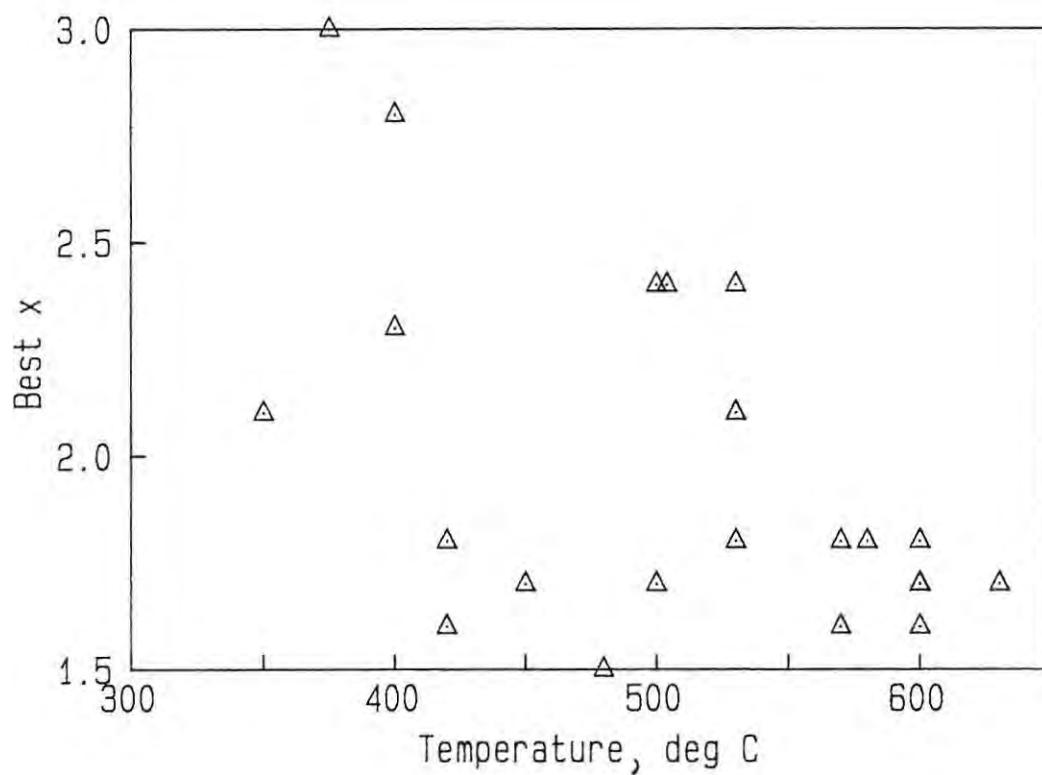


Figure 10.2 The best value of x in the contracting-geometry equation as a function of temperature
(a) air
(b) oxygen

which best describes the experimental data. This trend has been mentioned in Chapter 8, where TG curves obtained at lower temperatures tended to fit the R3 model, while at higher temperature the R2 model provided a better fit. At the higher temperatures, the lower limit of x is $\sim 1,7$ to $1,8$, and not $2,0$ as originally expected. This effect can be physically explained in terms of the relative rates of interface advance in the different directions, as has been shown in Figure 10.1.

For the pellets used in this study

$$\frac{2r_0}{h_0} = \frac{13 \text{ mm}}{2,5 \text{ mm}} = 5,2$$

and from Figure 6.3, it has been shown that $p = 4,90$.

Therefore

$$p < 2r_0/h_0$$

It is hence conceivable that an exponent of (say) $1/1,8$ in equation (10.8) does have real significance.

It has often been emphasized that the fitting of TG data to established kinetic models may not be sufficient to describe the kinetic behaviour of a system, and that the model chosen must be supported by evidence obtained using other experimental techniques. In this study the kinetic analysis of isothermal thermogravimetric data has led to the suggestion that the reaction is under chemical control, governed by the R2 model at higher temperatures and the R3 model at lower temperatures. Examination of the cross-

sections of partially-reacted pellets by SEM techniques has supported the mathematical equations which fit the experimental data well. The SEM has moreover shown that the R2 and R3 models are limiting cases of a more general contracting-geometry model. The model has therefore been extended to allow for different rates of interface migration in pellets of different shapes and sizes, and leads to a rate equation of the form

$$1 - (1 - \alpha)^{1/x} = kt \quad (10.8)$$

where, for the oxidation of CrCl_3 pellets, x has values from ~ 1.6 to 3.0 , and depends on the particular experimental conditions employed.

The above model applies to the oxidation of CrCl_3 pellets and it is uncertain whether this model would also apply to the oxidation of CrCl_3 flakes. The pellets were made by uniaxial compression, with the direction of the compression perpendicular to the flat sides of the pellet. Because CrCl_3 crystals are a flat plate-like shape, the crystals tend to align themselves so that their flat sides are also perpendicular to the direction of compression. It is therefore expected that the porosity in the x,y -direction will be greater than in the direction of compression. If the reaction were under diffusion control, the rate of reaction in the x,y -direction would then be expected to be enhanced, thereby giving rise to the contracting-area model. Experimental and theoretical results suggest, however, that the reaction is not under diffusion control, and so the proposed contracting-geometry rate expression is expected to

hold for the oxidation of CrCl_3 single crystals as well as for the oxidation of pellets.

10.3 The rate-limiting step of the reaction

In Chapter 2, three possible rate-limiting steps were identified for the irreversible oxidation of CrCl_3 - rate control by diffusion of the reactant gas through the boundary gas layer, by diffusion of the reactant gas through the pellet to the reaction site, or by the chemical reaction itself.

Thermogravimetric results, discussed in Chapter 5, showed that since the flowrate of the reactant gas had no effect on the rate of reaction under the experimental conditions used, the possibility of diffusion of the boundary gas layer providing the major resistance to reaction could be discounted. TG results showing the effects of pellet porosity, oxygen partial pressure, and the addition of other metal oxides gave inconclusive evidence on whether or not mass transport in the product is rate-limiting. Other TG evidence indicated that the chemical reaction is likely to provide the major resistance to the oxidation reaction. The measurements of the bulk physical properties of the two solid phases of the reaction (Chapter 7) have shown that the porosity of the Cr_2O_3 is ~75%, while the porosity of the unreacted CrCl_3 core is ~12%; diffusion of oxygen through the Cr_2O_3 will therefore offer less resistance to the

reaction. Analysis of the SEM measurements (Chapter 6) demonstrated that the reaction proceeds by means of well-defined reactant-product interfaces which move inwards from the surface of the pellet. Such contracting-geometry behaviour may describe a reaction under either diffusion or chemical control (Section 8.2).

Evidence that the chemical process offers the greatest resistance to reaction for the oxidation of CrCl_3 is presented in Chapter 8. The kinetic rate expression which consistently best fits the experimental data is the contracting-area model, which is derived for a chemical rate-controlling process on the basis that the rate of interface advance is constant. This linear rate of interface advance is supported by SEM measurements (Figure 7.4). The rate of interface advance for a reaction limited by mass transfer through the Cr_2O_3 product layer would have decreased with increasing conversion, as the diffusion path length increased. It has therefore been concluded that the rate of oxidation of CrCl_3 pellets in the temperature range 400 to 600°C and in the α -range 0,15 to 0,90 is limited by the rate of the chemical reaction.

The evidence cited above in support of a chemically-controlled reaction is, however, mainly indirect evidence. A major observation detracting from this argument is that although the unreacted CrCl_3 core has a relatively high porosity (~12%), the reaction nevertheless occurs at a well-defined interface. The formation of CrOCl in Section 5.8.1

also cannot be dismissed as arising solely from a competing side-reaction; the possibility exists that this species is in fact an intermediate of the oxidation reaction. It has been shown (Figure 5.17) that under extreme reaction conditions the formation of CrOCl results in an impervious layer between the CrCl_3 and the Cr_2O_3 , which then inhibits further reaction. It is hence conceivable that under less extreme conditions this species still forms and, although it remains undetected, may be an integral step in the reaction mechanism. Evidence in Section 5.8.1 appeared to indicate that once this species had formed it could not be further oxidised to Cr_2O_3 ; however, this may be misleading. It would not be unexpected to find that in the conversion of chromium chloride to chromium oxide, a chromium-chloride-oxide intermediate species was formed. CrCl_3 and CrOCl have similar crystal structures, which means that the conversion from the chloride to the oxide-chloride is expected to occur readily.

It has been argued in Chapter 8 that a linear rate of interface advance is evidence for chemical control, and that a reaction limited by the rate of gaseous diffusion through the product layer will show a decreasing rate of interface advance. This is, however, only true if the thickness of the product layer under consideration increases with time. If an intermediate product layer is formed between the Cr_2O_3 product layer and the CrCl_3 core, and the thickness of this product layer remains constant with time, then although gaseous diffusion through this layer may provide the

greatest resistance to reaction, the rate of interface advance will be constant.

It is evident that the determination of the rate-limiting step and elucidation of the mechanism of the reaction for this reaction system may not be as straightforward as originally concluded. A closer investigation of the process(es) occurring at the interface is required. The structural relationships between the various solid species and the necessity for single crystal studies now become important. This study has identified the kinetic behaviour of a bulk sample; the kinetics and mechanism of the oxidation of CrCl_3 on a micro-scale still remain incompletely resolved.

10.4 A general rate expression

As discussed in Chapter 2, a number of steps all contribute to a particular reaction. These steps involve both chemical and mass-transfer processes. The rate expressions discussed in the present work are derived from simplified models which assume that one process is very much slower than all the others and hence determines the overall rate.

In recent years, it has become more common practice to derive a general rate expression to describe the kinetic behaviour over the entire reaction, incorporating contributions from all the possible resistances to reaction which

may be encountered^{69,70}. Such a rate expression will take into account the effects of the chemical reaction, the inward and outward diffusion of reactant and product gases, as well as heat-transfer effects. In the various limiting cases, one of these steps will have a lower rate than the others, and will then be rate-controlling.

In general, at the beginning of a reaction when the solid and gaseous reactants are in direct contact, the rate of the overall reaction should be controlled by the chemical reaction, as no diffusion process is involved. At the other extreme, as the reaction interface moves further into the solid, the diffusion distance for the gaseous reactant becomes greater, and the diffusion rate continuously decreases. Eventually, for a sufficiently large and compact sample, the rate will probably become diffusion-controlled. As the transition from one controlling step to another must be continuous, a more complex rate expression is required. Such an equation can be derived by considering the rates of diffusion and chemical reaction simultaneously. This approach has been used by a number of researchers^{69,70}.

Most derivations of a general rate equation have been based on consideration of a spherical particle reacting according to the unreacted shrinking-core model, with equal rates of interface advance in all three dimensions. The solution of the resulting differential equations is often complicated, and numerical methods may be required. In the present system the situation is considerably more complex, with a

disc-shaped pellet reacting at different rates in different directions. No attempt will be made to establish the general rate equation for this system; rather a qualitative discussion of the implications of such an approach is presented.

The rate of oxidation of CrCl_3 pellets has been shown to be under chemical reaction control at temperatures from 400 to 600°C in the α -range 0,15 to 0,90. At lower temperatures and low conversions, the rate is probably limited by the rate of formation of nuclei of Cr_2O_3 . Once these nuclei form, stresses and crystal-lattice imperfections are induced in the adjacent reactant and the nuclei grow rapidly over the surface to form a continuous reaction interface. At temperatures above 600°C, the rate of the chemical reaction is extremely fast due to the exponential dependence of reaction rate on temperature, and the overall rate becomes limited by the rate at which oxygen can be provided at the reaction site. This effect is more pronounced in air than in oxygen because of the relative oxygen partial pressures. In cases of extreme oxygen starvation, an alternate product, CrOCl , may form.

The relative contributions of these rate-limiting factors are obviously affected by experimental parameters such as surface area, pellet size, pellet porosity and crystal lattice imperfections, and there is still considerable scope for a quantitative examination of these factors.

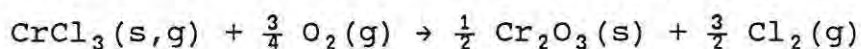
Also of significance in deriving a general rate expression for this particular system, is the observation that the relative rates of interface advance in the two major directions appear to be dependent on experimental conditions (Figure 10.2). At the lower reaction temperatures, these rates are similar, but at higher temperatures, preferential reaction from the circumferential sides of the pellet appears to take place.

In summary, to describe the kinetic behaviour of a particular reaction system completely, a number of physical and chemical effects should be taken into account, and a general rate expression derived. However, in many systems, this process is often not necessary, or even probable, for practical purposes and may not be justified by the quality of the experimental data available. In the present system, it has been shown that provided the limitations of the proposed model are understood, useful information concerning the kinetic behaviour over a wide range of reaction conditions can be obtained.

11. CONCLUSIONS

A fundamental study of the factors affecting the rate and extent of the oxidation of chromium(III) chloride pellets under various experimental conditions has been undertaken. The following conclusions have been drawn :

- (i) CrCl_3 reacts with oxygen to form chromium(III) oxide and chlorine gas according to the reaction



- (ii) The rate of reaction is measurable at temperatures of 400°C and above, and the oxidation can be carried out in either air or oxygen atmospheres.

The rate of the reaction increases with increasing temperature, increasing oxygen partial pressure, increasing subdivision of the solid reactant, and on the addition of other metal oxides to the starting material.

The rate of the reaction is not affected by changes in the reactant gas flowrate or in the porosity of the CrCl_3 pellets under the experimental conditions used.

- (iii) The reaction appears to occur in a single step, and, under most experimental conditions studied, Cr_2O_3 is the only solid product detected. However, under

certain extreme conditions, the formation of CrO_2Cl_2 or CrOCl has been observed. It is uncertain whether these species are formed as a result of competing side-reactions or as intermediate species in the oxidation reaction.

CrO_2Cl_2 formation becomes significant when the oxidation is carried out in pure oxygen at a low temperature or low heating rate.

CrOCl is observed under conditions of low oxygen partial pressure and high heating rates, i.e. conditions such that the reaction rate depends on the rate of mass transfer of oxygen to the reaction site. When a complete layer of CrOCl is formed on the CrCl_3 surface, further oxidation is inhibited.

- (iv) Under most experimental conditions studied, the rate of the reaction is thought to be limited by the rate of the chemical reaction, and the kinetic behaviour may be described by a contracting-geometry rate expression for over ~90% of the reaction. The reaction proceeds by the linear advance of a well-defined reactant-product interface which moves inwards from the surface of the pellet. Two rate constants describe the rate of the reaction, the rate of interface advance from the sides of the disc-shaped pellet being greater than the rate of interface advance from the top and bottom of the pellet. The

ratio of these rates is dependent on the particular experimental conditions employed.

- (v) The Cr_2O_3 produced by the solid-gas oxidation of CrCl_3 is comparable, in terms of both chemical and physical properties, with that manufactured commercially by wet chemical processes.

12. SUGGESTIONS FOR FURTHER WORK

(i) Oxidation of single crystals

All experimental work in this study has been on 1 g CrCl_3 pellets. Although the conclusions drawn from these experiments appear to indicate that the results can be extrapolated to describe the behaviour of single crystals of CrCl_3 , this can only be confirmed by experimental evidence.

(ii) Oxidation at low temperatures

This study has shown that the kinetic model proposed holds only in the temperature range 400 to 600°C. Below 400°C significant deviations from the model occur, particularly when the reaction is carried out in pure oxygen. A more detailed investigation of this behaviour should be undertaken.

(iii) Different pellet sizes and relative dimensions

The present study has examined the oxidation of CrCl_3 pellets of fixed mass and dimensions. The kinetic expression proposed contains terms involving the ratio of the pellet diameter to the pellet thickness. Different pellet configurations should be used to validate this model.

(iv) SEM analysis

The SEM analysis of partially-reacted pellets was carried out only under a single set of experimental

conditions. Different rates of migration of the reactant-product interface in different directions were observed. These observations should be extended to include other temperatures, to see whether these different rates have different temperature dependences.

(v) **Gas-phase oxidation**

As mentioned in Chapter 10, it may be desirable from a commercial point of view that the oxidation be carried out with both reactant species in the gaseous phase. Such a study is expected to give substantially different kinetic results to the present study. Experimental techniques such as mass spectrometry or vapour-phase spectroscopy would be required for such a study.

(vi) **Physical properties of Cr_2O_3**

A quantitative study of the dependence of the physical properties of the oxide particles produced on the experimental conditions used for their production could be useful, especially for commercial applications.

(vii) **Effect on the oxidation of impurities in the CrCl_3**

The CrCl_3 starting material used in the present work was produced from electrolytic chromium and was therefore relatively pure. As mentioned in Chapter 1, it is envisaged that industrial applications of this

would use CrCl_3 produced from the chlorination of chromite or ferrochromium. Such CrCl_3 would be contaminated by small amounts of other transition-metal chlorides. A study of the effects of these impurities on the rate of reaction and on the physical properties of the oxide would be useful.

(viii) Parameters affecting the rate constant

In this work, discussion of the rate constants obtained has been limited. These have been shown (Section 8.2) to depend quantitatively on factors such as the partial pressure of the gaseous reactant, its diffusivity, the pellet dimensions, or the relative densities of the solid reactant and product. Further investigation of the fundamental nature of the rate constant could be carried out.

(ix) Mechanism of reaction

Although this study has defined and attempted to account for the bulk kinetic behaviour of the system, the process(es) occurring at the reactant-product interface have not been fully explained, and the possibility of the formation of an intermediate species cannot yet be discounted. There is considerable scope for a closer investigation of the conditions under which alternate products form and their effect on the reaction mechanism.

(x) Oxidation of other chromium(III) halides

Of more fundamental interest, the kinetics and mechanism of oxidation of other chromium(III) halides could be investigated. It is possible that the oxidation of CrF_3 may have potential industrial applications in the future.

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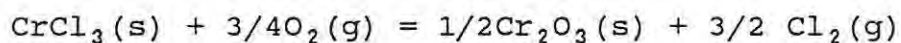
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APPENDIX A CALCULATION OF ENERGY BALANCE

Basis : 1 mol CrCl_3

Assumptions :

- (i) O_2 enters the system at 25°C ;
- (ii) O_2 utilisation efficiency is 50%, therefore 2 stoichiometric units are introduced;
- (iii) CrCl_3 has been preheated to the reaction temperature of 600°C ;
- (iv) Reaction occurs at 600°C and goes to completion;
- (v) Cl_2 and excess O_2 leave the reactor at 600°C .

Mass balance :

For 1 mol CrCl_3 - 1,5 mol O_2 required
 - 1,5 mol Cl_2 produced
 - 0,5 mol Cr_2O_3 produced.

Energy balance :

CrCl_3 in	: 1,0 mol @ 600°C	-497,35 kJ
O_2 in	: 1,5 mol @ 25°C	0,00 kJ
		-497,35 kJ

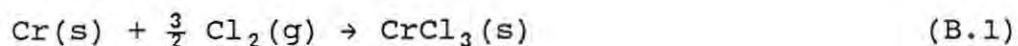
Cr ₂ O ₃ out :	0,5 mol @ 600°C	-530,28 kJ
O ₂ out :	0,75 mol @ 600°C	13,72 kJ
Cl ₂ out :	1,5 mol @ 600°C	31,00 kJ
		-485,55 kJ

Therefore energy out - energy in = 11,80 kJ

Thus the process is slightly endothermic.

APPENDIX B METHOD FOR THE PREPARATION OF CrCl_3

Anhydrous chromium(III) chloride was produced on a batch scale by the high temperature chlorination of chromium metal according to the reaction



The experimental apparatus is shown in Figure B.1. Electrolytic chromium of 99,99% purity and industrial-grade chlorine (Sappi) were the starting materials. Approximately 9 g of metal (-5 mm, +2 mm) was supported between clean, dried silica wool in a silica tube of internal diameter 38 mm in a packed-bed configuration, and then placed in a Kanthal-wound resistively-heated, 1,5 kW horizontal tube furnace. The temperature of the furnace was regulated by a Pye Ether Transitrol controller; temperatures were measured using R-type (Pt-Pt13%Rh) thermocouples. Gas flowrates were measured using calibrated rotameters. After purging the system with high-purity nitrogen to remove all oxygen, the furnace was heated to the required temperature and the chlorine gas allowed to enter the reactor. On completion of the reaction, the chlorine flow and the furnace were switched off, but the nitrogen flow was maintained until the system had cooled to room temperature.

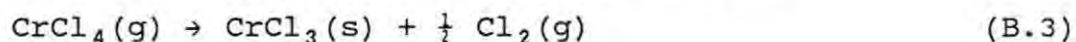
The chlorination reaction was typically carried out at 860 to 900°C, using a chlorine partial pressure of ~42,0 kPa, and a total gas flowrate of 500 cm³ min⁻¹. Nitrogen was

used as the diluent/carrier gas. The reaction was usually complete within 30 to 40 minutes.

Since chromium(IV) chloride is known to be the most stable chromium chloride species to exist in the presence of excess chlorine at the reaction temperature^{21,25}, the reaction which is thought to take place in the bed is



However, at temperatures below 800°C, the tetrachloride gas disproportionates according to the reaction



Since CrCl_4 is a gas, the reaction product is transported along the reaction tube and the dissociation product CrCl_3 is deposited downstream of the original chromium bed, as shown in Figure B.1. The purple flaky crystals are then recovered manually from the reaction tube, crushed by hand with a mortar and pestle, and used "as received" for the oxidation experiments.

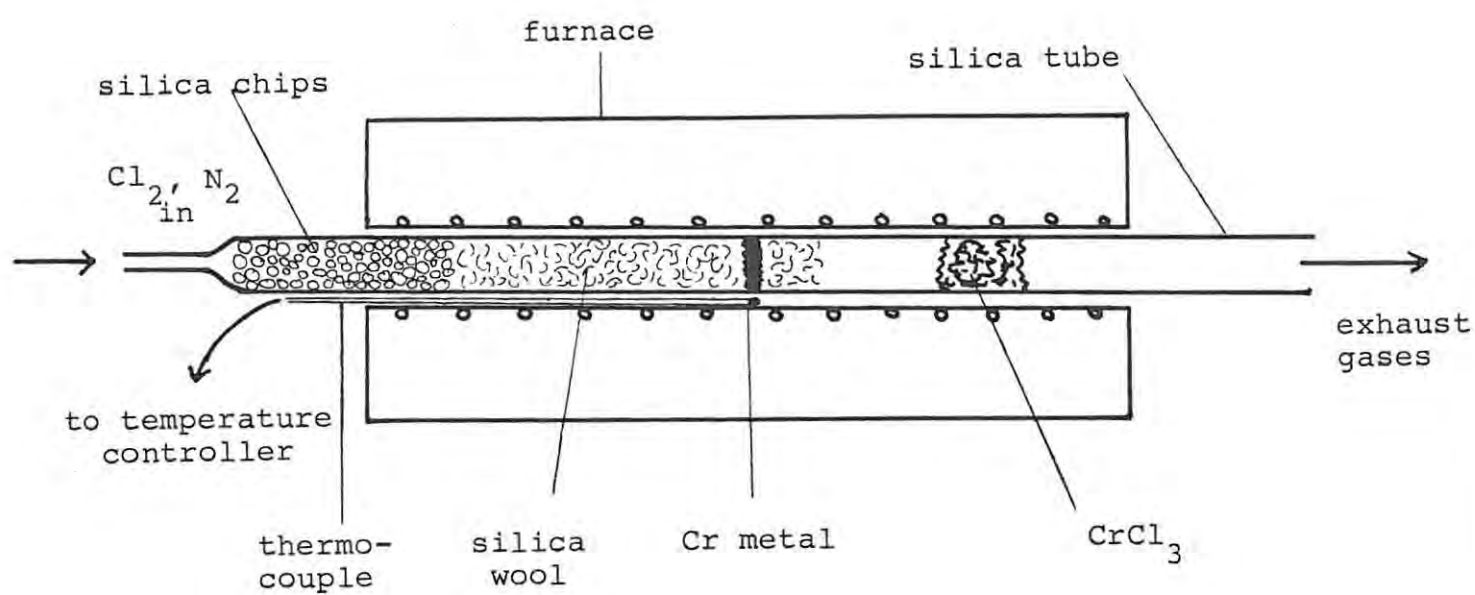


Figure B.1 Apparatus used for the chlorination of chromium metal to produce CrCl_3

APPENDIX C TYPICAL ANALYSIS OF A PARTIALLY-REACTED PELLET
CROSS-SECTION FROM SEM ATOMIC-NUMBER CONTRAST
IMAGE

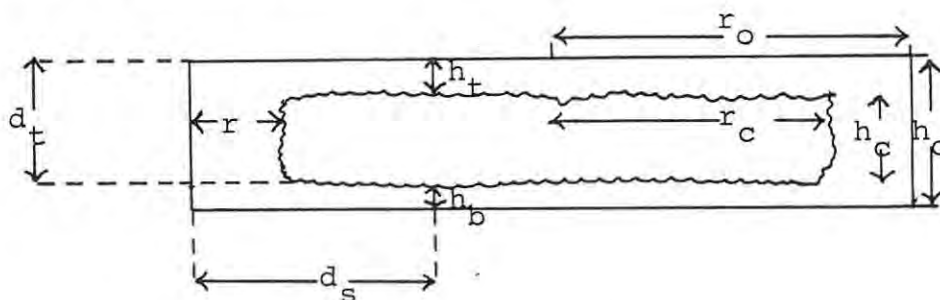
Reaction conditions : Reacted at 600°C in static air for 5 minutes. A photograph of the cross-section is shown in Figure 7.2(b).

The scale was determined by measuring the distance between two fixed points on the SEM screen using the SEM software, and comparing this distance with that measured (using a ruler) on the dot-matrix printout. For convenience, all measurements refer to the printout image.

Scale : $7,90 \text{ cm} \equiv 2,87 \text{ mm}$

Therefore $1 \text{ mm on printout} \equiv 0,0363 \text{ mm on actual cross-section.}$

Since "end effects" are pronounced in certain cross-sections, measurements are only made on the "linear" region of the reactant-product interface. The measurements made are shown below.



Reference points are the left-hand side of the pellet ($d_s = 0$) for measurements along the top (h_t) and bottom (h_b), and the top of the pellet ($d_t = 0$) for measurements along the sides (r).

Thickness of the product layer on the top and bottom :

d_s (mm)	20	40	60	80	100	120	140	160	180	200
h_t (mm)	5,5	4,8	4,0	4,0	5,5	3,0	4,0	4,2	3,5	3,8
h_b (mm)	7,0	8,0	6,5	4,2	5,0	3,0	3,8	4,2	3,2	2,0

d_s (mm)	220	240	260	280	300	320	340	360		
h_t (mm)	4,5	3,0	2,5	4,5	5,0	4,5	3,0	3,0		
h_b (mm)	5,5	3,0	5,2	3,0	5,0	7,5	-	-		

Thickness of the product layer on the sides :

d_t (mm)	10	20	30	40	50	60	70
r_{LHS} (mm)	17	13	5,0	4,8	7,5	9,5	12
r_{RHS} (mm)	17	11	9,5	9,5	9,0	8,0	16

Average thickness top and bottom = 4,1 mm

Average thickness sides = 10,6 mm

Thickness of product layers as a fraction of the total dimension:

Top and bottom = 4,1 mm/80 mm = 5,2%

Sides = 10,6 mm/372 mm = 2,9%

Volume of original pellet = $\pi r_o^2 h_o = \pi (372/2 \text{ mm})^2 \cdot 80 \text{ mm}$
 = $8,70 \times 10^6 \text{ mm}^3$

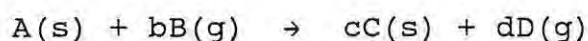
Volume of CrCl_3 core remaining = $\pi r_c^2 h_c = \pi (351/2 \text{ mm})^2 \cdot 72 \text{ mm}$
 = $6,93 \times 10^6 \text{ mm}^3$

So, fractional conversion, α_s = 20,3%

Compare with fractional conversion calculated from the mass loss, α_m = 17,8%.

APPENDIX D DERIVATION OF RATE EXPRESSIONS FOR A DISC-
SHAPED PELLET EXHIBITING CONTRACTING-GEOMETRY
KINETIC BEHAVIOUR

Consider a disc-shaped pellet of initial height, h_0 , and radius, r_0 , reacting according to the equation

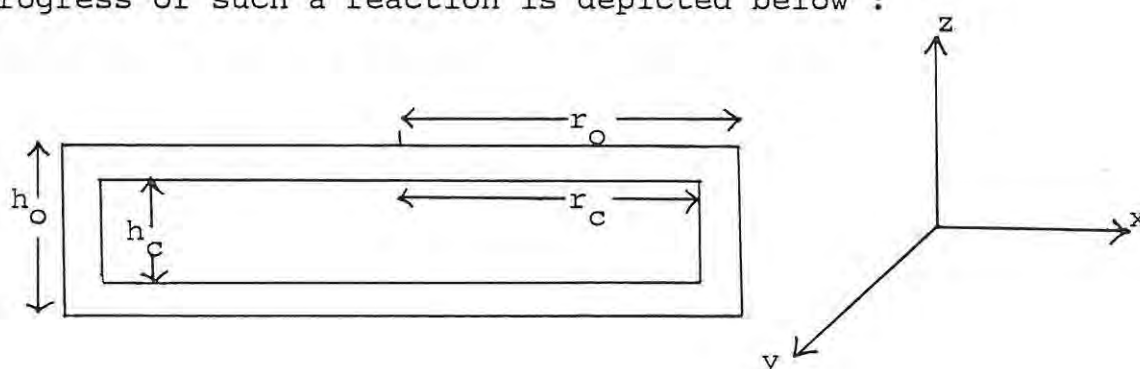


It is assumed that

- (i) the reaction occurs at a well-defined reactant-product interface;
- (ii) the product layer is not removed from the unreacted core, and the dimensions of the final product are the same as those of the starting material;
- (iii) the unreacted core is considered to be essentially non-porous, while the product layer is considered to be porous.

It is further assumed that the movement of the interface occurs at equal rates in the x-, y- and z-directions. Therefore, if a is the ratio of the pellet height to diameter, then $a = h/2r$ at any time t .

The progress of such a reaction is depicted below :



The fractional conversion of the product C at any time t is given (for TG experiments) by

$$\alpha = \frac{m_0 - m_i}{m_0 - m_f} \quad (D.1)$$

$$\alpha = \frac{\rho_A \pi r_0^2 h_0 - \rho_A \pi r_c^2 h_c}{\rho_A \pi r_0^2 h_0} \quad (D.2)$$

$$\alpha = \frac{r_0^3 - r_c^3}{r_0^3} \quad \text{since } h = 2ra \quad (D.3)$$

$$\alpha = 1 - (r_0/r_c)^3 \quad (D.4)$$

Therefore

$$r_c = r_0 (1 - \alpha)^{1/3} \quad (D.5)$$

where ρ_A is the density of solid reactant A

r_c and h_c are the radius and height of the unreacted core of A at time t .

The rate of reaction is determined by the rate of interface advance, dr_c/dt . This may be governed either by the rate of diffusion of the reactant gas B through the product layer C, or by the rate of the chemical reaction itself at the reaction site.

Diffusion Control :

Both the reactant gas B and the reactant-product interface advance with time towards the centre of the pellet. The shrinkage of the unreacted core, however, occurs at a much slower rate, and the interface can therefore initially be assumed to be stationary.

The rate of diffusion of the reactant gas B to the reaction site is proportional to the concentration gradient along which the diffusion occurs, and is governed by Fick's first law.

$$-\frac{1}{A} \frac{dN_B}{dt} = D \frac{dC}{dr_c} \quad (D.6)$$

where A is the surface area of the unreacted core of A

N_B is the number of molecules of the reactant gas B

D is the diffusion coefficient

C is the concentration (partial pressure) of reactant gas B.

The surface area of a disc-shaped pellet is given by

$$A = 2\pi r^2 + 2\pi rh \quad (D.7)$$

and since $h = 2ra$

$$\begin{aligned} A &= 2\pi r_c^2 + 4\pi r_c^2 a \\ &= 2\pi r_c^2 (1 + 2a) \end{aligned} \quad (D.8)$$

Substituting into equation D.6

$$-\frac{dN_B}{dt} = 2\pi r_c^2 (1 + 2a) D \frac{dC}{dr_c} \quad (D.9)$$

Integrating across the ash layer from the initial radius, r_0 , to the radius of the core, r_c , at any time t

$$-\frac{dN_B}{dt} \int_{r_0}^{r_c} \frac{1}{r_c^2} dr_c = 2\pi(1 + 2a)D \int_C^0 dC \quad (D.10)$$

$$-\frac{dN_B}{dt} \left(\frac{1}{r_c} - \frac{1}{r_0} \right) = 2\pi(1 + 2a)DC \quad (D.11)$$

If the change of the radius of the core, r_c , with time is taken into account, then it is expected that as the thickness of the ash layer increases, the rate of diffusion will decrease.

$$\text{Now } dN_B = \rho_A dV = dN_A/b \quad (\text{D.12})$$

For a cylindrical disc

$$V = \pi r^2 h = 2\pi r_c^3 a \quad (\text{D.13})$$

Therefore

$$dN_A = b\rho_A 2\pi a r_c^2 dr_c \quad (\text{D.14})$$

Substituting into equation D.11

$$- b\rho_A 2\pi a \int_{r_0}^{r_c} \left(\frac{1}{r_c} - \frac{1}{r_0} \right) r_c^2 dr_c = 2\pi(1+2a)DC \int_0^t dt \quad (\text{D.15})$$

$$- \left[\int_{r_0}^{r_c} r_c dr_c - \int_{r_0}^{r_c} \frac{r_c^2}{r_0} dr_c \right] = \frac{(1+2a)DC}{b\rho_A a} t \quad (\text{D.16})$$

$$- \left[\frac{1}{2} r_0^2 - \frac{1}{2} r_c^2 - \frac{1}{3} r_0^2 - \frac{r_c^3}{3r_0} \right] = \frac{(1+2a)DC}{b\rho_A a} t \quad (\text{D.17})$$

$$1 - 3 \left[\frac{r_c}{r_0} \right]^2 + 2 \left[\frac{r_c}{r_0} \right]^3 = - \frac{6(1+2a)DC}{b\rho_A a r_0^2} t \quad (\text{D.18})$$

$$\text{Now, since } r_c = r_0(1-\alpha)^{1/3} \quad (\text{D.5})$$

equation (D.18) can be reduced to

$$1 - 3(1-\alpha)^{2/3} + 2(1-\alpha) = - \frac{6(1+2a)DC}{b\rho_A a r_0^2} t \quad (\text{6.19})$$

This rate expression is now of the form

$$f(\alpha) = kt$$

and it is readily seen that the apparent rate constant, k , for the reaction will be given by

$$k = - \frac{6(1 + 2a)DC}{b\rho_A ar_0^2} \quad (D.20)$$

Therefore, if the reaction is under diffusion control, the rate of the reaction will be dependent on the dimensions of the pellet (r_0 and a), the diffusion coefficient (D), the partial pressure of the reactant gas (C) and the density of the solid reactant (ρ_A).

The rate of interface advance is given by the rate of change of the radius of the unreacted core. Differentiation of equation D.18 with respect to r_c gives

$$\frac{dt}{dr_c} = - \frac{6r_c}{kr_0^2} + \frac{6r_c^2}{kr_0^3} \quad (D.21)$$

$$= - \frac{6(r_0 r_c - r_c^2)}{kr_0^3} \quad (D.22)$$

Therefore

$$\frac{dr_c}{dt} = - \frac{kr_0^3}{6(r_0 r_c - r_c^2)} \quad (D.23)$$

The rate of interface advance of the reactant-product interface for a reaction under diffusion control is not constant with time; it is dependent on the radius of the unreacted core, r_c .

Chemical Control :

For a solid-gas reaction controlled by the rate of the chemical reaction at the reactant product interface, it is

assumed that the reaction is first order with respect to the reactant gas B.

Then

$$-\frac{dN_A}{dt} = k_g AC \quad (D.24)$$

where dN_A is the change of mass of reactant A

k_g is the first order rate constant

A is the surface area of the unreacted core A

C is the concentration of reactant gas B.

Therefore

$$-\frac{d(\rho_A \pi r_c^2 (2r_c a))}{dt} = k_g C (2\pi r_c (2r_c a) + 2\pi r_c^2) \quad (D.25)$$

$$-2\rho_A \pi a \frac{dr_c^3}{dt} = k_g C 2\pi r_c^2 (2a + 1) \quad (D.26)$$

$$-b\rho_A \pi a r_c^2 dr_c = k_g C 2\pi r_c^2 (2a + 1) dt \quad (D.27)$$

$$-b\rho_A \pi a r_c^2 \int_{r_0}^{r_c} dr_c = k_g C 2\pi r_c^2 (2a + 1) \int_0^t dt \quad (D.28)$$

$$-3a\rho_A (r_0 - r_c) = -(2a + 1)k_g Ct \quad (D.29)$$

Substituting (D.5) into (D.29)

$$-3a\rho_A (r_0 - r_0(1 - \alpha)^{1/3}) = -(2a + 1)k_g Ct \quad (D.30)$$

$$1 - (1 - \alpha)^{1/3} = \frac{(2a + 1)}{3a\rho_A r_0} k_g Ct \quad (D.31)$$

This is the rate expression for the contracting-volume (3-dimensional shrinking core) model. Since this equation has the form

$$f(\alpha) = kt$$

the apparent rate constant for the reaction of a disc-shaped pellet under chemical control is given by

$$k = \frac{(2a + 1)k_g C}{3a\rho_A r_0} \quad (D.32)$$

The rate of a reaction under chemical control will therefore be determined by the dimensions of the pellet (a , r_0), the density of the solid reactant A (ρ_A) and the partial pressure of the gaseous reactant B (C).

The rate of interface advance for this kinetic behaviour is obtained from the first derivative of equation (D.29).

$$-3a\rho_A(r_0 - r_c) = -(2a + 1)k_g Ct \quad (D.29)$$

$$r_c = r_0 - \frac{(2a + 1)k_g Ct}{3a\rho_A} \quad (D.33)$$

$$\frac{dr_c}{dt} = \frac{(2a + 1)k_g C}{3a\rho_A} \quad (D.34)$$

Therefore, in contrast to the situation for a reaction under diffusion control (equation (D.23)), the rate of interface advance for a reaction under chemical control is constant with respect to time.

A similar analysis can be carried out for the derivation of the respective rate expressions for the two-dimensional situation. If it is now assumed that a disc-shaped pellet reacts only by interface advance in the x -, y -plane, and that no reaction occurs from the flat ends of the pellet, then at

any time t , $h_c = h_0 = 2r_0 a$.

The fractional conversion is then given by

$$\alpha = \frac{\rho_A \pi r_0^2 h_0 - \rho_A \pi r_c^2 h_0}{\rho_A \pi r_0^2 h_0} \quad (D.35)$$

$$= \frac{r_0^2 - r_c^2}{r_0^2} \quad (D.36)$$

$$= 1 - (r_c/r_0)^2 \quad (D.37)$$

Therefore

$$r_c = r_0 (1 - \alpha)^{1/2} \quad (D.38)$$

Diffusion control :

$$- \frac{1}{A} \frac{dN_B}{dt} = D \frac{dC}{dr_c} \quad (D.39)$$

Now

$$A = 2\pi r h = 2\pi r_c (2r_0 a) = 4\pi r_0 a r_c \quad (D.40)$$

Therefore

$$- \frac{dN_B}{dt} = 4D\pi r_0 a r_c \frac{dC}{dr_c} \quad (D.41)$$

$$- \frac{dN_B}{dt} \int_{r_0}^{r_c} \frac{1}{r_c} dr_c = 4D\pi r_0 a \int_C^0 dC \quad (D.42)$$

$$- \frac{dN_B}{dt} \ln r_c \Big|_{r_0}^{r_c} = 4D\pi r_0 a C \quad (D.43)$$

$$- \frac{dN_B}{dt} (\ln r_0 - \ln r_c) = 4D\pi r_0 a C \quad (D.44)$$

$$\text{Now } dN_B = \rho_A dV = dN_A/b \quad (D.45)$$

$$\text{And } V = \pi r^2 h = 2\pi r_c^2 r_0 a \quad (D.46)$$

Therefore

$$dN_A = 2\pi r_0 a b r_c \rho_A dr_c \quad (D.47)$$

Substituting (D.45) and (D.47) into (D.44)

$$- 2\pi r_0 a b \rho_A \int_{r_0}^{r_c} (\ln r_0 - \ln r_c) r_c dr_c = 4D\pi r_0 a C \int_0^t dt \quad (D.48)$$

$$- \left[\int_{r_0}^{r_c} r_c \ln r_0 dr_c - \int_{r_0}^{r_c} r_c \ln r_c dr_c \right] = \frac{2DC}{b\rho_A} \int_0^t dt \quad (D.49)$$

$$- \left[\left[\frac{1}{2} \ln r_0 (r_c^2) \right]_{r_0}^{r_c} - \left[\frac{r_c^2}{2} \ln r_c - \frac{r_c^2}{2} \right]_{r_0}^{r_c} \right] = \frac{2DC}{b\rho_A} t \quad (D.50)$$

Therefore

$$- 2r_c^2 \ln r_0 + r_0^2 + 2r_c^2 \ln r_c - r_c^2 = - \frac{8DC}{b\rho_A} t \quad (D.51)$$

$$\text{Now, since } r_c = r_0(1 - \alpha)^{1/2} \quad (D.38)$$

equation (D.51) can be simplified to

$$\alpha + (1 - \alpha) \ln(1 - \alpha) = kt \quad (D.52)$$

$$\text{where } k = -8DC/b\rho_A \quad (D.53)$$

The rate of interface advance is obtained from the first derivative of equation (D.51) with respect to time.

$$\frac{dt}{dr_c} = \frac{1}{k} (-4r_c \ln r_0 + r_0^2 + 2 \frac{r_c^2}{r_c} + 4r_c \ln r_c - 2r_c) \quad (D.54)$$

Therefore

$$\frac{dr_c}{dt} = \frac{k}{-4r_c (\ln r_0 - \ln r_c)} \quad (D.55)$$

$$\frac{dr_c}{dt} = \frac{2DC}{r_c b \rho_A \ln(r_0/r_c)} \quad (D.56)$$

Chemical control :

$$- \frac{dN_A}{dt} = k_g AC \quad (D.57)$$

Therefore

$$- \frac{d(b\rho_A \pi r_c^2 (2r_0 a))}{dt} = k_g C 4\pi r_0 a r_c \quad (D.58)$$

$$- b\rho_A \pi 2r_0 a dr_c^2 = k_g C 4\pi r_0 a r_c dt \quad (D.59)$$

$$- b\rho_A \int_{r_0}^{r_c} dr_c = k_g C \int_0^t dt \quad (D.60)$$

$$- b\rho_A (r_0 - r_c) = k_g C t \quad (D.61)$$

Simplifying and substituting (D.38) gives

$$1 - (1 - \alpha)^{1/2} = - \frac{k_g C}{b\rho_A r_0} t \quad (D.62)$$

This is the rate expression for the contracting-area model, where the apparent rate constant is given by

$$k = - \frac{k_g C}{b\rho_A r_0} \quad (D.63)$$

Rearranging (D.61) gives

$$r_c = \frac{k_g C}{b\rho_A} t + r_0 \quad (D.64)$$

Therefore

$$\frac{dr_c}{dt} = \frac{k_g C}{b\rho_A} = \text{constant} \quad (D.65)$$

This confirms that the rate of interface advance for a reaction under chemical rate control is constant with time, although the rate of interface advance for a diffusion-controlled reaction depends on the dimensions of the unreacted core (and hence the thickness of the product layer) at any time t (equation (D.56)).

APPENDIX E COMPUTER PROGRAMS FOR KINETIC ANALYSIS

E.1 ALPHA

```

100 REM *****
110 REM * THIS PROGRAM CONVERTS TG CURVES *
120 REM * IN % MASS LOSS TO ALPHA CURVES *
130 REM * AND CREATES ALPHA - TIME DATA *
140 REM * AND ALPHA - REDUCED-TIME DATA *
150 REM *****
160 DIM TG%(1668),AL%(1668),A$(21),TM(1668),RT(1668)
170 D$ = CHR$(4)
180 HOME : INVERSE : PRINT "
190 VTAB 3: PRINT "
200 VTAB 2: PRINT " "; HTAB 39: PRINT "
210 NORMAL : VTAB 2: HTAB 3: PRINT "CONVERSION OF TG DATA TO ALPHA DATA"
220 VTAB 6: PRINT "INSERT MASTER FILE DISC (D2)"
230 VTAB 8: INPUT "ENTER MASTER FILE NAME : ";NAAM$
240 VTAB 15: PRINT "      CALCULATION IN PROGRESS
250 PRINT : PRINT "      PLEASE DO NOT SWITCH OFF !"
260 GOSUB 1000: REM READ IN DATA
270 GOSUB 2000: REM CALCULATE ALPHA
280 VTAB 15: PRINT "      ": VTAB 17: PRINT
"
290 VTAB 10: INPUT "DO YOU WANT TO STORE ALPHA DATA ? ";A$
300 IF A$ < > "Y" AND A$ < > "N" THEN GOTO 290
310 IF A$ = "N" THEN GOTO 330
320 GOSUB 3000: REM STORE ALPHA DATA
330 PRINT : PRINT : PRINT "DO YOU WANT TO CALCULATE ALPHA - TIME"
340 INPUT "DATA ? ";A$
350 IF A$ < > "Y" AND A$ < > "N" THEN GOTO 340
360 IF A$ = "N" THEN GOTO 380
370 GOSUB 4000
380 PRINT : PRINT : PRINT "DO YOU WANT TO CALCULATE ALPHA -
390 INPUT "REDUCED-TIME DATA ? ";A$
400 IF A$ < > "Y" AND A$ < > "N" THEN GOTO 390
410 IF A$ = "N" THEN GOTO 430
420 GOSUB 5000
430 PRINT : PRINT : INPUT "ANOTHER CALCULATION ? ";A$
440 IF A$ < > "Y" AND A$ < > "N" THEN GOTO 430
450 IF A$ = "N" THEN GOTO 470
460 GOTO 180
470 PRINT D$;"RUN TGMENU,D1"
1000 REM *****
1010 REM * READ IN MASTER AND TG DATA *
1020 REM *****
1030 PRINT D$;"OPEN";NAAM$;"",D2"
1040 PRINT D$;"READ";NAAM$
1050 FOR I = 1 TO 21: INPUT A$(I): NEXT I
1060 PRINT D$;"CLOSE";NAAM$
1070 AR = VAL (A$(18))
1080 ND = VAL (A$(21))
1090 PML = - 1E7
1100 PRINT D$;"OPEN";NAAM$ + ".TG,D2"
1110 PRINT D$;"READ";NAAM$ + ".TG"
1120 FOR I = 1 TO ND
1130 INPUT TG%(I)
1140 IF TG%(I) > PML THEN PML = TG%(I)

```



```

1150 NEXT I
1160 PRINT D$;"CLOSE";NAAM$ + ".TG"
1170 RETURN
2000 REM *****
2010 REM * CALCULATION OF ALPHA *
2020 REM *****
2030 FOR I = 1 TO ND
2040 AL%(I) = INT ((TG%(I) / PML) * 10000 + .5)
2050 NEXT I
2060 RETURN
3000 REM *****
3010 REM * STORE ALPHA DATA *
3020 REM *****
3030 PRINT : PRINT "INSERT DISC TO STORE ALPHA DATA (D2)"
3040 HTAB 7: VTAB 20: PRINT "PRESS 'RETURN' TO CONTINUE "
3050 GET R$: PRINT
3060 VTAB 20: PRINT "
3070 VTAB 13: PRINT "ALPHA DATA IS STORED AS ";NAAM$ + ".AL"
3080 PRINT D$;"OPEN";NAAM$ + ".AL,D2"
3090 PRINT D$;"DELETE";NAAM$ + ".AL"
3100 PRINT D$;"OPEN";NAAM$ + ".AL"
3110 PRINT D$;"WRITE";NAAM$ + ".AL"
3120 FOR I = 1 TO ND: PRINT AL%(I): NEXT I
3130 PRINT D$;"CLOSE";NAAM$ + ".AL"
3140 RETURN
4000 REM *****
4010 REM * CALCULATE ALPHA - TIME DATA *
4020 REM *****
4030 HOME : INVERSE : PRINT "
3: PRINT "
: HTAB 38: PRINT "
4040 NORMAL : VTAB 2: HTAB 3: PRINT "CALCULATION OF ALPHA - TIME DATA"
4050 VTAB 6: PRINT "TIME UNITS IN "
4060 PRINT : PRINT " (A) MINUTES"
4070 PRINT " (B) HOURS"
4080 PRINT : INPUT "ENTER CHOICE : ";TM$
4090 IF TM$ < > "A" AND TM$ < > "B" THEN GOTO 4080
4100 IF TM$ = "A" THEN TM = 1
4110 IF TM$ = "B" THEN TM = 60
4120 TM(1) = (AR / 60) / TM
4130 FOR I = 2 TO ND: TM(I) = TM(I - 1) + (AR / 60) / TM: NEXT I
4140 PRINT : PRINT "INSERT DISC FOR ALPHA-TIME DATA (D2)"
4150 HTAB 7: VTAB 20: PRINT "PRESS 'RETURN' TO CONTINUE"
4160 GET R$: PRINT
4170 HTAB 7: VTAB 20: PRINT "
4180 VTAB 15: PRINT "DATA STORED AS ";NAAM$ + ".TIME.AL"
4190 PRINT D$;"OPEN";NAAM$ + ".TIME.AL,D2"
4200 PRINT D$;"DELETE";NAAM$ + ".TIME.AL"
4210 PRINT D$;"OPEN";NAAM$ + ".TIME.AL"
4220 PRINT D$;"WRITE";NAAM$ + ".TIME.AL"
4230 PRINT ND / 5
4240 FOR I = 1 TO ND STEP 5: PRINT TM(I): PRINT AL%(I) / 10000: NEXT I
4250 PRINT D$;"CLOSE";NAAM$ + ".TIME.AL"
4260 RETURN
5000 REM *****
5010 REM * CALCULATE REDUCED-TIME DATA *
5020 REM *****

```

```

5030 HOME : INVERSE : PRINT "                                     ": VTAB
      3: PRINT "                                     ": VTAB 2: PRINT " "
      ;: HTAB 39: PRINT " "
5040 NORMAL : VTAB 2: HTAB 3: PRINT "CALCULATION OF ALPHA-RED.TIME DATA"
5050 MN = 1E7
5060 FOR I = 1 TO ND
5070 IF ABS (0.5 - (AL%(I) / 10000)) > MN THEN GOTO 5100
5080 MN = ABS (0.5 - (AL%(I) / 10000)):
5090 T50 = TM(I)
5100 NEXT I
5110 FOR I = 1 TO ND:RT(I) = TM(I) / T50: NEXT I
5120 VTAB 6: PRINT "INSERT DISC TO STORE DATA (D2)"
5130 HTAB 7: VTAB 20: PRINT "PRESS 'RETURN' TO CONTINUE"
5140 GET R$: PRINT
5150 HTAB 7: VTAB 20: PRINT "
5160 VTAB 8: PRINT "DATA IS STORED AS ";NAAM$ + ".RTM.AL"
5170 PRINT D$;"OPEN";NAAM$ + ".RTM.AL,D2"
5180 PRINT D$;"DELETE";NAAM$ + ".RTM.AL"
5190 PRINT D$;"OPEN";NAAM$ + ".RTM.AL"
5200 PRINT D$;"WRITE";NAAM$ + ".RTM.AL"
5210 PRINT ND / 5
5220 FOR I = 1 TO ND STEP 5: PRINT RT(I): PRINT AL%(I) / 10000: NEXT I
5230 PRINT D$;"CLOSE";NAAM$ + ".RTM.AL"
5240 RETURN

```

E.2 KINETICS

```

100 REM *****
110 REM * THIS PROGRAM CALCULATES THEORETICAL *
120 REM * ISOTHERMAL KINETIC FUNCTIONS FROM *
130 REM * ALPHA-TIME CURVES *
140 REM *****
150 D$ = CHR$(4)
160 DIM AL(400),FA(400),TM(400),YTH(400),RS(400)
170 HOME : INVERSE : PRINT "
180 VTAB 3: PRINT "
190 VTAB 2: PRINT " : HTAB 38: VTAB 2: PRINT "
200 VTAB 2: NORMAL : HTAB 11: PRINT "ISOTHERMAL KINETICS"
210 PRINT : PRINT : PRINT " THIS PROGRAM CALCULATES ISOTHERMAL"
220 PRINT " KINETIC FUNCTIONS FROM EXPERIMENTAL "
230 PRINT " ALPHA-TIME DATA OR ALPHA-REDUCED TIME"
240 PRINT " DATA."
250 HTAB 7: VTAB 20: PRINT "PRESS 'RETURN' TO CONTINUE"
260 GET R$: PRINT
270 HOME : PRINT : PRINT " TO RUN THIS PROGRAM, THE DATA MUST BE"
280 PRINT " STORED AS ALPHA-TIME OR ALPHA-REDUCED"
290 PRINT " TIME FILES."
300 PRINT : PRINT " IF YOUR DATA IS NOT IN THIS FORM THEN"
310 PRINT " PRESS 'ESCAPE' TO EXIT FROM THE "
320 PRINT " PROGRAM."
330 VTAB 22: HTAB 7: PRINT " PRESS 'RETURN' TO CONTINUE."
340 GET R$: PRINT : IF R$ = CHR$(27) THEN GOTO 650
350 HOME : PRINT : PRINT " A NUMBER OF KINETIC MODELS ARE "
360 PRINT " AVAILABLE FOR FITTING THE DATA."
370 PRINT : PRINT " THE KINETIC FUNCTIONS ARE OF THE FORM"
380 PRINT : PRINT " F(A) = KT"
390 PRINT : PRINT " WHERE A=ALPHA "
400 PRINT " K=RATE CONSTANT"
410 PRINT " T=TIME"
420 PRINT : PRINT " IF THE MODEL CHOSEN REPRESENTS"
430 PRINT " THE EXPERIMENTAL SYSTEM ACCURATELY,"
440 PRINT " THEN A PLOT OF F(A) VS T WILL BE A "
450 PRINT " STRAIGHT LINE WITH SLOPE K."
460 PRINT : PRINT " THIS PROGRAM CALCULATES THE THEORET-"
470 PRINT " ICAL FUNCTIONS, PLOTS F(A) AGAINST"
480 PRINT " TIME AND CALCULATES THE CORRELATION"
490 PRINT " COEFFICIENT FOR THE LINE."
500 PRINT : PRINT : HTAB 7: PRINT "PRESS 'RETURN' TO CONTINUE"
510 GET R$: PRINT
520 GOSUB 1000
530 GOSUB 2000
540 GOSUB 3000
550 GOSUB 4000
560 GOSUB 5000
570 GOSUB 6000
580 GOSUB 7000
590 HOME : TEXT : VTAB 3: INPUT " DO YOU WANT TO TRY ANOTHER EQN ? ";A$
600 IF A$ < > "Y" AND A$ < > "N" THEN GOTO 590
610 IF A$ = "Y" THEN GOTO 530
620 PRINT : INPUT " DO YOU WANT TO ENTER NEW DATA ? ";A$
630 IF A$ < > "Y" AND A$ < > "N" THEN GOTO 620
640 IF A$ = "Y" THEN GOTO 520

```

```

650 PRINT D$;"RUN MENU,D1"
1000 REM *****
1010 REM * INPUT DATA *
1020 REM *****
1030 HOME : INPUT " ENTER MASTER FILE NAME : ";NAAM$
1040 PRINT : PRINT : PRINT " IS YOUR DATA AS"
1050 PRINT : PRINT " (A) ALPHA - TIME FILES"
1060 PRINT " (B) ALPHA - REDUCED-TIME FILES"
1070 PRINT : INPUT " ENTER (A) OR (B) : ";B$
1080 IF B$ < > "A" AND B$ < > "B" THEN GOTO 1070
1090 IF B$ = "A" THEN T$ = ".TIME"
1100 IF B$ = "B" THEN T$ = ".RT"
1110 AX = - 1E7;AN = 1E7
1120 PRINT D$;"OPEN";NAAM$ + T$ + ".AL,D2"
1130 PRINT D$;"READ ";NAAM$ + T$ + ".AL"
1140 INPUT ND
1150 ND = INT (ND)
1160 FOR I = 1 TO ND: INPUT TM(I): INPUT AL(I)
1170 IF AL(I) > AX THEN AX = AL(I)
1180 IF AL(I) < AN THEN AN = AL(I)
1190 NEXT I
1200 PRINT D$;"CLOSE";NAAM$ + T$ + ".AL"
1210 RETURN
2000 REM *****
2010 REM * SELECT MODEL REQUIRED *
2020 REM *****
2030 HOME : INVERSE : PRINT " KINETIC EXPRESSIONS : F(A) = KT"
2040 PRINT : PRINT "ACCELERATORY A-T CURVES"
2050 NORMAL : PRINT "1. POWER LAW A^(1/N)"
2060 PRINT "2. EXPONENTIAL LAW LN A"
2070 INVERSE : PRINT "SIGMOID A-T CURVES"
2080 NORMAL : PRINT "3. AVRAMI EROFEEV LN(1-A)^(1/N)"
2090 PRINT "4. PROUT-TOMPKINS LN(A/(1-A))"
2100 INVERSE : PRINT "DECELERATORY A-T CURVES"
2110 NORMAL : PRINT "5. CONTRACTING AREA 1-(1-A)^(1/2)"
2120 PRINT "6. CONTRACTING VOLUME 1-(1-A)^(1/3)"
2130 PRINT "7. 1-D DIFFUSION A^2"
2140 PRINT "8. 2-D DIFFUSION (1-A)LN(1-A)+A"
2150 PRINT "9. 3-D DIFFUSION 1-3(1-A)^(2/3)"
2160 PRINT " +2(1-A)"
2170 PRINT "10. JANDER (1-(1-A)^(1/3))^2"
2180 PRINT "11. GINST/BROUNS. (1-2A/3)-"
2190 PRINT " (1-A)^(2/3)"
2200 PRINT "12. 1ST ORDER -LN(1-A)"
2210 PRINT "13. 2ND ORDER 1/(1-A)"
2220 PRINT "14. 3RD ORDER (1-(1-A))^2"
2230 PRINT : INPUT "ENTER NUMBER OF MODEL : ";MD
2240 IF MD < 1 OR MD > 14 THEN GOTO 2230
2250 IF MD = 1 OR MD = 3 THEN INPUT "ENTER THE VALUE OF N : ";N
2260 RETURN
3000 REM *****
3010 REM * CONVERT A TO F(A) *
3020 REM *****
3030 HOME : VTAB 12: PRINT " CALCULATION IN PROGRESS"
3040 PRINT : PRINT " PLEASE DO NOT SWITCH OFF!"
3050 FOR I = 1 TO ND
3060 ON MD GOSUB 3090,3100,3110,3120,3130,3140,3150,3160,3170,3180,3190,3
200,3210,3220
3070 NEXT I
3080 RETURN

```

```

3090 FA(I) = AL(I) ^ (1 / N):MD$ = "P" + STR$(N): RETURN
3100 FA(I) = LOG (AL(I)):MD$ = "E1": RETURN
3110 FA(I) = LOG ((1 - AL(I)) ^ (1 / N)):MD$ = "A" + STR$(N): RETURN
3120 FA(I) = LOG (AL(I) / (1 - AL(I))):MD$ = "B1": RETURN
3130 FA(I) = 1 - (1 - AL(I)) ^ (1 / 2):MD$ = "R2": RETURN
3140 FA(I) = 1 - (1 - AL(I)) ^ (1 / 3):MD$ = "R3": RETURN
3150 FA(I) = AL(I) ^ 2:MD$ = "D1": RETURN
3160 FA(I) = (1 - AL(I)) * LOG (1 - AL(I)) + AL(I):MD$ = "D2": RETURN
3170 FA(I) = 1 - 3 * ((1 - A) ^ (2 / 3)) + 2 * (1 - A)
3180 FA(I) = (1 - (1 - AL(I)) ^ (1 / 3)) ^ 2:MD$ = "D3": RETURN
3190 FA(I) = (1 - 2 * AL(I) / 3) - (1 - AL(I)) ^ (2 / 3):MD$ = "D4": RETURN

3200 FA(I) = - LOG (1 - AL(I)):MD$ = "F1": RETURN
3210 FA(I) = 1 / (1 - AL(I)):MD$ = "F2": RETURN
3220 FA(I) = (1 / (1 - AL(I))) ^ 2:MD$ = "F3": RETURN
4000 REM *****
4010 REM * CALCULATE STATISTICAL FUNCTIONS *
4020 REM *****
4030 REM *** CALCULATE CORRELATION COEFFICIENT ***
4040 XY = 0: SX = 0: SY = 0: XSQ = 0: YSQ = 0: A = 0: B = 0: C = 0: FLG = 0
4050 FOR I = 1 TO ND
4060 SY = SY + FA(I): SX = SX + TM(I): XY = XY + TM(I) * FA(I)
4070 XSQ = XSQ + TM(I) * TM(I): YSQ = YSQ + FA(I) * FA(I)
4080 NEXT I
4090 B = (ND * XY - SX * SY) / (ND * XSQ - SX * SX)
4100 A = (SY - B * SX) / ND
4110 C = (ND * XY - SX * SY) / (((ND * XSQ - SX * SX) * (ND * YSQ - SY * S
Y)) ^ .5)
4120 REM *** CALCULATE EQN OF BEST LINE ***
4130 FOR I = 1 TO ND: YTH(I) = A + B * TM(I): NEXT I
4140 REM *** CALCULATE STD ERROR OF THE REGRESSION ***
4150 DSQ = 0: D = 0
4160 FOR I = 1 TO ND
4170 D = FA(I) - (B * TM(I) + A)
4180 DSQ = DSQ + D * D
4190 NEXT I
4200 SS = SQR (DSQ / (ND - 2))
4210 REM *** STD ERROR OF SLOPE OF REGRESSION LINE ***
4220 XAV = SX / ND: XD = 0
4230 FOR I = 1 TO ND
4240 X = TM(I) - XAV
4250 XD = XD + X * X
4260 NEXT I
4270 SB = SS / ( SQR (XD))
4280 PSB = (100 * SB) / B
4290 IF FLG = 1 THEN PR# 1
4300 HOME : PRINT : PRINT " RUN "; NAAM$
4310 PRINT " ===== "
4320 PRINT : PRINT " THE BEST STRAIGHT LINE THROUGH THE "
4330 PRINT " PLOT OF F(A) VS TIME FOR THE "; MD$
4340 PRINT " MODEL IS "
4350 PRINT : PRINT " F(A) = A + B*(TIME) "
4360 PRINT : PRINT " WHERE A = "; A
4370 PRINT " B = "; B
4380 PRINT : PRINT " AND HAS A CORRELATION COEFFICIENT OF "
4390 PRINT " "; C; "."
4400 PRINT : PRINT " THE STD ERROR OF THE REGRESSION IS "
4410 PRINT " "; SS; " "
4420 PRINT " THE STD ERROR OF THE SLOPE OF THE "

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4430 PRINT " REGRESSION LINE IS ";SB
4440 PRINT " AND THE % ERROR OF THE SLOPE IS ";PSB;". "
4450 IF FLG = 1 THEN PR# 0: IF FLG = 1 THEN GOTO 4500
4460 PRINT : PRINT : INPUT " DO YOU WANT A PRINTOUT OF CONSTANTS? ";A$
4470 IF A$ < > "Y" AND A$ < > "N" THEN GOTO 4460
4480 IF A$ = "N" THEN GOTO 4500
4490 FLG = 1: GOTO 4290
4500 RETURN
5000 REM *****
5010 REM * PLOT F(A) VS TIME *
5020 REM *****
5030 MAX = - 1E7
5040 FOR I = 1 TO ND
5050 IF ABS (FA(I)) > MAX THEN MAX = ABS (FA(I))
5060 IF ABS (YTH(I)) > MAX THEN MAX = ABS (YTH(I))
5070 NEXT I
5080 HGR : HCOLOR= 3
5090 HPLLOT 0,0 TO 279,0 TO 279,150 TO 0,150 TO 0,0
5100 HOME : VTAB 22: INVERSE : PRINT " PLOT OF ";MD$;" MODEL & BEST STRAI
    GHT LINE "
5110 FOR I = 2 TO ND
5120 P1 = TM(I - 1) / TM(ND) * 279
5130 P2 = TM(I) / TM(ND) * 279
5140 IF P1 < 0 THEN P1 = 0
5150 IF P1 > 279 THEN P1 = 279
5160 IF P2 < 0 THEN P2 = 0
5170 IF P2 > 279 THEN P2 = 279
5180 P3 = 75 - FA(I - 1) / MAX * 75 + .5
5190 P4 = 75 - FA(I) / MAX * 75 + .5
5200 IF P3 < 0 THEN P3 = 0
5210 IF P3 > 75 THEN P3 = 75
5220 IF P4 < 0 THEN P4 = 0
5230 IF P4 > 75 THEN P4 = 75
5240 HPLLOT P1,P3 TO P2,P4
5250 P5 = 75 - YTH(I - 1) / MAX * 75 + .5
5260 P6 = 75 - YTH(I) / MAX * 75 + .5
5270 IF P5 < 0 THEN P5 = 0: IF P5 > 75 THEN P5 = 75
5280 IF P6 < 0 THEN P6 = 0: IF P6 > 75 THEN P6 = 75
5290 HPLLOT P1,P5 TO P2,P6
5300 NEXT I
5310 VTAB 23: HTAB 7: PRINT "PRESS 'RETURN' TO CONTINUE"
5320 GET R$: PRINT : NORMAL : TEXT
5330 RETURN
6000 REM *****
6010 REM * STORE TIME - F(A) DATA *
6020 REM *****
6030 HOME : PRINT : INPUT " DO YOU WANT TO STORE TIME-F(A) DATA : ";A$
6040 IF A$ < > "Y" AND A$ < > "N" THEN GOTO 6030
6050 IF A$ = "N" THEN GOTO 6200
6060 PRINT : PRINT " INSERT DISC FOR DATA STORAGE (D2)"
6070 VTAB 23: HTAB 7: PRINT "PRESS 'RETURN' TO CONTINUE"
6080 GET R$: PRINT
6090 VTAB 23: HTAB 7: PRINT "
6100 VTAB 6: PRINT " DATA IS STORED AS ";NAAM$ + ".TIME." + MD$
6110 PRINT D$;"OPEN";NAAM$ + ".TIME." + MD$;" ,D2"
6120 PRINT D$;"DELETE";NAAM$ + ".TIME" + MD$
6130 PRINT D$;"OPEN";NAAM$ + ".TIME" + MD$
6140 PRINT D$;"WRITE";NAAM$ + ".TIME." + MD$
6150 PRINT ND
6160 FOR I = 1 TO ND

```



```

6170 PRINT TM(I): PRINT FA(I)
6180 NEXT I
6190 PRINT D$;"CLOSE";NAAM$ + ".TIME." + MD$
6200 RETURN
7000 REM *****
7010 REM * CALCULATE RESIDUALS *
7020 REM *****
7030 RX = - 1E7:RN = 1E7
7040 FOR I = 1 TO ND:RS(I) = FA(I) - YTH(I)
7050 IF RS(I) > RX THEN RX = RS(I)
7060 IF RS(I) < RN THEN RN = RS(I)
7070 NEXT I
7080 IF ABS (RN) > RX THEN RX = ABS (RN)
7090 PRINT : PRINT " DO YOU WANT TO STORE RESIDUAL-ALPHA "
7100 INPUT " DATA ? ";A$
7110 IF A$ < > "Y" AND A$ < > "N" THEN GOTO 7090
7120 IF A$ = "N" THEN GOTO 7240
7130 PRINT : PRINT " INSERT DISC FOR DATA STORAGE (D2)"
7140 VTAB 20: HTAB 7: PRINT "PRESS 'RETURN' TO CONTINUE"
7150 GET R$: VTAB 20: HTAB 7: PRINT "
7160 VTAB 10: PRINT " DATA STORED AS ";NAAM$;";";MD$;".RES.AL"
7170 PRINT D$;"OPEN";NAAM$ + "." + MD$ + ".RES.AL"
7180 PRINT D$;"DELETE";NAAM$ + "." + MD$ + ".RES.AL"
7190 PRINT D$;"OPEN";NAAM$ + "." + MD$ + ".RES.AL"
7200 PRINT D$;"WRITE";NAAM$ + "." + MD$ + ".RES.AL"
7210 PRINT ND
7220 FOR I = 1 TO ND: PRINT RS(I): PRINT AL(I): NEXT I
7230 PRINT D$;"CLOSE";NAAM$ + "." + MD$ + ".RES.AL"
7240 PRINT : PRINT " DO YOU WANT A PLOT OF RESIDUALS"
7250 INPUT " VS ALPHA ? ";A$
7260 IF A$ < > "Y" AND A$ < > "N" THEN GOTO 7240
7270 IF A$ = "N" THEN GOTO 7500
7280 HGR : HCOLOR= 3
7290 HPLLOT 0,0 TO 279,0 TO 279,150 TO 0,150 TO 0,0
7300 HPLLOT 139,0 TO 139,150
7310 HOME : VTAB 22: HTAB 3: INVERSE : PRINT "PLOT OF RESIDUAL FUNCTION V
S ALPHA"
7320 IF ABS (AN) > AX THEN AX = ABS (AN)
7330 FOR I = 2 TO ND
7340 P1 = 139 + RS(I) / RX * 139
7350 P2 = 139 + RS(I - 1) / RX * 139
7360 IF P1 < 0 THEN P1 = 0
7370 IF P1 > 279 THEN P1 = 279
7380 IF P2 < 0 THEN P2 = 0
7390 IF P2 > 279 THEN P2 = 279
7400 P3 = AL(I) / AX * 150
7410 P4 = AL(I - 1) / AX * 150
7420 IF P3 < 0 THEN P3 = 0
7430 IF P3 > 150 THEN P3 = 150
7440 IF P4 < 0 THEN P4 = 0
7450 IF P4 > 150 THEN P4 = 150
7460 HPLLOT P2,P4 TO P1,P3
7470 NEXT I
7480 HTAB 7: VTAB 23: PRINT "PRESS 'RETURN' TO CONTINUE"
7490 GET R$: PRINT : NORMAL : TEXT
7500 RETURN

```

E.3 GEOMODEL

```

100 REM *****
110 REM * THIS PROGRAM CALCULATES THE BEST *
120 REM * VALUE OF N IN THE GENERAL *
130 REM * CONTRACTING-VOLUME RATE EXPRESSION *
140 REM *****
150 D$ = CHR$(4)
160 DIM AL(400),FA(400),TM(400),YTH(400),C(50),SS(50),PSB(50)
170 HOME : INVERSE : PRINT "
180 VTAB 3: PRINT "
190 VTAB 2: PRINT " : HTAB 38: VTAB 2: PRINT "
200 VTAB 2: NORMAL : HTAB 11: PRINT "ISOTHERMAL KINETICS"
210 GOSUB 1000
220 GOSUB 2000
230 GOSUB 4000
240 HOME : TEXT : VTAB 3
250 INPUT " DO YOU WANT TO ENTER NEW DATA ? ";A$
260 IF A$ < "Y" AND A$ < "N" THEN GOTO 250
270 IF A$ = "Y" THEN GOTO 210
280 END
1000 REM *****
1010 REM * INPUT DATA *
1020 REM *****
1030 HOME : INPUT " ENTER MASTER FILE NAME : ";NAAM$
1040 AX = - 1E7:AN = 1E7
1050 PRINT D$;"OPEN";NAAM$ + ".TIME.AL,D2"
1060 PRINT D$;"READ ";NAAM$ + ".TIME.AL"
1070 INPUT ND
1080 ND = INT (ND)
1090 FOR I = 1 TO ND: INPUT TM(I): INPUT AL(I)
1100 IF AL(I) > AX THEN AX = AL(I)
1110 IF AL(I) < AN THEN AN = AL(I)
1120 NEXT I
1130 PRINT D$;"CLOSE";NAAM$ + ".TIME.AL"
1140 RETURN
2000 REM *****
2010 REM * CONVERT A TO F(A) *
2020 REM *****
2030 HOME : VTAB 12: PRINT " CALCULATION IN PROGRESS"
2040 PRINT : PRINT " PLEASE DO NOT SWITCH OFF!"
2050 FOR J = 15 TO 30
2060 N = J / 10
2070 FOR I = 1 TO ND
2080 FA(I) = 1 - (1 - AL(I)) ^ (1 / N)
2090 NEXT I
2100 GOSUB 3000
2110 NEXT J
2120 RETURN
3000 REM *****
3010 REM * CALCULATE STATISTICAL FUNCTIONS *
3020 REM *****
3030 REM *** CALCULATE CORRELATION COEFFICIENT ***
3040 XY = 0: SX = 0: SY = 0: XSQ = 0: YSQ = 0: A = 0: B = 0: C = 0: FLG = 0
3050 FOR I = 1 TO ND

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← X

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3060 SY = SY + FA(I):SX = SX + TM(I):XY = XY + TM(I) * FA(I)
3070 XSQ = XSQ + TM(I) * TM(I):YSQ = YSQ + FA(I) * FA(I)
3080 NEXT I
3090 B = (ND * XY - SX * SY) / (ND * XSQ - SX * SX)
3100 A = (SY - B * SX) / ND
3110 C = (ND * XY - SX * SY) / (((ND * XSQ - SX * SX) * (ND * YSQ - SY * S
    Y)) ^ .5)
3120 C(J) = (INT (C * 10000)) / 10000
3130 REM *** CALCULATE EQN OF BEST LINE ***
3140 FOR I = 1 TO ND:YTH(I) = A + B * TM(I):NEXT I
3150 REM *** CALCULATE STD ERROR OF THE REGRESSION ***
3160 DSQ = 0:D = 0
3170 FOR I = 1 TO ND
3180 D = FA(I) - (B * TM(I) + A)
3190 DSQ = DSQ + D * D
3200 NEXT I
3210 SS = SQR (DSQ / (ND - 2))
3220 SS(J) = (INT (SS * 10000)) / 10000
3230 REM *** STD ERROR OF SLOPE OF REGRESSION LINE ***
3240 XAV = SX / ND:XD = 0
3250 FOR I = 1 TO ND
3260 X = TM(I) - XAV
3270 XD = XD + X * X
3280 NEXT I
3290 SB = SS / (SQR (XD))
3300 PSB = (100 * SB) / B
3310 PSB(J) = (INT (PSB * 10000)) / 10000
3320 RETURN
4000 REM *****
4010 REM * PRINTOUT OF STATISTICS *
4020 REM *****
4030 HOME : PRINT : PRINT " RUN ";NAAM$
4040 PRINT " =====
4050 PRINT J / 10; TAB( 8);C(J); TAB( 20);SS(J); TAB( 30);PSB(J)
4060 NEXT J
4070 IF FLG = 1 THEN PR# 0
4080 IF FLG = 1 THEN GOTO 4140
4090 PRINT : INPUT "DO YOU WANT A PRINTOUT ? ";A$
4100 IF A$ < > "Y" AND A$ < > "N" THEN GOTO 4090
4110 IF A$ = "N" THEN GOTO 4140
4120 PR# 1:FLG = 1
4130 GOTO 4030
4140 RETURN

```

