

The production of anhydrous metal chlorides in fluidized beds : the chlorination of rutile

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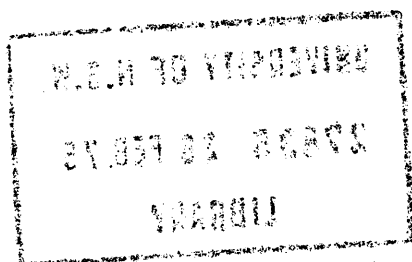


THE
PRODUCTION OF ANHYDROUS METAL CHLORIDES
IN FLUIDIZED BEDS

The Chlorination of Rutile

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I should like to express my thanks to the N.S.W. University of Technology for the scholarship position which made this work possible, to Professor J.P. Baxter for his encouragement and advice at all stages of the work, to all my friends on the staff of the School of Chemical Engineering for their encouragement and assistance, and to the Imperial Chemical Industries for allowing me leave of absence to carry out the work and for their assistance in preparation of this thesis.

This is to certify that the work
described herein was wholly
carried out by me at the School
of Chemical Engineering of the
N.S.W. University of Technology
during the period January, 1951
to July, 1954

W.R.S. Briggs
16th November, 1955

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ABSTRACT

This thesis reports a literature survey and investigation of the chlorination of rutile in the presence of carbon under fluid bed conditions. Experiments on the development of a suitable chlorination apparatus, the determination of the optimum reaction conditions and investigation of the mechanism of the chlorination reaction are described.

It has been shown that the fluid bed chlorination is eminently suited to the production of titanium tetrachloride giving complete conversion of the chlorine feed and very high production rates. Calculations based on experimental results and thermodynamic data show that at optimum operating temperature (900°C) a furnace would be fully autothermic for reaction bed volumes greater than 0.2 ft^3 , having an output of 150 lb. of titanium tetrachloride per hour per cubic foot of bed volume. The optimum conditions for fluid bed chlorination and the design of a suitable furnace are detailed.

Investigation of the reaction mechanism has shown that both the oxides of carbon are formed, and that solid carbon must be present in the bed if high reaction rates are to be achieved.

The energy of activation has been determined at 20 cal/gm.mol. The reaction is of fractional (0.6) apparent order with respect to chlorine, is autocatalysed by titanium tetrachloride and unaffected by concentrations of carbon monoxide and carbon dioxide. A possible reaction mechanism has been postulated.

CHAPTER I

Introduction

When a stream of fluid is passed upwards through a bed of finely divided solids at such a rate that all particles are separated from one another and are free to move about, the bed is said to be fluidized. Such a bed of solids possesses certain well defined characteristics, which make fluidization particularly useful in operation in which it is necessary to contact or react gases and solids. These advantages are:-

- (a) The bed is maintained in violent motion, resulting in excellent mixing and uniform composition throughout.
- (b) The bed temperature is uniform, very small temperature gradients occurring between the walls and centre, and top and bottom of the bed.
- (c) Heat transfer between a wall and a fluid bed is much greater than between a wall and a gas.
- (d) Very fine solids fluidize ^{at} a low flow rate. This makes it easy and economical to produce fluid beds with high specific surfaces, resulting in high reaction rates for heterogeneous reactions.
- (e) The fluid properties of the bed allow solid materials when fluidized to be handled in a manner similar to a liquid, that is, to be run through pipes and to be controlled by valves, thus making for simplicity in continuous operation.

This process then has obvious advantages in the preparation of volatile anhydrous metal chlorides, particularly in those cases such as the chlorination of Rutile, Ilmenite, Aluminium Oxide etc., in which it is necessary to use carbon as a reducing agent to remove oxygen. For these the fluid bed technique, as well as insuring good temperature control and flexible plant operation, would also insure uniform bed compositions.

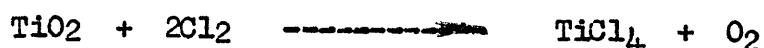
In this project it was proposed initially to investigate the

Chlorination of rutile, with the view of establishing optimum conditions for the commercial operation under fluid bed conditions and then to extend the work to the chlorination of Ilmenite, Bauxite, and Zircon. As the work on the chlorination of rutile proceeded, it was decided however to limit the project ^{to} this chlorination and to endeavour to elucidate the reaction mechanism.

Titanium tetra-chloride was first prepared in 1825 by George and later by Dumas, Wohler, Pierre, Merz and Damarday (1). These early workers reacted chlorine at an elevated temperature with a variety of titaniferous materials including the relatively pure metal, alloys, carbides, cyanonitride, dioxide and ores. When oxygen containing materials were used, a carbonaceous reducing agent was added to the charge to absorb oxygen, or a reducing gas (e.g. carbon monoxide) was passed in with the chlorine, (2). Carbon tetrachloride, chloroform, and sulphur chloride have also been used in the chlorination of the dioxide.

Since 1900, references to the preparation of titanium tetrachloride by chlorination of the rutile and ilmenite ores and titanium dioxide pigment have been confined largely to the patent literature, and to work published in the U.S.S.R. by a team headed by Pamfilov, and in Australia by McTaggart.

In the reaction of chlorine with titanium dioxide, the reaction



does not take place readily, other than at high temperatures, (3). A reducing agent, such as carbon or carbon monoxide is therefore introduced to take up oxygen and prevent reversal of the reaction. Under these conditions the chlorination may be carried out at lower temperatures and at higher

reaction rates.

The usual commercial practice in the chlorination of the ore or the pigment has been to form the materials into briquettes, in which the solid reducing agent is incorporated. This is done to facilitate ease of handling of the materials, to prevent choking of the furnace and dust carry over and to bring the reducing agent into intimate contact with the titanium bearing material. In the fluid bed process materials in the particle size range of 100 to 150 mesh are blended by mixing, and the mixture of solids charged to the reactor in which the bed so formed, is fluidized by the chlorine feed. Under the conditions of fluidization the bed composition is then held uniform throughout.

In order to evaluate the worth of the fluid bed chlorination process for commercial operation, it is necessary to know the optimum condition under which the reaction occurs, the characteristics of the fluid bed under reaction conditions, and the heat requirements of the reactor, while a general understanding of the process is advanced by a knowledge of the reaction mechanism. To determine the optimum conditions of the reaction, the effects on reaction rate of bed depth, chlorine feed rate, temperature, particle size of the constituents and the ratio of carbon to rutile in the bed were investigated, noting at the same time the composition of the tail gases and the characteristics of the bed.

Published work has thrown very little light on the mechanism occurring in the chlorination. It is, in some cases, contradictory, and does not suggest any mechanism which can account for the high reaction rates obtained in a complex heterogeneous system involving reaction between a gas and two

solids. To elucidate this mechanism the effects on the reaction rate of variation of the partial pressures of chlorine, carbon dioxide, carbon monoxide, and titanium tetrachloride, were determined. Chlorinations were also carried out in the absence of any reducing agent, and using carbon monoxide instead of carbon as the reducing agent. The results of these experiments together with those from the experiments carried out on optimum conditions of chlorination were then correlated and a reaction mechanism deduced.

CHAPTER IISurvey of the Literature of Titanium TetrachloridePhysical Properties of Titanium Tetrachloride

Molecular Weight:	189.73
Form:	Colourless to light yellow liquid
Refractive Index:	1.61
Specific Gravity:	1.726
Melting Point:	-23°C
Boiling Point:	136.4°C

Chemical Properties of Titanium Tetrachloride

Titanium tetrachloride dissolves in cold water to form clear solutions, which are hydrolysed readily to form a series of basic chlorides.

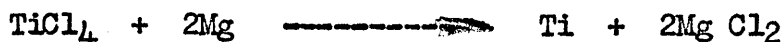
$\text{TiCl}_3(\text{OH})$, $\text{TiCl}_2(\text{OH})_2$, $\text{TiCl}(\text{OH})_3$ and finally $\text{Ti}(\text{OH})_4$. Hydrolysis may be prevented by the presence of hydrochloric acid.

The liquid tetrachloride fumes in moist air, reacting with water to give the basic chlorides mentioned above.

A solution of titanium tetrachloride in ethanol forms an insoluble white addition compound with hydrogen peroxide.

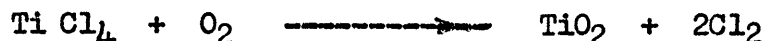
Titanium tetrachloride reacts with powdered antimony and silver, and with hydrogen to form the trichloride. Reduction with sodium amalgam forms the dichloride.

Titanium tetrachloride reacts with molten magnesium in the absence of oxygen to form titanium metal and magnesium chloride.

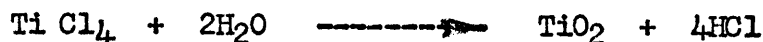


With liquid hydrogen sulphide the tetrachloride reacts to form a compound $\text{TiCl}_4 \cdot 2\text{H}_2\text{S}$.

Titanium dioxide may be formed directly from the tetrachloride by reaction with oxygen at 1000°C when the reaction



takes place. The dioxide may also be formed directly by vapour phase hydrolysis at $300^\circ - 400^\circ\text{C}$.



Titanium tetrachloride reacts with alcohols to form titanate esters.

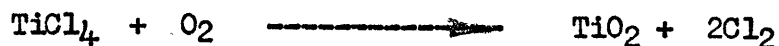
Uses of Titanium Tetrachloride

Titanium tetrachloride finds its major application as a raw material for the production of titanium metal, yearly being used in larger tonnages in the new jet aviation age, by the Kroll, or similar process, according to the reaction.



These processes are at present the most important methods of preparation of the metal.

Titanium dioxide pigment may also be prepared by thermal splitting of the tetrachloride with oxygen at 1000°C according to the reaction



This product has many advantages compared with that from the sulphate process, and will, it is expected, be increasingly used in new plants.

Titanium tetrachloride also finds application in the preparation of seed rutile crystals used in the manufacture of the pigment by the sulphate process. This seed crystal is prepared by controlled hydrolysis of the tetrachloride, followed by heating at the transition point of the oxides, to convert anatase to the rutile form. It is necessary to use a seed crystal in the sulphate process to obtain a suitable product.

During the last few years titan~~o~~-organic compounds such as butyl titanate and other titanium esters prepared from the tetrachloride have found application in the field of heat resistant and anti fouling paints.

Titanium tetrachloride has also found application as a smoke screen material for military application. This application has absorbed large quantities of the material in times of war.

Titanium Dioxide and Rutile Chlorination

Titanium tetrachloride has been prepared by chlorination of both pigment titanium dioxide and rutile ore containing up to ten percent of iron and other impurities. The usual commercial practice in the chlorination of the ore or pigment is to form the material into briquettes, to facilitate ease of handling, and to prevent choking of the furnace and dust carryover. When a solid reducing agent is used this material is also incorporated in the briquette.

Briquetting Processes

The term "briquetting" is used to designate the formation of hard

aggregates of the mixture to be chlorinated, independent of the means employed to accomplish this end. Thus the process may be carried out by machine, or press, or simply by rolling into balls by hand. The briquette should have sufficient mechanical strength to withstand handling and breakdown in the furnace, and sufficient porosity to allow chlorine penetration.

McTaggart (5) describes a method of briquette forming using binders followed by pressure. Agents such as starch solution, and solutions of sugar, dextrose, dextrin and molasses etc. may be used as bonding agents, while pressures between 200 and 6000 pounds per sq. inch are used. This worker reports excellent briquette formed with 15% starch solution at 4000 p.s.i. and 75% molasses solution at 200 p.s.i.

McTaggart also reports another method of briquette formation. This method involved the mixing of the mixture to be chlorinated with a crude tar to give a thick pasty mass. This mass is spread on an iron tray making a layer one half inch to three quarters of an inch in thickness, and then heated strongly beneath. When gases were evolved from the tarry mass these were ignited, and when all volatile matter had burned off, and mass was allowed to cool, broken into suitably sized lumps, and ignited out of contact with air at six to seven hundred degrees centigrade. The product was a hard, quite strong, and very porous coke-like material. Results of chlorination carried out showed briquette formed by the latter process to be slightly inferior to the starch bonded type.

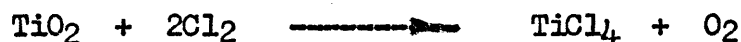
Pamfilov (3) formed briquettes by bonding a mixture of ground ore and charcoal with birch tar, and coking first at $400^{\circ} - 500^{\circ}\text{C}$ until all volatile matter had been driven off, and then at $800^{\circ} - 850^{\circ}\text{C}$ for two hours. A porous product allowing penetration of chlorine was obtained (6) by coking at a red heat a briquetted mixture of titanium dioxide and peat or sawdust. Muskat and Taylor (7) reported the formation of briquettes having the desired properties, by mixing various proportions of finely ground ore and carbon with 12% molasses. This mixture was formed into briquettes and baked at 400°C to remove volatile hydrocarbons.

Of the methods of briquetting to which reference was available, that described by McTaggart, in which tar was burned off, would seem to be the most economical.

Pamfilov (3) reports no difference in reaction rate for chlorination of briquettes and of unbriquetted mixture contained in boats. However, as the latter charge was dried in air at a temperature of three to four hundred degrees centigrade, resulting in burning some carbon in the charge, his results cannot be taken as conclusive. The formation of briquettes must have a definite effect upon the reaction velocity, this being a function of the surface area of both carbon and titanium dioxide exposed to reaction with chlorine. Briquetting which does not allow for entry of chlorine, either by non-porosity or by deposition of a surface layer of carbon on titanium dioxide particles during coking, will decrease the velocity of the chlorination. It would also seem to be possible that the initiation of the chlorination may be facilitated by the coking process, by formation of active centres on the dioxide by reduction by the hydrocarbon.

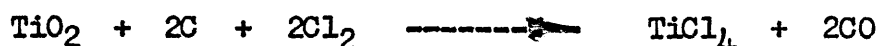
Temperature of Chlorination

Kangro and Jahn (8) report that a temperature of at least eight hundred degrees centigrade is required to achieve a one percent yield per hour from the reaction



while it is reported (9) in work on the chlorination of ilmenite in the absence of a reducing agent, that the reaction of the titanium compound begins at 815°C.

Dumas (1) described the reaction of chlorine with titanium dioxide and carbon to give titanium tetrachloride according to the reaction



when heated to a red heat. Watt and Bell state that titanium tetrachloride may be formed by passing carbon tetrachloride over the dioxide heated to bright redness. Barton (10) patented the production of titanium tetrachloride by the reaction of chlorine at 650°C with the clinker formed by coking a mixture of titanium dioxide and soft coal.

Pamfilov and Shtandel (3) report a chlorination of pure titanium dioxide and carbon of one hour duration, in which chlorine was passed at two litres per hour, giving the following results:

<u>Temperature °C</u>	<u>% TiO₂ Chlorinated</u>
420	3.3
490	42.7
580	83.69

indicating that the reaction commences at approximately 400°C. These workers claim that addition of 0.2% of Manganese dioxide catalyses the chlorination, reducing the most favourable temperature for optimum yields from above

500°C to 480°C. Addition of more catalyst produces no further effect. In these experiments percentage chlorination was plotted against temperature. With added manganese dioxide a maximum is shown at about 480°C. In the series of experiments without added manganese dioxide, chlorination was carried out up to only 520°C, no flattening of the curves being reached. Doubt is cast on these results by later work by Pamfilov and Chikher (4), who state that the maximum yield occurred only when chlorinating in boats, chlorination of briquettes giving no such maximum. They considered this may have been due to the stopping, the reaction, by burning out the carbon in the charge. The influence of manganese dioxide as a catalyst is reported by them to fade with increase in temperature, and to be unnoticeable at high temperatures.

Pamfilov et alia (11) reported that the reaction was catalysed by the use of a small portion of rare earth chlorides, resulting in a lowering of 100° - 200°C in the reaction temperature. McTaggart (5) states, that in test carried out, addition of 1% and 5% rare earth chlorides produced no effect upon reaction velocity or temperature of the reaction initiation.

The most satisfactory published work on the temperature of reaction, is that of McTaggart (5). This worker passed chlorine at a rate which was known to be slightly in excess of that which the charge could take up, while increasing the temperature in 10°C steps. The yield of titanium tetrachloride obtained (cc/10 min.) was then plotted against temperature of reaction. This graph is reproduced in Figure 2.2. From these results it appears that the optimum temperature of chlorination is approximately 700° - 800°C.

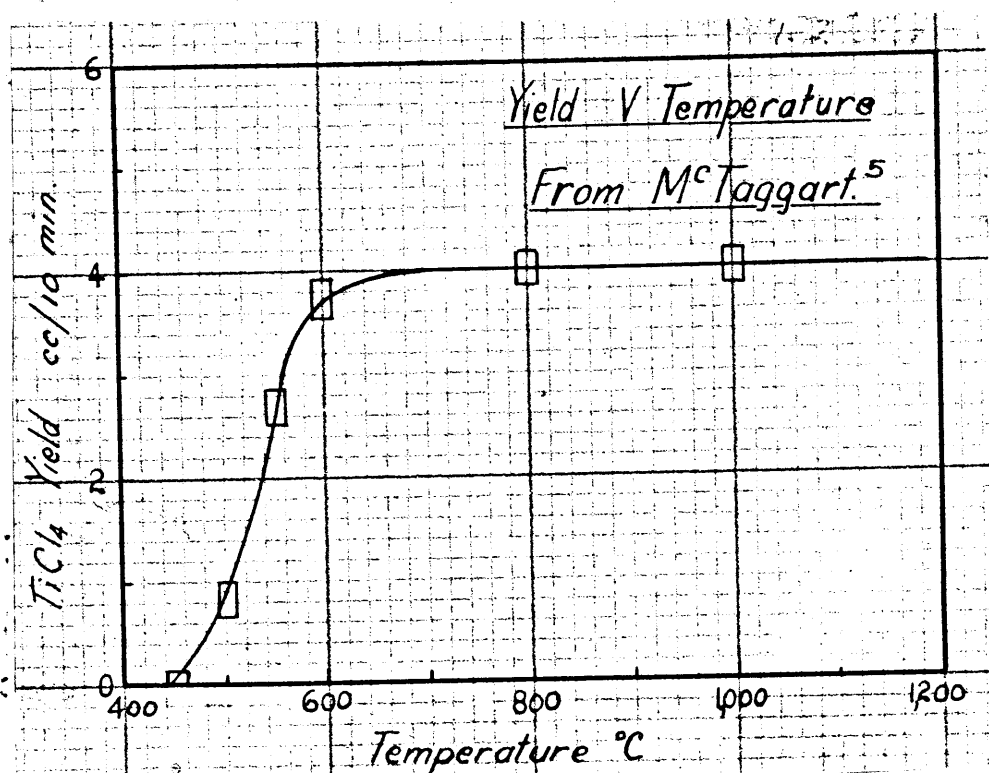


Figure 2.1

McTaggart reports that the reaction for all types of briquettes, independent of the grain size and binder commences at about 450°C. This was indicated by the appearance of white fumes of titanium tetrachloride in the condenser, while passing chlorine through the charge, and increasing the temperature in 10°C steps.

Further evidence of the optimum temperature for the chlorination of rutile or titanium dioxide is presented by Brallier (12) who states that the required temperature of chlorination is 700°C. This worker used the addition of titanium carbide, titanium cyanitride or silicon (13) to supply added heat to maintain an autothermic reaction. Belchetz (14) has taken out a patent for the chlorination of finely ground rutile and carbon in a fluidized bed at 700°C - 950°C, under which conditions it is claimed that the reaction is autothermic, provided undue heat losses are prevented.

It would appear from the work of Pamfilov (3) and McTaggart (5) that the reaction of titanium dioxide with chlorine in the presence of carbon, commences at $400^{\circ} - 450^{\circ}\text{C}$ and that a maximum is reached at approximately 700°C , above which temperature further increase produces no increase in titanium tetrachloride yield. In view of later work, claims as to the effectiveness of manganese dioxide and rare earth chlorides as chlorination catalysts may be discounted.

Variation of Reaction Rate with Particle Size

In a heterogeneous reaction, in which the velocity may be expected to be governed by reaction at an interface, the reaction velocity must be proportional to the surface area of the solid exposed to gaseous chlorine provided excess chlorine is present.

The only published data on the effect of particle size on reaction rate is that due to McTaggart (5). In this series of experiments, four sizes of rutile were tested, as well as titanium white pigment. Chlorine was passed at rates of 100, 200 and 250 cc/minute through 100 grams of starch (10% soln.) bonded rutile carbon briquettes pressed at 4000 lb/in². Different chlorine rates were used to ensure that sufficient chlorine was entering to completely satisfy the charge. The results of these experiments are reproduced in Figures 2.2 and 2.3.

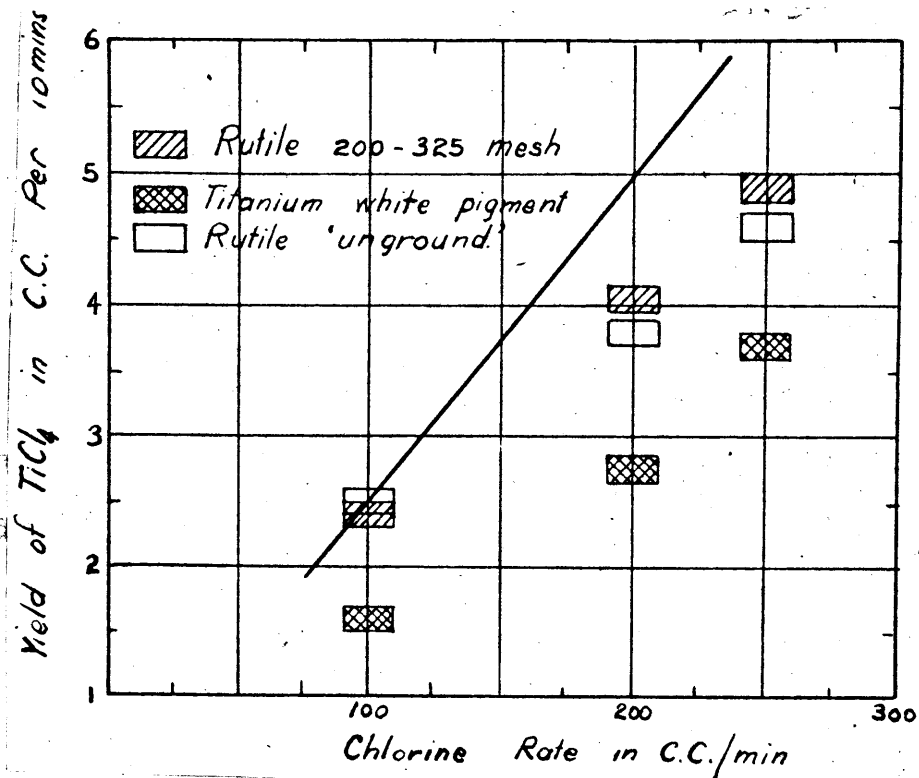


Figure 2.2

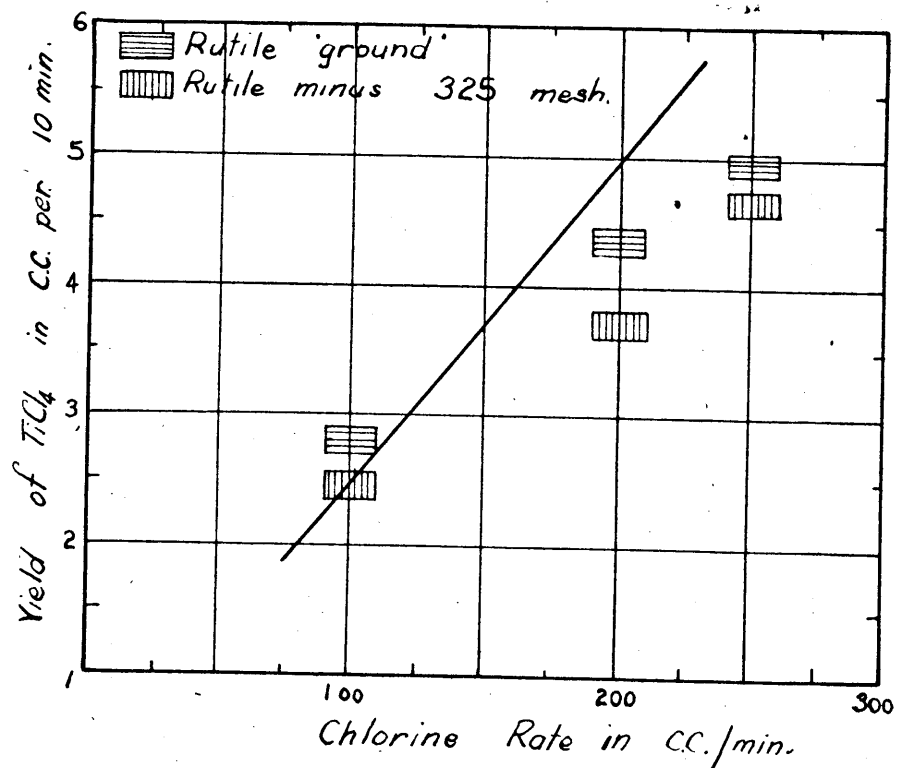


Figure 2.3

From these results no correlation of reaction rate and particle size appears. The reactivity of briquetted titanium dioxide pigment, contrary to theoretical considerations is shown to be definitely inferior to the various sizes of rutile used, while uniform particle size will briquette under pressure into a product with little porosity to allow entry of chlorine, while large and non-uniform particles should result in a more porous product. This would seem to be born out in the results of McTaggart. It is expected that in a fluidized bed chlorination, in which a homogeneous mixture of carbon and titanium dioxide particles is fluidized in a stream of chlorine, the particle size of both titanium dioxide and carbon should show a definite correlation with reaction rate. Reaction rates obtainable for a given volume of bed under fluidized conditions should be higher than those obtainable under fixed bed briquette chlorination, as a very much greater specific surface would be available for reaction than is possible in the latter case.

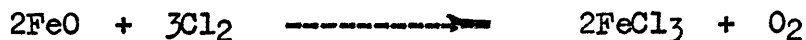
Chlorine Efficiency

McTaggart (5) claims on the result of pilot plant work chlorine efficiencies of 90-94% for an optimum chlorine velocity, above which the chlorine efficiency falls off. This conversion of chlorine also falls if chlorination is carried beyond 70-75% of the charge. I.G. Faben reports (16) indicate up to 93% chlorine efficiency on a commercial operation. It may be concluded therefore that high conversion of chlorine may be obtained if sufficient materials is present in the bed through which chlorine is being passes.

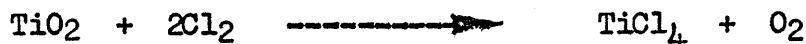
Chlorination of Ilmenite

Separation of Iron and Titanium by Chlorination

In the chlorination of Ilmenite, two chlorination reactions take place



and



the chlorination of iron oxides taking place more readily and at a lower temperature than the titanium chlorination. A patent has been taken out by Saklatwalla (9) making use of this fact to achieve separation of the iron and titanium in Ilmenite ore. Finely ground ore was selectively chlorinated at 800°C, at which temperature iron only was attacked, ferric chloride being removed as the vapour, leaving a residue of the titanium dioxide and other impurities. Chlorination of titanium dioxide was reported to begin at 815°C.

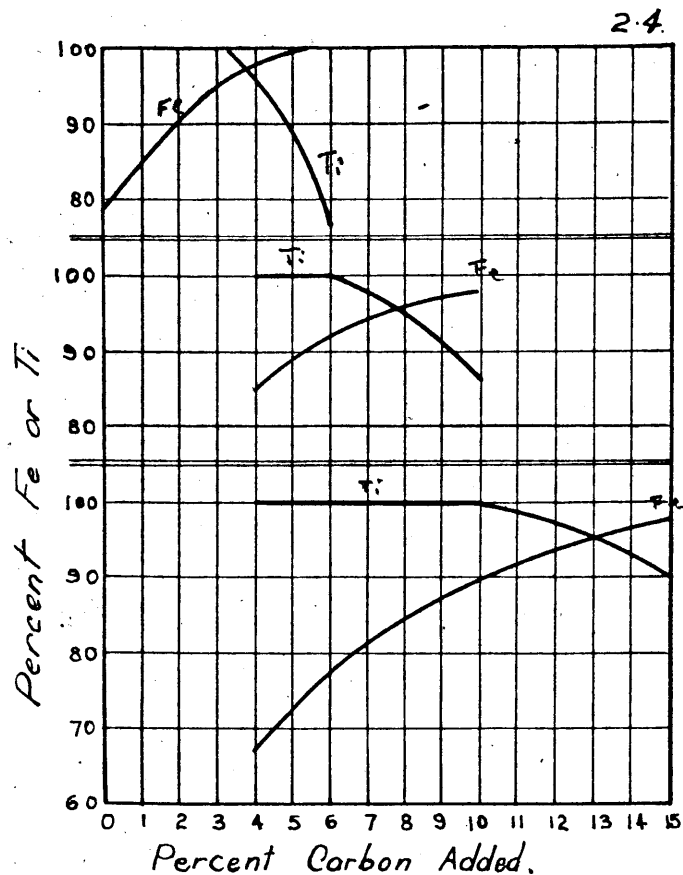
It is reported by Pamfilov (3) that titanium tetrachloride reacts with iron oxides to give ferric chloride and titanium dioxide. This was shown by chlorination of successively loaded briquettes of titanomagnetite concentrates and carbon in a tube furnace. Briquettes away from the chlorine inlet showed an increase in their titanium dioxide content, while the ferric oxide decreased. These workers claim that the chlorination of the iron oxides commences at about 280°C compared with 450°C for titanium dioxide as discussed above.

Use has been made (11) of this difference in reaction temperature to separate iron and titanium. The briquetted mixture of ilmenite ore and carbon was chlorinated first at 350°C at which temperature iron was attacked. When all iron had been removed, the temperature was raised to 550°C - 600°C within which range titanium dioxide was chlorinated. It was claimed that a product was

obtained containing traces only of the chlorides of iron silicon and vanadium.

Donaldson (18) took out a patent for the separation of iron and titanium by heating the ore with carbon at 1000°C when all iron compounds were reduced to the metal. The iron was then removed by chlorination at between 350° and 1000°C , and the residue of titanium dioxide chlorinated in the usual manner in the presence of carbon. Titanium tetrachloride has also been formed (19) by chlorinating a briquetted mixture of ilmenite and coal at 750°C , followed by fractional distillation of the volatile chloride.

Muskat and Taylor (7) report that although iron may be removed by chlorination of Ilmenite in the absence of reducing agent, the process is incomplete, and a considerable quantity of titanium dioxide is lost during the chlorination. They report that the direction of the chlorination to remove iron may be controlled by the concentration of reducing agent, such as carbon, present in the charge during chlorination; and that at an optimum carbon concentration most of the iron may be removed without substantial titanium losses. With carbon concentration above this figure chlorination of titanium commences. This carbon concentration is dependant upon the content of iron in the ore, and to some extent upon the chlorination temperature. Within the range $700^{\circ} - 1150^{\circ}\text{C}$, however, carbon concentration varies little with temperature. In this work the effect of introduction of air with chlorine was also studied. The results of this work is shown in Figures 2.4 and 2.5 reproduced from the patent papers.



Chlorine of Ilmenite at 980° C.
Fe. Removed to Ti Recovery with varying
carbon Concentration.

Figure 2.4

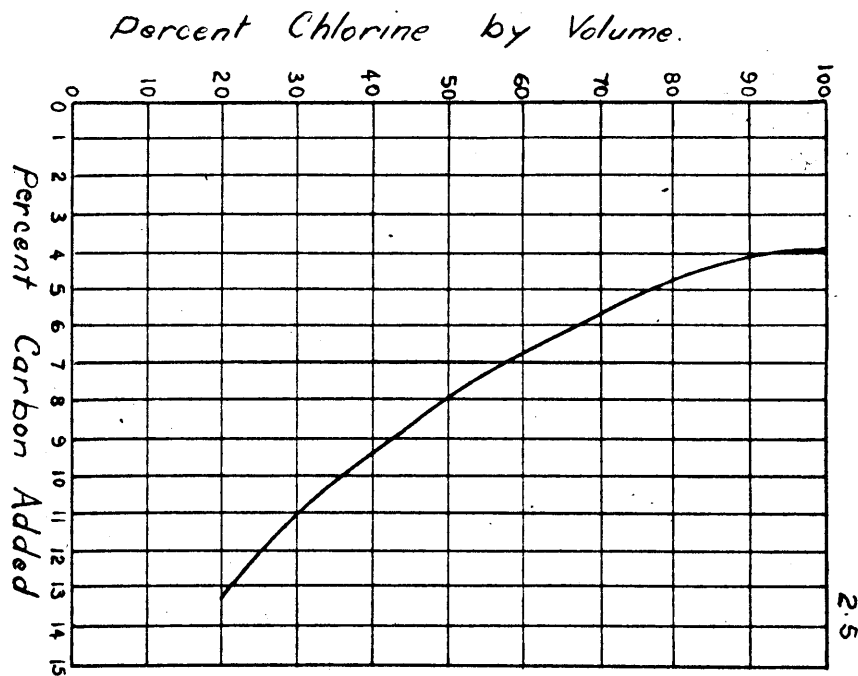
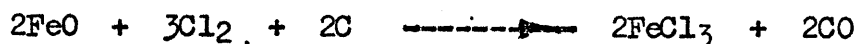


Figure 2.5

From the graph for chlorination in the absence of oxygen, it may be seen that titanium dioxide does not react until sufficient carbon has been added to allow most of the iron to be chlorinated, the figure of 3% added carbon, corresponding to approximately 4% carbon in the briquettes, is approximately the stoichiometric concentration for the reaction



assuming the formula for ilmenite as FeTiO_3 , that is no associated iron. At the chlorination temperature (980°C), carbon monoxide will be formed in preference to the dioxide. It is reported (20) that the amount of carbon introduced, as carbon, carbon monoxide, phosgene, etc., should be theoretical amount required to reduce the iron to the metallic state.

Similar results were claimed (21) for the chlorination at 815°C in the absence of oxygen of briquettes of ilmenite containing 7.2% carbon, resulting in 98% removal of iron, and a loss of only 4% titanium. In this patent the residue titanium dioxide was chlorinated at 600°C in the presence of a gaseous reducing agent to yield a relatively pure titanium tetrachloride. The reaction was carried out at such a rate to maintain the temperature at 600°C without any external heat input.

It would seem, therefore, that in the presence of a reducing agent, a large percentage of iron in ilmenite ore is chlorinated before titanium dioxide begins to react. Also iron begins to react at a lower temperature than titanium.

Chlorination in the absence of oxygen provides the sharper separation of iron and titanium. Addition of air or oxygen to the chlorination gas tends

to flatten out the separation curves, and increases the amount of carbon required in the charge to achieve separation. Lower titanium recoveries are also obtained. Little advantage then seems to occur from the addition of oxygen.

Separation of Iron and Titanium Chlorides

Several processes are mentioned in the patent and general literature for separation of the chloride mixtures resulting from chlorination of ilmenite, titanomagnetite and other iron containing titanium ores. Difficulty is experienced in handling the chloride mixture which condenses as a mush of solid ferric chloride and liquid titanium tetrachloride, blocking the condensation system. Muskat and Taylor (22) report that fractional condensation is difficult to achieve, as ferric chloride distributes itself throughout the condensation system, a large proportion remaining dispersed as colloidal particles in the uncondensed gases. If, however, a substantial portion of the titanium tetrachloride is condensed with the ferric chloride most of the solid ferric chloride is removed. The method adopted by these workers involves condensing the ferric chloride and part of the titanium tetrachloride in a condenser fitted with scrapers, which discharge the mixture to a second scraper. Here the mixture of chlorides is heated to recover the titanium tetrachloride, and the ferric chloride is discharged from the vessel by means of the scrapers. It is reported that the separation of the chloride is improved by the presence of a diluent gas, the gaseous mixture passing from the first condenser being used for the purpose. Titanium tetrachloride is then condensed from the resultant gas mixture by a spray condenser recirculating cold titanium tetrachloride. The apparatus said to be employed in the work is shown in Figure 2.3 reproduced from the patent papers.

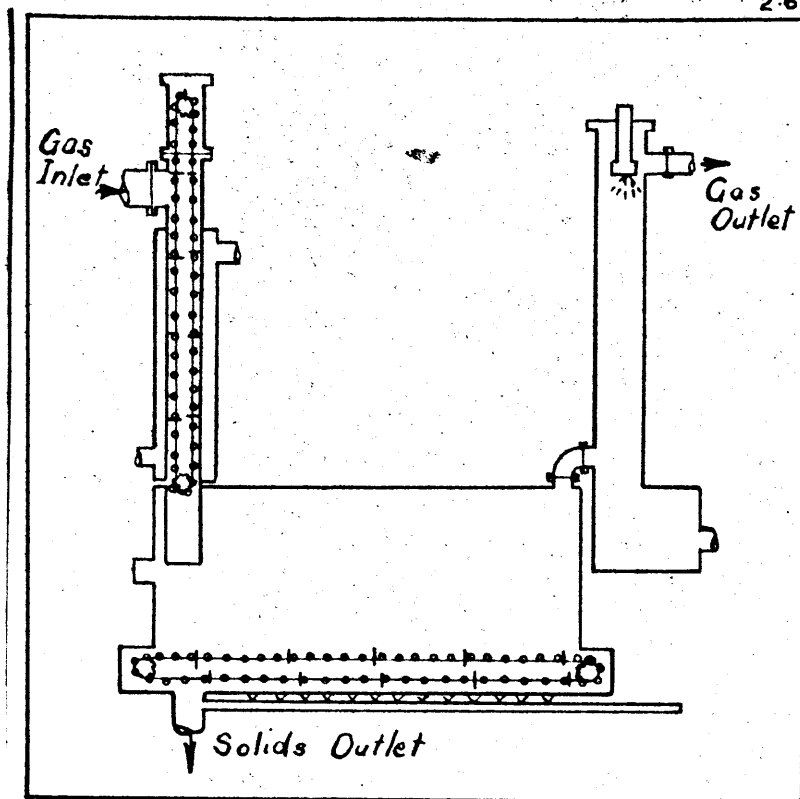


Figure 2.6

Another approach to the problem is that of Pechukas (23) who sought to achieve fractional condensation by passing the vapours through three spray scrubbers in series. The bulk of the ferric chloride was removed in the first scrubber by washing the mixed vapours with a chloride, e.g. silicon or carbon tetrachloride, at 135°C . Titanium tetrachloride, and some ferric chloride as a colloidal suspension pass to the second scrubber and are scrubbed with liquid titanium tetrachloride. This removes the remainder of the ferric chloride, and some titanium tetrachloride. The remainder of the titanium tetrachloride is removed in a third scrubber by scrubbing with cold titanium tetrachloride.

A variation of this method is described in a patent taken out by Kraus (24). The resultant gas mixture of titanium tetrachloride, ferric chloride, carbon monoxide, carbon dioxide, and chlorine from the reactor is passed to a cyclone

where it meets a spray of liquid titanium tetrachloride. This latter is vapourised while ferric chloride is condensed as a solid being removed from the bottom of the cyclone. The remaining gas passes to a surface condenser where titanium tetrachloride is removed.

An alternative method is suggested by Belchetz (14) making use of the insolubility of ferric chloride in titanium tetrachloride. The flow sheet in his patent on the fluidized chlorination of ilmenite shows the condenser discharge passing to a receiver, from which the slurry of ferric chloride is pumped, part to a filter where ferric chloride is removed, part through a cooler and back to the receiver to cool the slurry. The temperature in the receiver may thus be controlled to allow the ferric chloride crystals to grow to filterable size. Any titanium tetrachloride in the gas leaving the receiver is condensed in a refrigerated condenser. It is claimed that should the slurry in the receiver become too thick to be readily pumped, titanium tetrachloride may be returned to the receiver from the filter. This method does not seem to allow for deposition of solid ferric chloride in the condenser, although it seems probable that this could be prevented by introduction of liquid titanium tetrachloride into the condenser.

Of the methods described above those of Muskat and Taylor and Belchetz would appear to be most successful. The method of Kraus seems rather optimistic in hoping to achieve complete removal of ferric chloride and vapourisation of added titanium tetrachloride in what must at best be one theoretical stage. The process would be ideal if the patentee's claim could be substantiated, but without practical tests this seems unlikely. The method of Pechukas suffers in that a third contaminant is introduced in the first scrubber, and that liquid titanium tetrachloride containing ferric chloride

is obtained from the second scrubber. The method suggested by Belchetz has the advantage that no heat need be supplied to revapourise the tetrachloride, and that provided the filters are working satisfactorily a product containing not more than 0.02% iron will be obtained. Operation of this separation should also be more simple than that of Muskat and Taylor. The final choice between these two systems will depend on the energy and labour requirements, which seems to favour the former.

Use of Gaseous Reducing Agents

The use of gaseous reducing agents introduced with the chlorine, in place of carbon in the charge was first mentioned in 1878 (2). It has been claimed (4) that the use of gaseous reducing agents has advantages in eliminating the necessity of calcining of briquettes to eliminate hydrocarbons. These workers also claim the reaction using carbon monoxide as a reducing agent to be more exothermic. This has been verified, by calculation of the free energy changes for the reaction, to be the case at temperatures below 800°C, but above this temperature less exothermic than when using solid carbon (see Appendix I). In experimental chlorination using carbon monoxide as the reducing agent, the reaction commences (4) at approximately 500°C, as in the case of chlorination in the presence of solid carbon. The work carried out showed no maximum yield to be reached with increase in temperature. No substantial differences in reaction using carbon monoxide instead of carbon were found.

Similar results to those obtained using carbon, have been claimed by Muskat and Taylor (20) for the chlorination of Ilmenite using gaseous reducing agents, such as carbon monoxide, phosgene, hydrogen, sulphur chloride, carbon tetrachloride etc. The results reported in this patent, however, deal only

with the use of carbon monoxide, with which very similar results to those using carbon were claimed. In chlorination in the range $850^{\circ} - 1000^{\circ}\text{C}$ an amount of reducing agent slightly in excess of the theoretical amount required to reduce the iron oxides to the metal resulted in selective chlorination of the iron, while above this concentration both iron and titanium were chlorinated. It is reported that above 600°C the reaction proceeds with such rapidity, and with sufficient evolution of heat to operate autothermally.

According to Chauvinet (25) phosgene is less satisfactory than a mixture of carbon monoxide and chlorine, due to the exothermic nature of the decomposition of the carbonyl chloride. Chloroform has also been used (26) as a chlorinating agent, reacting to give titanium tetrachloride carbon monoxide and hydrogen chloride.

It is also reported that di- or higher sulphur chlorides may be used for chlorination, reacting to give titanium tetrachloride and sulphur dioxide.

Titanium Compounds Other than Oxides

References are available to the chlorination of carbides, alloys and clays containing titanium.

It is reported by Oreshkin (27) that chlorine reacts with the carbide more readily than with a mixture of dioxide and carbon, the reaction taking place at 200°C . Stahler (28) reported the chlorination of carbide formed by fusing rutile or ilmenite with coke gives good yields. The slag formed from titaniferous clays used in an aluminium furnace is reported (29) to react readily with chlorine at $400^{\circ} - 500^{\circ}\text{C}$.

Patents have been taken out for the recovery of titanium tetrachloride from clay at $300^{\circ} - 450^{\circ}\text{C}$ (32). These processes have not, however, been successfully operated on a commercial scale.

Furnace Operation

As will be seen from the thermodynamic survey of possible reactions, the chlorination of titanium dioxide in the presence of carbon is exothermic. Reference to the literature shows that if the chlorination is carried out with a sufficiently large mass of material, and if undue heat losses do not occur, the heat liberated by the reaction is sufficient to maintain the mass at the reaction temperature ($600^{\circ} - 900^{\circ}\text{C}$), without the addition of any external heat. In one batch chlorination the preheated charge is dropped into the furnace initially heated by a wood fire, and chlorination proceeds without any further external heating. The furnace remains up to temperature, and the following preheated charge is introduced when the first is chlorinated. A continuous autothermic chlorination is described (34) in which a briquetted mixture of ilmenite ore and carbon is passed through a shaft furnace, the charge being fed and the unreacted material being removed by means of a star feeder. A bed approximately three feet deep was maintained and chlorine was passed upwards. A temperature of at least 700°C was maintained in portion of the bed. It was reported that the bed could be divided into zones, the top zone preheating the charge, the middle zone in which iron was chlorinated, and the bottom zone in which titanium dioxide chlorination took place. Temperature control was achieved by regulating the rate of feeding the charge and chlorine, and by the rate of discharge of the residue. Additional heat may be supplied by adding excess carbon to the charge, and air or oxygen with the chlorine.

A similar process using a gaseous reducing agent is described by Muskat and Taylor (20). The furnace was preheated to a suitable temperature (850°C) to initiate the reaction, by passing a blast of oxygen and air through a coke fire in the furnace. The charge of briquettes was then introduced, oxygen cut off, and the reducing gas and chlorine introduced. The reaction zone temperature is regulated by the rate of feeding and discharge of the ore, and the gas rate through the furnace. The patent claims that additional heat may be supplied by introducing carbon with the charge and oxygen with the gas mixture. Cooling of the reaction zone may be achieved by introduction of a diluent gas such as nitrogen or carbon dioxide with the inlet gas. Carbon dioxide is claimed to be particularly effective as a cooling agent. Since, however, substantially uniform results are obtained within the range 850° to 1250°C considerable latitude in temperature regulation is permissible.

As these processes employ a briquetted material, the briquetting processes requiring the heating of the briquettes to a fairly high temperature (c.a. 400°C), it is usual to discharge the briquette directly from the coking vessel to the chlorinator, in this way preheating the charge and conserving heat.

Another continuous autothermic process has been claimed by Belchetz (14), in which mixture of titanium dioxide and carbon, less than 200 mesh, was transferred by lean phase fluidization into a reactor in which a fluidized bed was formed. With a gas velocity of 1.5 ft. per second in the reactor, and a residence time of 15 seconds, it is claimed that when all feed materials were introduced at atmospheric temperatures, sufficient heat was liberated to maintain the reaction zone at $650^{\circ} - 950^{\circ}\text{C}$.

Furnace Construction

A typical furnace of the semi-continuous autothermic batch type is that used at Leverkusen by I.G. Farben (16). This furnace is a steel shell lined with fire brick, and fitted with an unlined quick opening charging door. Chlorine is passed in at the bottom, and the product gases taken off through a brick lined off take. They are then passed through two glass wool filters to remove dust. This furnace is shown in Figure 2.7 reproduced from a F.I.A.T. Report.

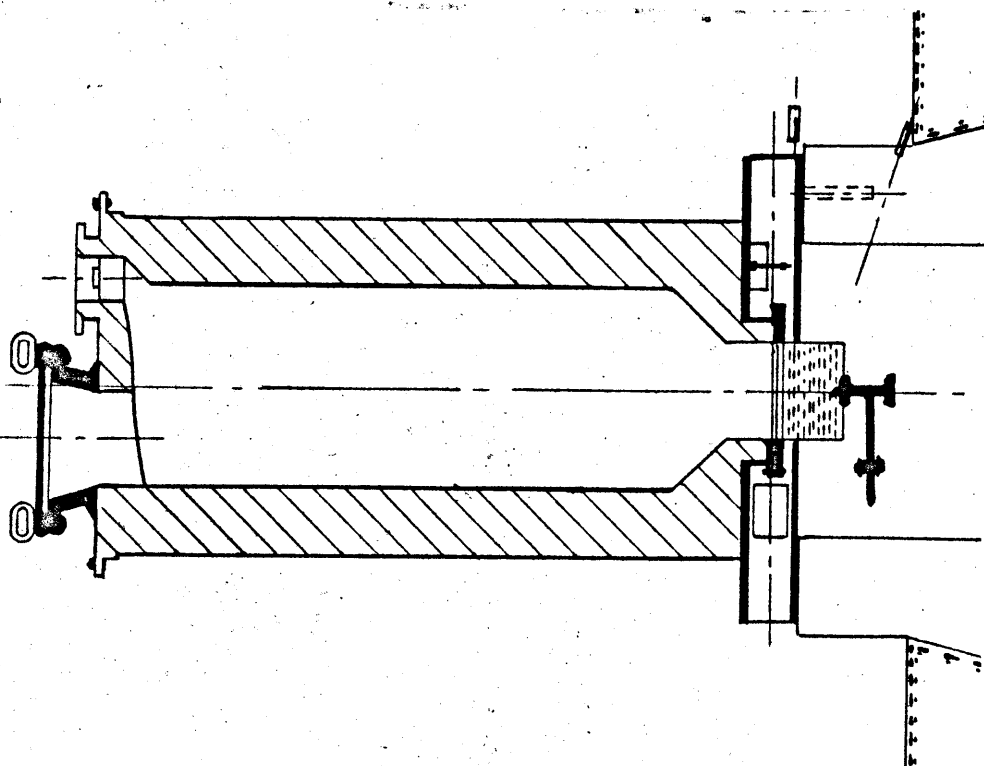


Figure 2.7

Figure 7.2

The furnace used in the pilot plant work at the Pittsburgh Plate Glass Co. (7, 20, 21, 22 & 23) for continuous chlorination is shown in Figure 2.8 reproduced from the patent papers. The patentees claim that the furnace may be constructed of fire brick, or other refractory material resistant to chlorine at the temperature employed. As no external heat is to be supplied

to the furnace, the use of heat conducting material is unnecessary. Figure 2.2 shows a furnace used with gaseous reducing agents. The inlet pipe is blocked off when using carbon in the charge.

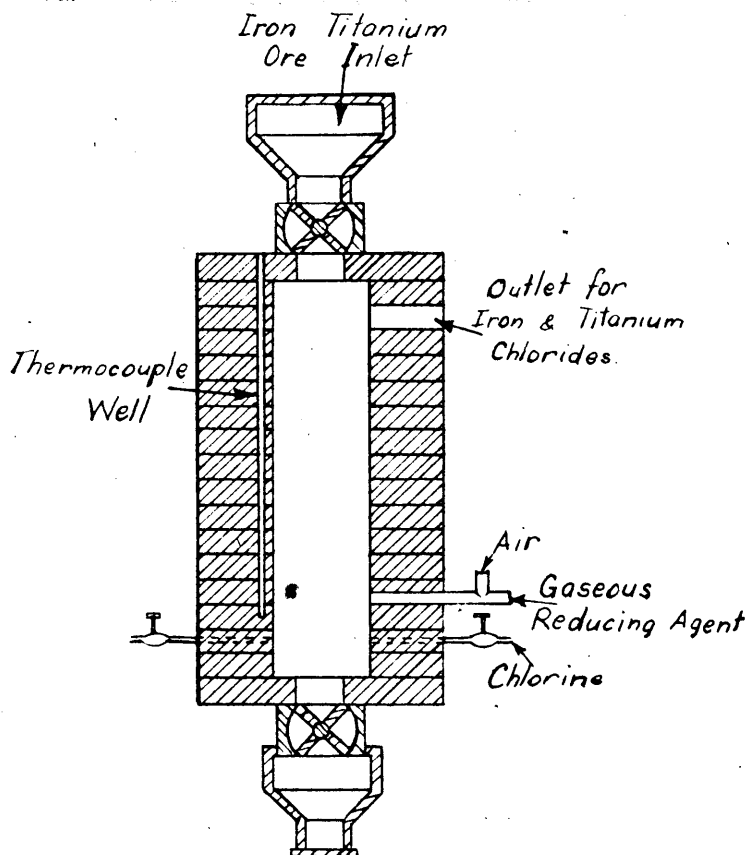


Figure 2.8

McTaggart (5) employed a pressed silicon carbide in the construction of a pilot plant furnace, and reported that no sign of attack or deterioration was evident after three hundred hours running.

Purification of Titanium Tetrachloride

Crude titanium tetrachloride obtained from the chlorination of titanium bearing materials usually contain dissolved chlorine, chlorides of iron,

silicon and vanadium as well as suspended ferric chloride and carbon dust.

McTaggart (5) reported the solubility of ferric chloride in titanium tetrachloride (estimated as iron) to be 0.02% at 20°C. Separation between the chlorides may be achieved by settling when the denser ferric chloride (S.G. 2.804 at 11°C) separates from titanium tetrachloride (S.G. 1.726) leaving a crystal clear bright yellow liquid. Ferric chloride may also be separated by filtration after cooling to room temperature. A deposit of ferric chloride giving better filtering properties may be obtained by holding the crude mixture at about 130°C, followed by slow cooling to allow the growth of large crystals of ferric chloride.

Impurities other than vanadium may be separated by fractional distillation. The yellow colour of the crude material is probably due to the presence of vanadium as the oxychloride or tetrachloride (35) both of which cannot be removed by fractional distillation.

Several methods of purification are described, including refluxing or standing over mercury, copper, reduced iron, sodium, potassium, sodium amalgam, etc. (1, 35 & 36). McTaggart (5) reports that, on test, only the method employing copper proved satisfactory. In this method titanium tetrachloride is refluxed over copper foil or turnings until colourless, and then distilled from the copper. In this way a water white product of high purity is obtained. Jenness and Annis (37) patented a method employing the addition of organic compounds to the crude material. Effective organic compounds are those which polymerise in the crude tetrachloride, reacting with the vanadium during polymerisation to form non-volatile easily separable compounds. The resultant compounds may be separated either mechanically or by distillation. Activated

carbon is also reported (38) to achieve separation of the impurities when used to treat either the liquid or the vapour. This worker suggests also the precipitation of impurities such as iron vanadium and manganese by means of active sulphides. Distillation from heavy metal soaps (39), alkali metal soaps (40), ferrous sulphate (41) or alkali metal hydroxides (42) have been suggested as methods of purification.

A pilot plant investigation on the purification of titanium tetrachloride has been carried out by Stoddard and Pietz of the Bureau of Mines (43). Full pilot plant data is given in this work for design of fractionating columns for the separation of silicon and titanium tetrachlorides. The removal of volatile impurities by treatment of the crude product with hydrogen sulphide, copper, oleic acid, fatty acids their salts, esters and certain amines, and naphthenic acid, its salts and certain esters was investigated, and treatment with copper or oleic acid was found to be the most satisfactory. One half percent of copper was found to be the minimum amount which will produce a colourless product. The crude tetrachloride was heated at 98.5°C with copper powder for fifteen minutes, and then distilled from the powder.

From the above data it may be concluded that impurities may most satisfactorily be separated from crude titanium tetrachloride as follows:

- (a) Ferric chloride may be reduced to 0.02% by settling and decantation, or by filtration.
- (b) Silicon tetrachloride and free chlorine may be separated by fractional distillation.
- (c) Vanadium, manganese, and traces of iron may be removed by heating the crude material with copper powder at 98.5°C , followed by distillation from the powder. Fractional distillation from the powder may replace section (b) above.

CHAPTER III

Discussion of the Literature Relating to the Mechanism of the Reaction

The reaction of chlorine and titanium dioxide in the presence of carbon may be one of the following overall reactions



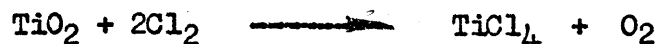
or



These reactions as written require the instantaneous reaction of a gas and two solids, which is an unlikely occurrence, for any chemical reaction which proceeds rapidly must occur through one or more relatively simple and kinetically probable steps, and the reactive species must have the opportunity to interact.

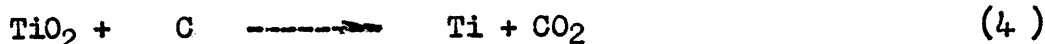
For these reactions the two simplest cases would seem to be that titanium dioxide may (a) react with chlorine, or (b) be reduced to the metal.

If the reaction takes place as in case (a) the reaction

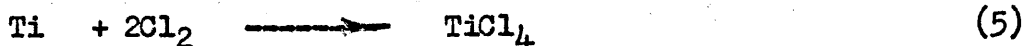


may occur, followed by the reaction of the oxygen formed with carbon to form the monoxide or dioxide. The possibility of the reaction between chlorine and carbon monoxide to form carbonyl chloride may be discounted at the reaction temperature, as the equilibrium partial pressures calculated by Godnev and Pamfilov (45) show that this compound will not exist at temperatures in the range of 400° - 1000°C.

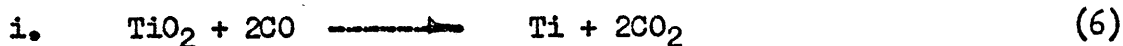
Should the oxide be first reduced to the metal the following scheme of reaction may occur:



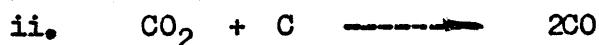
and



This first reaction requires the reaction of two solids, which for a fast reaction is improbable. This reaction may however be written in two steps:



and



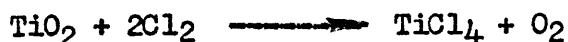
The possibilities of reactions (3) or (6) taking place has been investigated by a thermodynamic evaluation of the reactions in the temperature range of interest (Appendix I). Calculation of the equilibrium constant for the reactions show that at 1000°C the equilibrium constant

$$K_p = \frac{P_{\text{TiCl}_4} \times P_{\text{O}_2}}{P_{\text{TiO}} \times P_{\text{Cl}_2}^2} = 3.9 \times 10^{-5}$$

corresponds to a conversion of 1.25%; while the equilibrium constant

$$K_p = \frac{P_{\text{Ti}} \times P_{\text{CO}_2}^2}{P_{\text{TiO}_2} \times P_{\text{CO}}^2} = 1.6 \times 10^{-13}$$

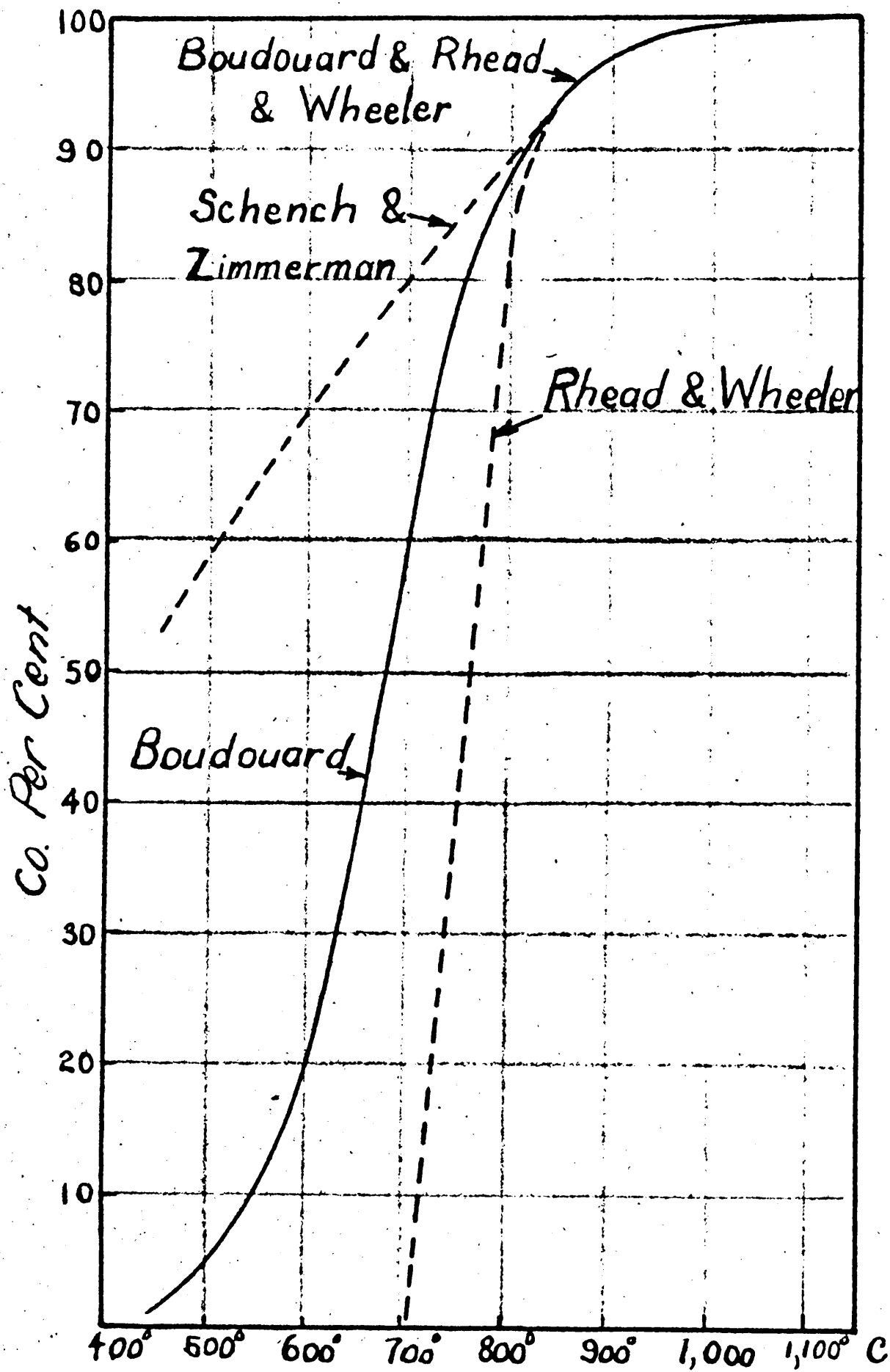
which gives a conversion of $4 \times 10^{-7}\%$. These values indicate that although in each case the equilibrium is unfavourable, the reduction to the metal as a first setp is not possible, while reaction (3) viz.



could be a first step in the chlorination in the presence of carbon.

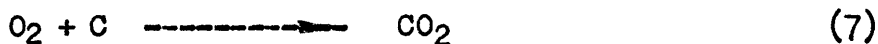
P. A. Smith

Although the theoretical equilibrium allows only a small conversion, complete reaction could be achieved by removal of the reaction products from the system as formed, by carrying the products away in a fast stream of gas, or by causing one of the products to react with a third compound. This occurs when carbon is present in the bed.

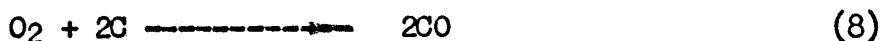


Kangro and Jahn (8) passed chlorine at 1.1 cc. per second over 1.5 to 3.0gm. of titanium dioxide contained in a boat placed in a tube furnace at 800°C and obtained only 8.6% chlorination of the oxide in one hour. Pamfilov and Shtandel (3) in the chlorination of the oxide in the presence of carbon under similar conditions (chlorine was passed 0.55 cc/sec. over the one gram of oxide) obtained 94.5% conversion in one hour. From these results, although the figures are at best qualitative, it would seem that for the chlorination in the absence of carbon no appreciable equilibrium shift resulting from the removal of the products was obtained, but in the presence of carbon the equilibrium of the reaction is shifted far to the right. The equilibrium constants, Table VI Appendix I for the possible reactions occurring give 100% conversion in each case..

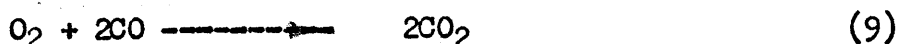
When carbon is present in the charge the simplest cause for the shift of the reaction equilibrium to the right would appear to be the reaction of oxygen with carbon, which may take place according to either of the following reactions:



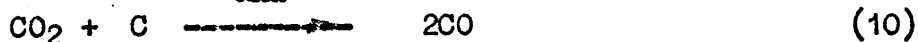
or



of which reaction (8) may itself take place in two steps:



and



Calculation of the equilibrium constants for reactions (7) and (8) - Table V Appendix I - shows an equal possibility of either reaction taking place. At equilibrium, however, the ratio of monoxide to dioxide will be corresponding to the equilibrium of reaction (10)/ Fig. 3.1

If carbon reacts as a solid according to reactions (7) and (8) then oxygen must be transferred to react at the carbon interface. Once oxygen has been removed from the titanium dioxide surface at which the reaction equilibrium exists, into the gas stream, the method^{of}/removal there, whether by sweeping away or by reaction with carbon, can have no effect on the equilibrium or the rate of the reaction. As it has been shown that high conversions can be obtained when carbon is present in the bed, it would seem that a reaction mechanism other than the reaction of oxygen with solid carbon is required.

Should carbon react as indicated in equations (9) and (10) carbon monoxide may be adsorbed on the titanium dioxide surface and react there with oxygen formed during the chlorination to yield carbon dioxide. Under these conditions the calculated equilibrium for the reaction occurring at the interface gives 100% conversion.

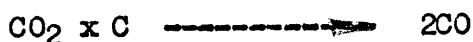
Thus the reaction of chlorine with titanium dioxide in the presence of carbon would seem to be most satisfactorily represented by the equations



and



The resultant gas mixture would then contain titanium tetrachloride, chlorine, carbon dioxide and carbon monoxide; the ratio of monoxide to dioxide depending upon the equilibrium of the reaction



at the temperature of the reaction. Figure 3.1 ~~F~~ Appendix-I shows the theoretical equilibrium for this reaction.

Godnev and Pamfilov (45) have calculated the partial pressures for chlorination at one atmosphere pressure, in the presence of carbon and show that at 400°C carbon dioxide is predominantly formed, while at 1000°C the equilibrium favours the formation of carbon monoxide. These values are given below.

Equilibrium Partial Pressures for the Chlorination in the
Presence of Carbon

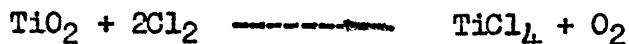
T°C	PCO	PCO ₂	PTiCl ₄	PCOCl ₂	PCl ₂
400	0.0054	0.4346	0.500	2.3×10^{-8}	1.38×10^{-7}
600	0.175	0.370	0.455	5.7×10^{-7}	1.47×10^{-5}
800	0.600	0.047	0.353	4.9×10^{-7}	7.4×10^{-5}
1000	0.6623	0.0027	0.335	9.9×10^{-8}	1.12×10^{-4}

These workers also claim that analysis of the gaseous mixture from chlorination gave compositions corresponding to the above table. This would be the case if the reaction mechanism postulated above occurred.

This concept of the reaction, is, however, contradicted by the work of McTaggart (5), who states that the material balance on chlorinations carried out by him on briquettes provided proof that little carbon dioxide could have been formed during the reaction. The possibility of the formation of carbon dioxide followed by reduction with carbon to form the monoxide is discounted by him in view to the reaction equilibrium at 700°C, which according to Stansfield (49) would give a carbon monoxide to dioxide ratio of 62:38, from which the usage of carbon would not correspond to the materials balance. These figures are not, however, backed up analysis of the gas mixture from the reactor.

In the reaction mechanism postulated above the following steps would take place in the propagation of the reaction in the bed.

1. the reaction



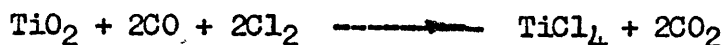
to form titanium tetrachloride and oxygen.

2. the reaction of oxygen with carbon to form carbon monoxide and carbon dioxide.
3. The reaction of carbon monoxide and chlorine with titanium dioxide to form titanium tetrachloride and carbon dioxide



4. The reaction of carbon dioxide with carbon to form carbon monoxide which reacts as in step three to continue the chlorination by that reaction.

Consideration of the reaction



as a basic step of the chlorination shows a heterogeneous reaction formally related to the catalytic reaction of gasses on a surface, in that the reaction is confined to the TiO_2 surface at any time, although all the products are volatile. The mechanism of such a surface reaction has been separated by Glasstone, Laidler and Eyring (44) into five stages.

1. The transport of the gaseous reactants to the surface
2. Adsorption of the gasses on the surface
3. Reaction on the surface
4. Desorption of the products
5. Transport of the liberated products from the surface into the bulk phase

In this separation stages one and five are diffusion processes, and if these were to exert control over the rate, the temperature coefficient of the reaction rate would be the same order as that for gaseous diffusion, increasing in proportion to the square root of the temperature, although in most known examples of heterogeneous reactions the temperature coefficients is exponential with increase in temperature.

These workers have also observed that most heterogeneous reactions have an energy of activation in the order of 30 kcal./mole., while for diffusion processes the energies of activation are probably very small, and that for the diffusion process to be controlling the film of stagnant gas on the surface would have to be of visible dimensions.

On the basis of these arguments it is now generally considered improbable that diffusion to or from the surface is the slow step in a reaction taking place at a surface, and that in general processes two and four may be expected to be the slow step in a heterogeneous reaction if the activation energy¹³ is high for the adsorption or desorption process, or is low for the surface reaction.

In a reaction taking place at a surface the rate of the reaction is governed by the concentration of the reactants at the surface, and only by the concentration in the bulk phase in so far as this affects the concentration at the surface.

The population of gaseous molecules on a surface is governed by the processes of either Physical or van der Waal's adsorption or Chemisorption. In a recent review of Heterogeneous Reactions Roberts and Anderson (46) state that in Physical adsorption the forces involved are of the same type and magnitude as in condensation of a liquid from a gas. These are non-specific and of the order of a few (< 5) kcal./mole., only. Below the critical temperature of the gas more than one adsorbed layer may be formed, but as the temperature rises the population of adsorbed molecules on the surface decreases, until as shown by the adsorption isotherm, there is no population of physically adsorbed N_2 or O_2 molecules above $600^\circ C$, or for H_2 molecules above room temperature, at which temperatures any reaction between the gas and the surface must take place at the instant of collision.

While the physical adsorption of a gas molecule on a surface involves only quite unspecific forces, the initiation of a chemical reaction between a gas molecule and the substrate implies a quite specific and more drastic mode of interaction involving either rearrangement of chemical bonds or an electron transference. The net energy balance of such a surface process is strongly exothermic and results in high or very high heats of adsorption. Unlike Physical adsorption this type of adsorption (chemisorption) is quite specific depending on the chemical nature of the solids and the gas, and not on the ease of liquifaction of the gas, as is the case for physical adsorption. Two types of chemisorption have been distinguished; where the heat of adsorption is less than about 20 kCal/mole. the adsorption process is reversible, and the chemisorbed gas may be desorbed at moderately low temperatures, and where the heat of adsorption is very large the chemisorption is practically irreversible and the adsorbed molecules are not recovered as such, but as the product of reaction between the adsorbed molecule and the substrate.

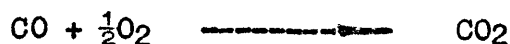
The rate of chemisorption of hydrogen and carbon monoxide on oxides increases rapidly with increase in temperature, and has been designated by H.S. Taylor as 'activated' adsorption.

Garner (47) studied the adsorption of carbon monoxide and hydrogen on a variety of difficultly reducible oxides, and found that adsorption taking place with a heat of adsorption of less than 20 kcal/mole. was reversible, while processes with a heat of adsorption greater than this amount were irreversible processes which are the first steps in the reduction of the oxides. Garner found that carbon monoxide was adsorbed reversibly on ZnO and that no surface carbonate (see below) was formed. On mixtures of ZnO and Cr₂O₃ the adsorption was however partly irreversible, up to 200°C the gas was evolved

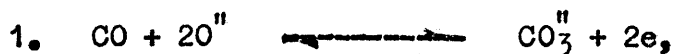
unchanged, but at 400°C carbon dioxide was evolved. On MnO 1.5 and Cr₂O₃ the adsorption is irreversible.

When carbon monoxide is adsorbed irreversibly with a heat of adsorption greater than 20 kCal/mole. CO₂ can be liberated by raising the temperature, but it is difficult to desorb at room temperature. If carbon dioxide is adsorbed the heat of adsorption is about 20 kCal/mole., and the gas is readily desorbed at room temperature, indicating no appreciable activation in the formation or dissociation of carbonate. When however carbon monoxide is adsorbed on an oxide the difficulty of the desorption shows the product to vary from the carbonate formed by the adsorption of carbon dioxide.

In the irreversible adsorption of carbon monoxide on MnO 1.5 and Cr₂O₃ the gas cannot be removed by evacuation at room temperature, but if the surface is reoxidised by the adsorption of a stiochiometric amount of oxygen, or by the initial adsorption of a mixture of carbon monoxide and oxygen, carbon dioxide is desorbed with a heat of desorption equal to the heat of adsorption of carbon monoxide. The total heats of adsorption and desorption for the carbon monoxide - oxygen - carbon dioxide system correspond to the heat of the reaction



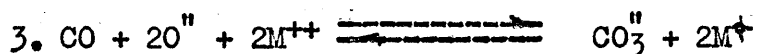
The mechanism which Garner has put forward to explain this process is that on oxides of the transition elements carbon monoxide reacts with two oxygen ions or atoms on the surface to give CO₃^{''} ions liberating two electrons,



the surface becoming unsaturated with respect to oxygen, which can be added in stiochiometric amounts, viz. $\frac{1}{2}\text{O}_2$ for each CO adsorbed.



For a bivalent metal the electrons set free would be held in the neighbourhood of the CO_3'' ion, and with this ion would form a resonation system.



The addition of $\frac{1}{2}O_2$ would then give



which will move the resonating system to the right, i.e. in the direction of the formation of the CO_3'' ion resulting in the desorption of CO_2 , which would explain the more ready evolution of carbon dioxide after the addition of oxygen.

Measurement of the rate of desorption of carbon dioxide shows that within a few calories the energy of activation is the same as the heat of adsorption. This type of reaction shows a close analogy with catalytic gas reactions as the solid acts as the medium for the transference of electrons.

Roberts and Anderson (46) observed the similarity of the reaction studied by Garner with the chlorination of metallic oxides by means of chlorine and carbon monoxide. For the reasons advanced above this process would seem to be the most likely mechanism for the chlorination of rutile in the presence of carbon, and from the above the chlorination of rutile would take place in the following steps:

1. The adsorption of CO on the oxide ion sites



2. The adsorption of Cl_2 on the metal ion sites



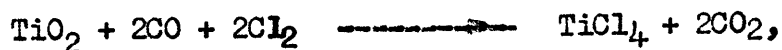
3. The desorption of CO_2



4. The desorption of volatile $TiCl_4$



Assuming the basic reaction in the chlorination in the presence of carbon to be



which would be proved if the chlorination takes place as readily in the presence of carbon monoxide as solid carbon, most light would be thrown on the mechanism of the reaction by determining the order of the reaction with respect to chlorine and carbon monoxide, and the extent to which the rate of the reaction is retarded by the concentration of the products.

The study of the mechanism of a reaction occurring in a fluid bed requires the use of a flow method of the type used by Gadsby, Hinshelwood and Sykes (48) for studying the kinetics of the steam - carbon system, as fluid bed conditions could not be achieved using a static technique. In this flow method a stream of gas would be passed through the fluid bed kept at a known temperature and the partial pressures of the gasses present in the reaction system varied separately, the total flow being kept constant, and the total pressure being maintained at atmospheric by use of nitrogen as an inactive carrier gas. The order of the reaction with respect to the reactants could then be determined from a plot of the reaction rate versus the partial pressure of the reactant, and the effect of the concentration of the products on the rate of reaction could be determined by varying the concentration of the products and plotting the rate versus the inlet partial pressure of the product. A comparison of the rates of reaction using solid carbon or carbon monoxide as the reducing agent could be obtained by determining the order of reaction of chlorine on a bed containing solid carbon, and for carbon monoxide on a bed containing only rutile, using a fixed partial pressure of chlorine, and then comparing the rates of reaction under conditions of equal chlorine partial pressure.

It should then be possible from the interpretation of the results of such experiments to show whether or not the reaction occurs by the adsorption of chlorine and carbon monoxide on the titanium dioxide surface, what type of control the concentration of the reactants exert on the rate of reaction, and if the rate is controlled by the concentration of the products.

CH AFTER IV

The Fluidization of Solids

The most comprehensive treatment of fluidization is given in the work of Leva and others published by the National Bureau of Standards ^{Mines} (50).

The term fluidization is applied to the condition which occurs when a fluid is passed upward through a bed of finely divided solids at such a velocity that the pressure drop through the bed is equal to the weight of the bed. Under this condition the bed expands and each particle is free to move about. This bed then possesses properties similar to a liquid and as a result the process has many applications where contacting of gasses and solids is necessary, the chief being the catalytic cracking of petroleum fractions and the roasting of various ores. The properties which have made this progress so important are:

- a. The fluid properties of the bed allow solid materials to be handled in a manner similar to a liquid, i.e. to be run through pipes and controlled by valves.
- b. The bed is maintained in violent motion, resulting in excellent mixing and uniform composition throughout.
- c. The bed temperatures are uniform, very little temperature differences existing between the top, bottom, centre and walls of the bed.
- d. The heat transference coefficients obtained between the fluid bed and a wall or pipe are very much greater than those obtained between a surface and a gas.
- e. Very fine solids fluidize at low flow rates, making it easy and economical to produce fluid beds with high specific surfaces. This results in high reaction rates for heterogeneous reactions.

Types of Fluidization

When a fluid is passed through a bed the behaviour of the bed in the fluid state varies widely with the fluid, the solid and the solid particle size. This behaviour has been classified broadly into particulate fluidization in which each particle moves independantly, and aggregative in

which the particles move in the bed in clusters. Particulate fluidization occurs in beds of solids fluidized with liquids, or occasionally when very light solids are fluidized with gasses, while the aggregative type is usually encountered in the fluidization of solids in a gas stream.

In aggregative fluidization a wide range of conditions can occur from channeling at one end of the range to slugging at the other. As in aggregative fluidization the solids have a tendency to move in clusters, so there is a similar tendency for the gas to pass through the bed in bubbles. When these bubbles forming ⁱⁿ the bed become an appreciable proportion of the cross sectional area of the reactor bridging occurs and slugs of solids are forced up the reactor. These slugs collapse as the solids run into the gas bubble and hence the condition is less evident in beds of free flowing materials. This passing of the gas through the bed in bubbles considerably reduced the contact of the gas and solid and thus reduces the efficiency of the process.

Channeling occurs when the gas cuts channels through the bed, and in extreme cases the remainder of the bed may be quite static. While slugging occurs in beds of coarse particles and is reduced by the addition of fine material, channeling is predominant with fine particle sizes, especially when the angle of repose of the solids is high. When this occurs channels may be cut through the bed and remain, as solids do not run back into the channels.

Some indication of the type of fluidization occurring in an opaque reactor may be gained from the pressure drop across the bed as registered by a manometer. In channeling beds the pressure drop remains static, while slugging conditions causes violent fluctuations in the pressure drop. Steady fluidization however is indicated by small rapidly occurring surges as the bed expands and contracts slightly on the average volume.

As slugging is one of the main problems in obtaining satisfactory fluid bed conditions a good deal of work has been done to determine the conditions under which slugging occurs.

Matheson Herbst and Holt (51) have shown the 'viscosity' of the bed as measured by a modified Stormer viscometer has a straight line relationship

with the slugging tendency of the bed, measured by the minimum height at which slugs occur divided by the diameter of the bed, the minimum slugging height decreasing with decrease in the 'viscosity'.

These workers investigated the effect of variables on the slugging tendency by determining their effect on the bed viscosity. Particle size was shown to have a large effect on the bed 'viscosity', the addition of a relatively small amount of fines to a bed of coarse material markedly reducing the 'viscosity' and slugging up to a concentration of about 30%, above which the trend is not so marked. It is also shown that the bed viscosity is a function of the bed density, as dependant on both the expansion of the bed and the density of the material, thus the addition of a low density material to a bed of heavy solids reduces the viscosity considerably.

Morse and Ballou (52) investigated the uniformity of fluidization and showed slugging to be affected by a number of factors. They showed that the presence of fines greatly improved the quality of fluidization, and that gas velocity, gas distribution and bed height were factors with a big effect on slugging. For fluidization of a metal oxide catalyst doubling the gas velocity from just above the initial fluidizing velocity trebled the size of the bubbles in the bed, while an increase to three and a half times took the bed to incipient slugging. The use of a gauze gas distributor was shown to improve the fluidization in the bottom of deep beds but had little effect at higher levels. Deep beds have a greater tendency to slug than shallow beds, but increase in the bed height has little effect on the quality of the fluidization at the bottom of the bed. The quality of fluidization through the bed was shown to decrease much more rapidly with materials which fluidize badly, slugs forming as the gas moves up the bed.

From this work it is clear that to obtain the best results with materials which have a tendency to slug beds should have the following characteristics:

- a. The particle size distribution should be wide, containing up to 30% of fine material.
- b. The bed density should be kept as low as possible, this could be assisted by the addition of a light material to the bed.
- c. The length to diameter ratio of the bed should be kept to a low figure, (not greater than 5).
- d. The distribution of gas at the bottom of the bed should be the best possible.

Mechanism of Fluidization

When a fluid is passed through a fixed bed of solids the pressure drop varies according to the Carmen equation

$$\frac{\Delta p}{l} = \frac{5M Sl^2 \bar{\phi} \mu}{gl \rho \bar{\phi}} \quad \text{for laminar flow where}$$

Δp = pressure drop through the bed

l = height of the bed

M = rate of fluid flow

Sl = surface area of particles and containing vessel per unit

$$\text{volume} = 6 \frac{(1 - \bar{\phi})}{\bar{\phi} d} + \frac{4}{D}$$

$\bar{\phi}$ = porosity of bed

$\bar{\phi}$ = particle sphericity

d = particle diameter

μ = fluid viscosity

ρ = bed density

g = gravitational constant

This equation holds for the inclined section of the pressure drop versus fluid velocity plot shown in Figure 4.1

When the velocity is increased to a value at which the pressure drop equals the weight of the bed, the bed expands as is shown by the down curve in the plot, and when no further expansion can occur without the particles separating, the bed is said to be fluidized. Once the bed is fluidized the pressure drop over the bed remains nearly constant varying only with the friction of the gas and solid particles with the walls.

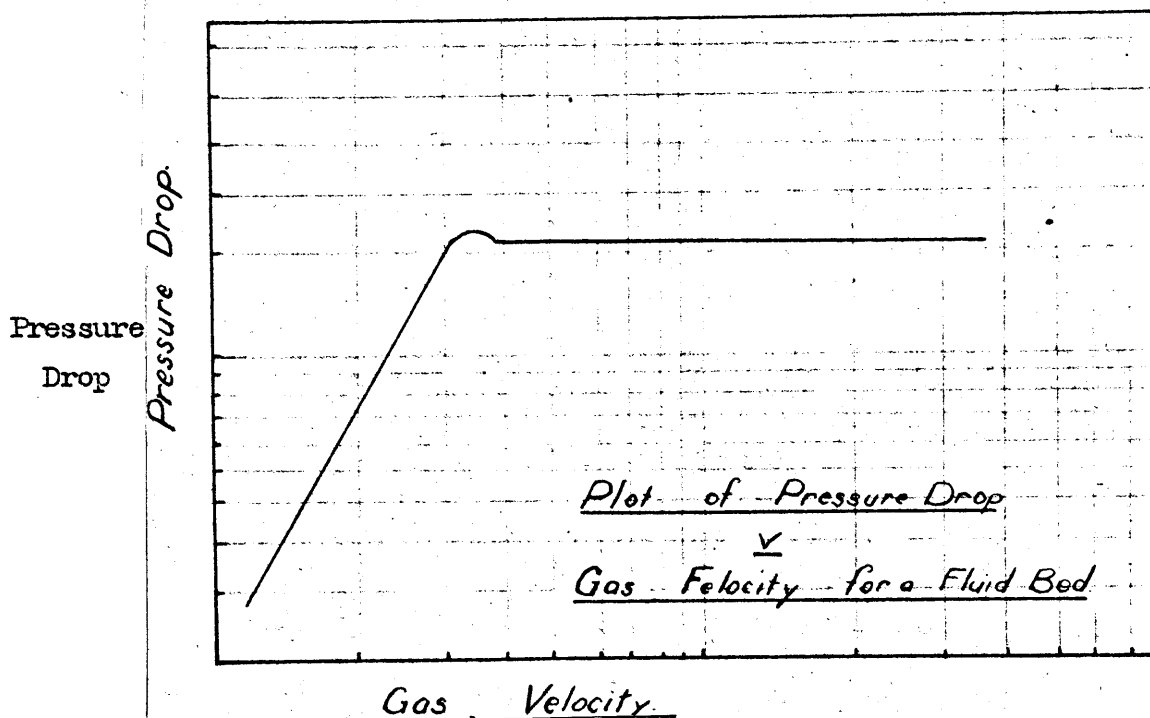


Figure 4.1

As the velocity of the gas through the bed is increased the bed expands and the most satisfactory correlation for a fluid bed is given by the Leva(53) equation

$$\frac{M \mu l_e}{\rho} = k \left[\frac{(1 - \delta)^2}{\delta^3} \right]^m$$

in which

M = mass flow of fluid

μ = fluid viscosity

l_e = ratio of bed height to fixed bed height at fluidization point

k = constant

m = constant

δ = maximum static bed porosity

ρ = fluid density

The constant 'm' is the gradient of a line obtained by plotting $\frac{M_{pl}}{\rho}$ against $\left(\frac{1 - \phi}{\phi}\right)^2$ on log-log paper and requires experimental fluidization, while the value 'k' may be determined by substituting the values of the other variables at the fluidization point.

A second useful correlation is a log-log plot of bed expansion versus Reynold's Number calculated on the particle diameter which gives a straight line. Thus in experimental work if the Reynold's Numbers for similar beds are constant for varying gas flows, temperatures and densities the quality of fluidization obtained should also be constant.

CHAPTER V

The Programme of the Experimental Investigation

The preceeding survey of the literature has shown the chlorination of briquettes formed from a mixture of rutile and carbon to be the process with the greatest present industrial significance for the production of titanium tetrachloride. In this process the briquettes, which are first roasted to remove volatile hydrocarbons, are charged to a shaft furnace at 400° to 600°C , and there reacted with chlorine. It is reported that the chlorination commences at 400° to 500°C , and that the optimum conditions for the reaction are in the range of 700° to 950°C , although McTaggart reports that no increase in the reaction rate was obtained above 700°C . Under these conditions the reaction is exothermic, no external heating of the reactor being required, and providing that there is sufficient material in the reactor, chlorine efficiencies of 93 to 95% are claimed. There is no reliable data on the effect of particle size on the reaction rate.

The previous work carried out on this chlorination has thrown very little light on the mechanism of the reaction taking place, and in some instances the reports are contradictory, although a fuller understanding of this would lead to a better appreciation of the most favourable conditions for the operation and improvement of the industrial process.

While reference (14) has been made to the chlorination of rutile in the presence of carbon under fluid bed conditions, very little data is given in this patent, and no real contribution to the literature on the subject has been made. No data is given for the characteristics of fluid beds of rutile and carbon, the conditions required to achieve optimum bed characteristics, or the effects of alteration of any of the reactor conditions.

In order to evaluate the worth of the fluid bed process for commercial operation, it is necessary to know the characteristics of fluid beds of rutile and carbon under operating conditions, the optimum conditions under which the reaction occurs, the process efficiency which could be obtained under operating conditions, and the heat requirements of the reactor.

The conditions for the operation of a fluid bed chlorination are first limited by the conditions under which efficient fluidization of a mixture of rutile and carbon may be achieved. As no data on these conditions were available in the literature, a preliminary investigation of the fluidization of rutile, carbon, and mixtures of rutile and carbon was required, and experiments were carried out using air as the fluidizing medium, before the design of the apparatus for chlorination.

The survey of the literature suggested that

- a. Temperature
- b. Rutile to carbon ratio
- c. Chlorine velocity through the bed
and
- d. Bed depth

were variables which should be investigated to determine the optimum conditions for the chlorination.

The previous work has shown that variation of temperature alters the rate of the reaction, and this variable is most important in achieving high rates of reaction. While most of the literature is in agreement that the reaction commences at temperatures in the range of 400° to 500°C, data on the optimum temperature for the reaction seemed to be open to question, and further investigation of this variable under fluid bed conditions was necessary.

As the reaction occurring must be a heterogeneous reaction between two solids and a gas, it is important to investigate the effect of variation of reaction rate with change in the surface area of both solids in the reaction zone. This will be governed by the amount of each material in the bed and the particle size of the rutile and the carbon. If the initial particle size of both rutile and carbon were kept constant, the effect of change in the surface area could be investigated by determining the change of the reaction rate with change in the amount of material in the bed, while variation of the ratio of the surface area of rutile to carbon available for reaction may be achieved by varying the ratio of rutile to carbon in the bed at constant particle size.

Change in the feed rate of chlorine to the bed could be expected to effect the rate of chlorination in two ways: to increase the rate due to increase of the partial pressure of chlorine at any point in the bed, or to decrease the conversion of chlorine due to slugging of the bed with resultant lower contact between the solid and the gas, passing the gas through the bed as bubbles without coming into contact with the solid.

Before any investigation of the variation of the reaction rate with temperature could be carried out, it is necessary to study the effects of change in chlorine rate and bed depth so that conditions could be chosen to supply sufficient chlorine to the bed to give an excess under all conditions, and to eliminate variations due to change in bed depth in correlating the effects of temperature.

As discussed in chapter three, the mechanism of the reaction would be most effectively studied using a flow system in which a constant volume of gas is passed through the bed held at a known temperature, and the partial

pressures of the gasses present in the reaction system would be varied separately the total pressure being maintained at atmospheric by the use of nitrogen as an inactive carried gas.

The factors discussed in the preceeding paragraphs lead to the drawing up of the following programme for the experimental investigation. In drawing up this programme it was thought advisable to use a sequential approach to the investigation, allowing the programme to be altered in the light of the experimental results.

A Programme for the Investigation of the Chlorination of Rutile
in the presence of Carbon in a Fluid Bed

- A. The investigation of the fluidizing characteristics of beds of rutile, carbon and mixtures of rutile and carbon, using air as the fluidizing medium in a glass column.
- B. Preliminary experiments on the chlorination of mixtures of rutile and carbon to ascertain the possibility of carrying the reaction out under fluid bed conditions, and to check the operation of the apparatus and the methods of analysis to be used on the system.
- C. Investigation of the fluid bed chlorination in the following steps:
 - i. Chlorination with constant charge particle size, bed composition and reaction temperature, varying the chlorine rate to the reactor.
 - ii. At constant conditions of charge particle size, bed composition, chlorine rate and temperature, carry out runs varying the bed height.
 - iii. With charge particle size, bed composition, initial bed weight, and chlorine feed rate constant make successive runs at bed temperatures between 450° and 950°C.
 - iv. At constant particle size, temperature and chlorine rate vary the carbon content of the bed.
- D. Investigation of the Reaction Mechanism in the following steps:
 - i. Variation of the partial pressure of chlorine in the gas to the reactor.

- ii. Variation of the partial pressure of carbon dioxide in the gas to the reactor.
- iii. Variation of the partial pressure of titanium tetrachloride in the gas to the reactor.
- iv. Variation of the partial pressure of carbon monoxide in gas to the reactor.

In step (i) the partial pressure of chlorine in the feed gas would be changed by adding nitrogen as a diluent gas, and reducing the chlorine rate to keep the total rate of flow constant, maintaining the pressure constant at atmospheric. In steps (ii), (iii), and (iv) the partial pressure of chlorine would be kept constant, and the partial pressure of the component (e.g. carbon dioxide) would be altered by adding this gas to the gas stream and adjusting the flow of nitrogen to keep a constant total rate of flow.

In each of these runs the variation of the weight of material in the bed, as measured by the pressure drop over the bed, and the rate of reaction, measured by the rate of condensation of titanium tetrachloride, would be determined, and analysis made of the tail gas and the residues of the chlorination. From these results materials balances could be calculated and the effects of the different variables correlated.

The results of the correlations of the variables obtained from the above experiments should then be sufficient for deciding upon the optimum conditions for the fluid bed chlorination and for evaluating the economic worth of the process. It should be also possible to decide the reactions which take place in the reaction of chlorine with rutile in the presence of carbon to form titanium tetrachloride, to determine the factors controlling the rate of the reaction and to calculate an energy of activation for the reaction, which would lead to a better understanding of the reaction mechanism.

CHAPTER VI

Preliminary Fluidization Experiments

As a preliminary to the chlorination in a fluid bed the fluidization of rutile and rutile-carbon mixtures was studied using air as the fluidizing medium.

The ore as received was a closely sized beach sand concentrate between 70 and 100 mesh Tyler Stand^{and}/Screen having a density of 4.25 gm/cc., and a bulk density of 2.39 gm/cc.

Fluidization of the material in a two inch diameter glass column gave violent slugging at high air velocities, slugs forming about one and a half inches above the distributor plate. This was with a bed five and a half inches deep. At low air velocities little solid movement occurred.

Fluidization of cuts of particle sizes of rutile ground in a ball mill resulted in channel formation in beds of particles less than 300 mesh, no solids falling into the channel through which all the gas passed. In the range of 200 to 300, channels were formed, but the material fluidized to some extent, while the 150 to 200 range resulted in some sluggish fluidization. As the particle size is increased the tendency to channel decreases while the tendency to slug increases, there being no cut of size at which smooth fluidization occurs.

Fluidization of mixed sizes showed the same tendencies of slugging and channeling exhibited in the fluidization of closely sized particles; far better fluidization is however obtained using mixed sizes, the optimum fluidization occurring for the grading given in column 'a' of Table 6.1. With this grading the formation of slugs and channels was reduced to a minimum,

and good solids circulation was obtained. The addition of more fines to the bed resulted in the formation of channels, until with a size distribution shown in column 'b' of Table 6.1 marked channeling and little agitation of the solids occurred.

Fluidization of a mixture of rutile and coke in the ratio of 3.3:1 by weight resulted in greatly improved fluidization, the lower bed density (1.66 gms/cc.) reducing the slugging tendency, smooth fluidization being obtained over a wide range of particle sizes. A size distribution such as given in column 'c' gave good fluidization characteristics at a superficial gas velocity of 4.3 ft/min. through the bed.

Table 6.1

Mesh	Wt. % of Material		
	a	b	c
40			1
70			5.5
100	10	7	33.1
140	25	10	27.2
200	15	10	27.7
-200	50	-	-
300		40	3.9
-300		33	1.6

A typical plot of the pressure drop over the fluidized bed versus the gas velocity for a material with the size analysis given in column 'c' is shown in Figure 6.1. The characteristic rise of pressure drop with increase in gas velocity for the fixed bed, the falling section during which the bed expands with increase in the velocity as the pressure drop becomes equal to the weight of the bed and the nearly horizontal section for fluidization when the bed is expanded and the pressure drop is equal to the weight of the bed are clearly shown. The slight increase in pressure drop during this flat section is due to friction between the containing walls and the bed of solids.

Experiments on fluidization carried out at an elevated temperature showed that at gas rates just above the minimum fluidizing velocity the temperature gradient across the bed was very large.

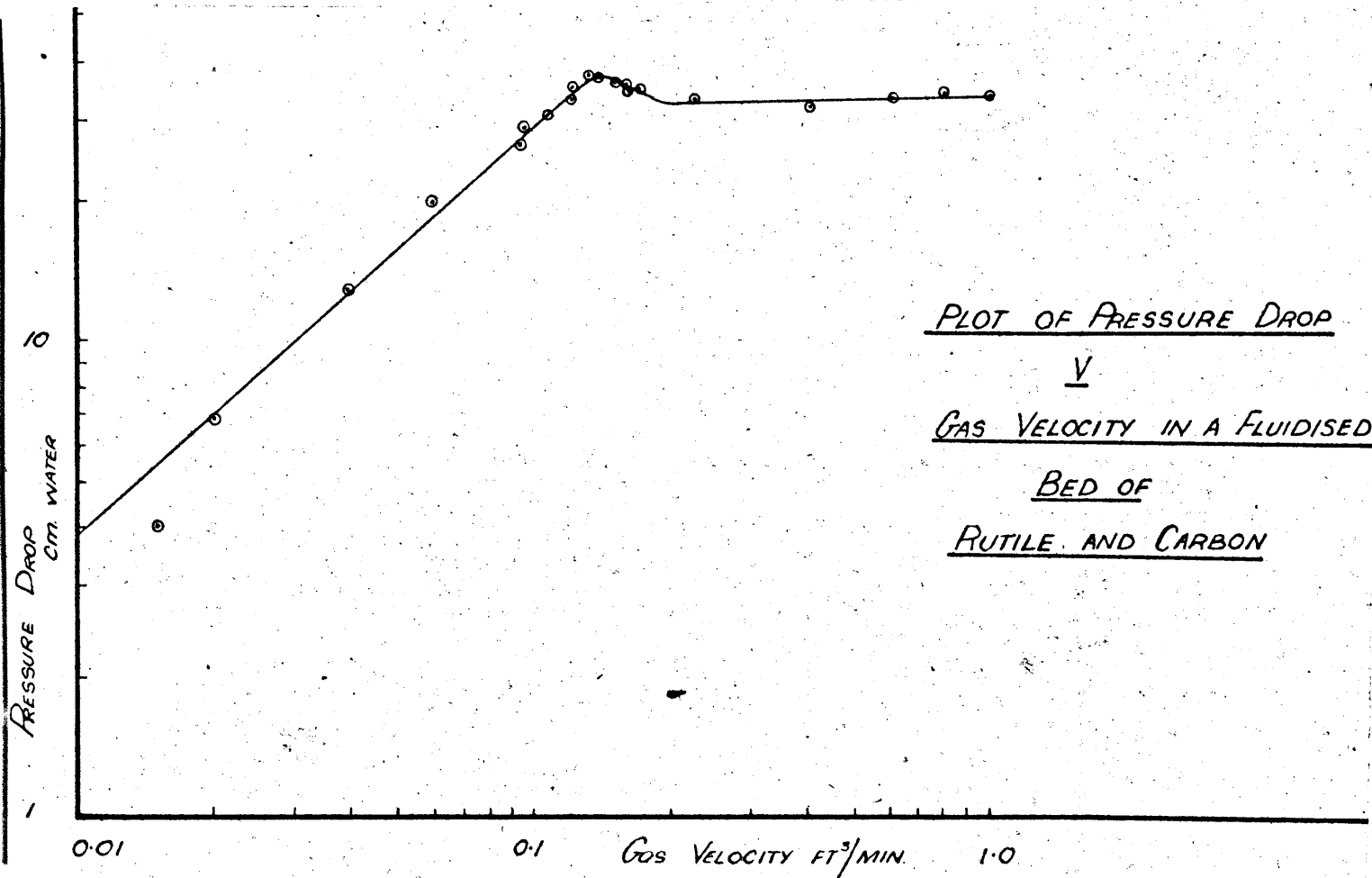


Figure 6.1

This shows that the agitation of the bed at these low velocities is very slight.

Figure 6.2 shows the temperature gradient variation in the bed with change in the gas rate. This gradient was measured between thermocouples five inches apart, the thermocouple indicating the lowest value being located one inch above the gas distributor through which the cold gas was fed into the bed. The temperature indicated by the top thermocouple remained constant at 420°C during the test, only the temperature in the bottom of the bed varying.

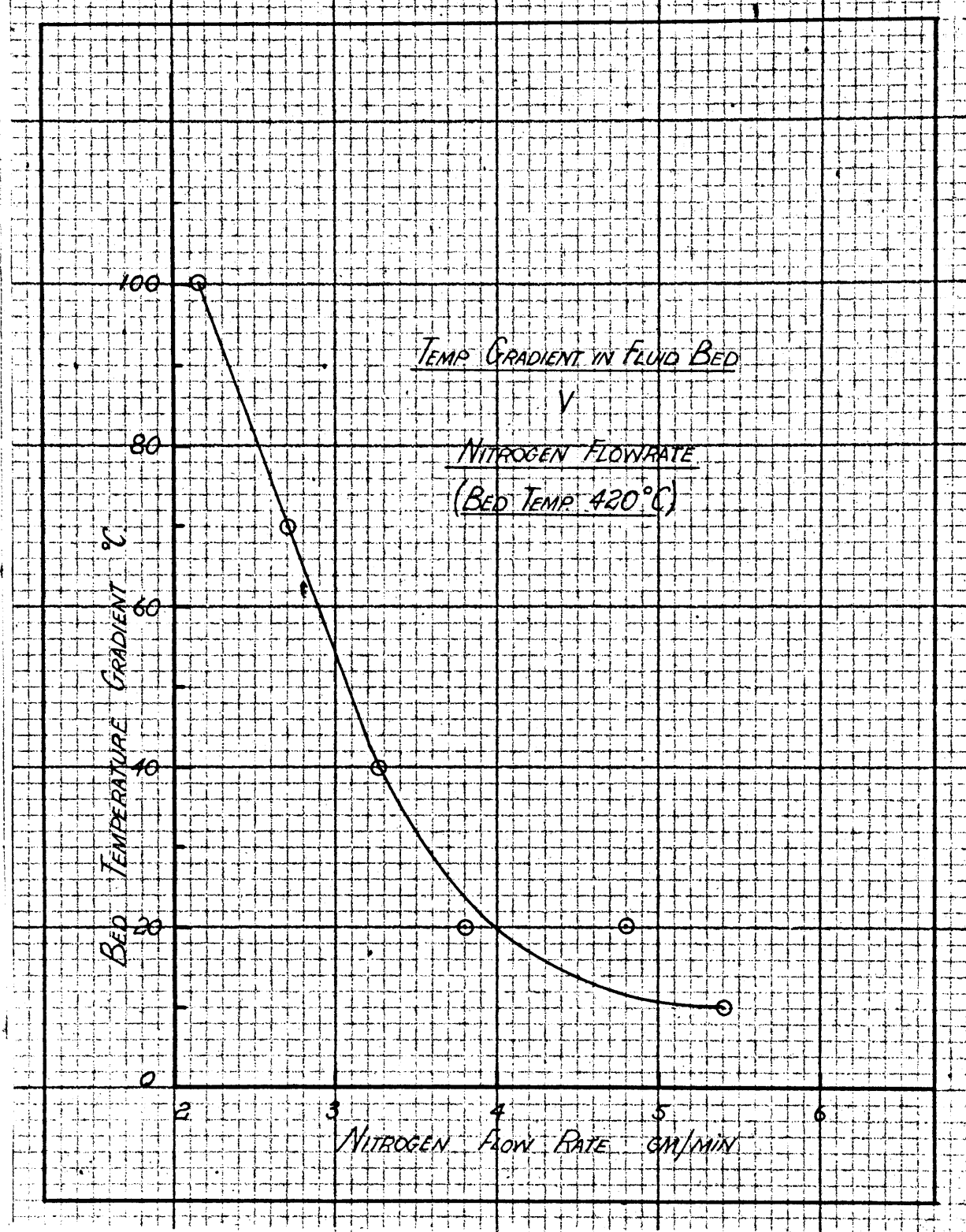


Figure 6.2

The correlation of the bed temperature gradient with the gas velocity and fluidization is better shown by plotting the variation of temperature gradient with gas velocity on the same graph as that showing the plot of pressure drop over the bed against the gas velocity. Figure 6.3 shows this plot.

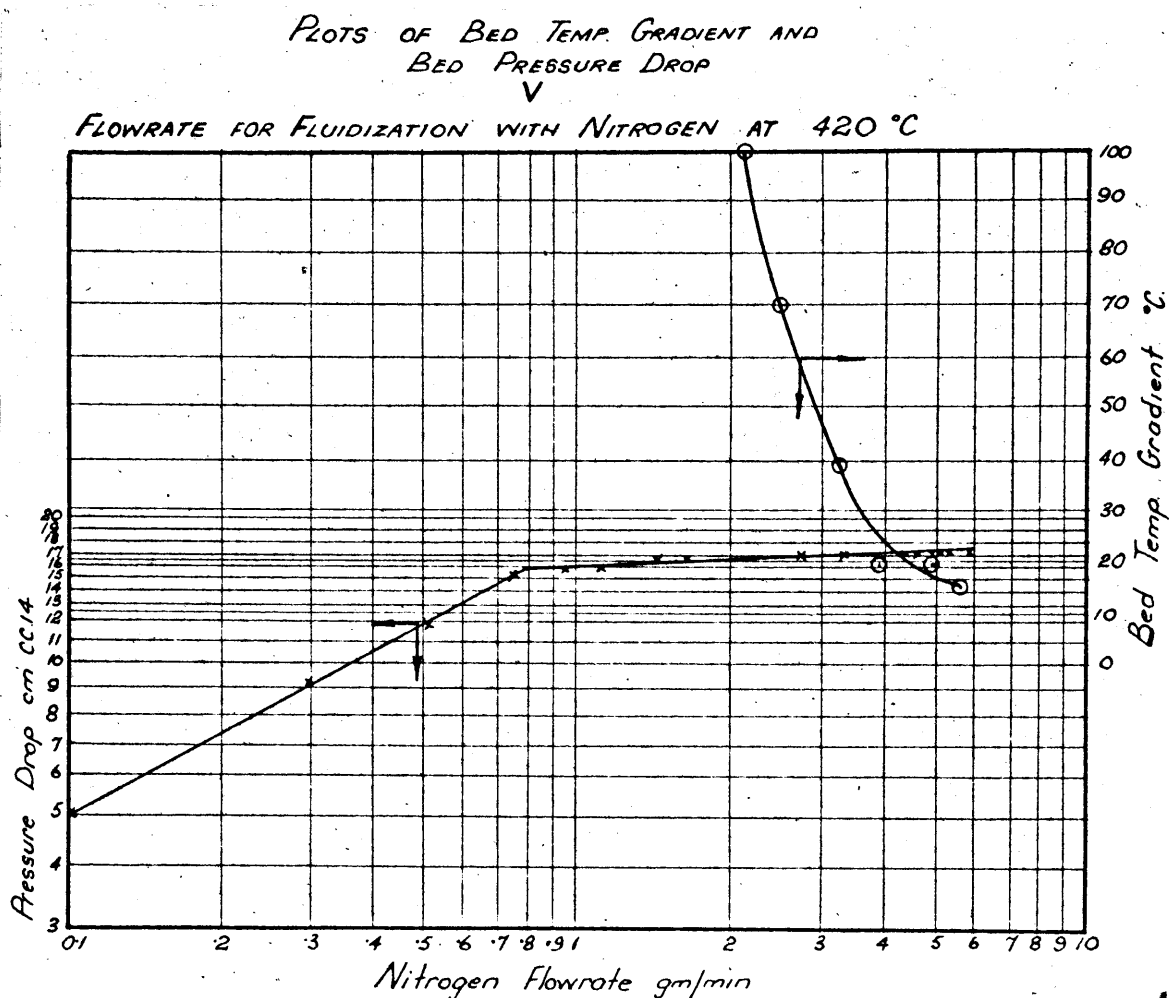


Figure 6.3

This indicates that the temperature gradient over the bed reaches a minimum at a gas velocity about five times the minimum fluidizing velocity. This decrease in temperature gradient with increase in the gas velocity shows the increased bed turnover and gas - solids contact occurring at the higher gas velocities. Measurement of the temperature over the bottom inch of the bed showed a rapid drop in temperature in this portion of the bed, the temperature at the distributor plate being about 150 to 200°C lower than the temperature in the body of the bed.

For efficient heat transference, uniform bed temperatures and uniform bed composition it is necessary therefore to operate with gas velocities greater than five times the minimum fluidizing velocity.

CHAPTER VII

The Development & Description of the Apparatus

The general arrangement of the apparatus used in the following experiments is shown in Figure 7.1.

The apparatus was set up so that chlorine, nitrogen, carbon monoxide, carbon dioxide and titanium tetrachloride, either separately or in combination, could be metered into the reactor in which chlorine was reacted with rutile and carbon under controlled conditions to form titanium tetrachloride and the oxides of carbon. This gas mixture then passed through the condensation system, in which titanium tetrachloride was condensed, to the liquid separation system to remove entrained liquid titanium tetrachloride, before passing to the stack.

The rate of the reaction was determined by measuring the rate of condensation of the titanium tetrachloride, making allowance for the amount of this material in the tail gas, which was sampled for analysis and the temperature and the flow rate measured.

Nitrogen and carbon dioxide were metered to the inlet of the reactor from the reducing valves at the cylinders, the flow rates being controlled by needle valves located in the lines before the meters.

Liquid chlorine from a ten pound cylinder was passed to a coil of quarter inch diameter copper tubing immersed in hot water and the gas formed in the coil was cooled and metered into the reactor. The flow rate was controlled by a needle valve located after the evaporating coil. The flow rates were checked against the total weight of chlorine used during the run.

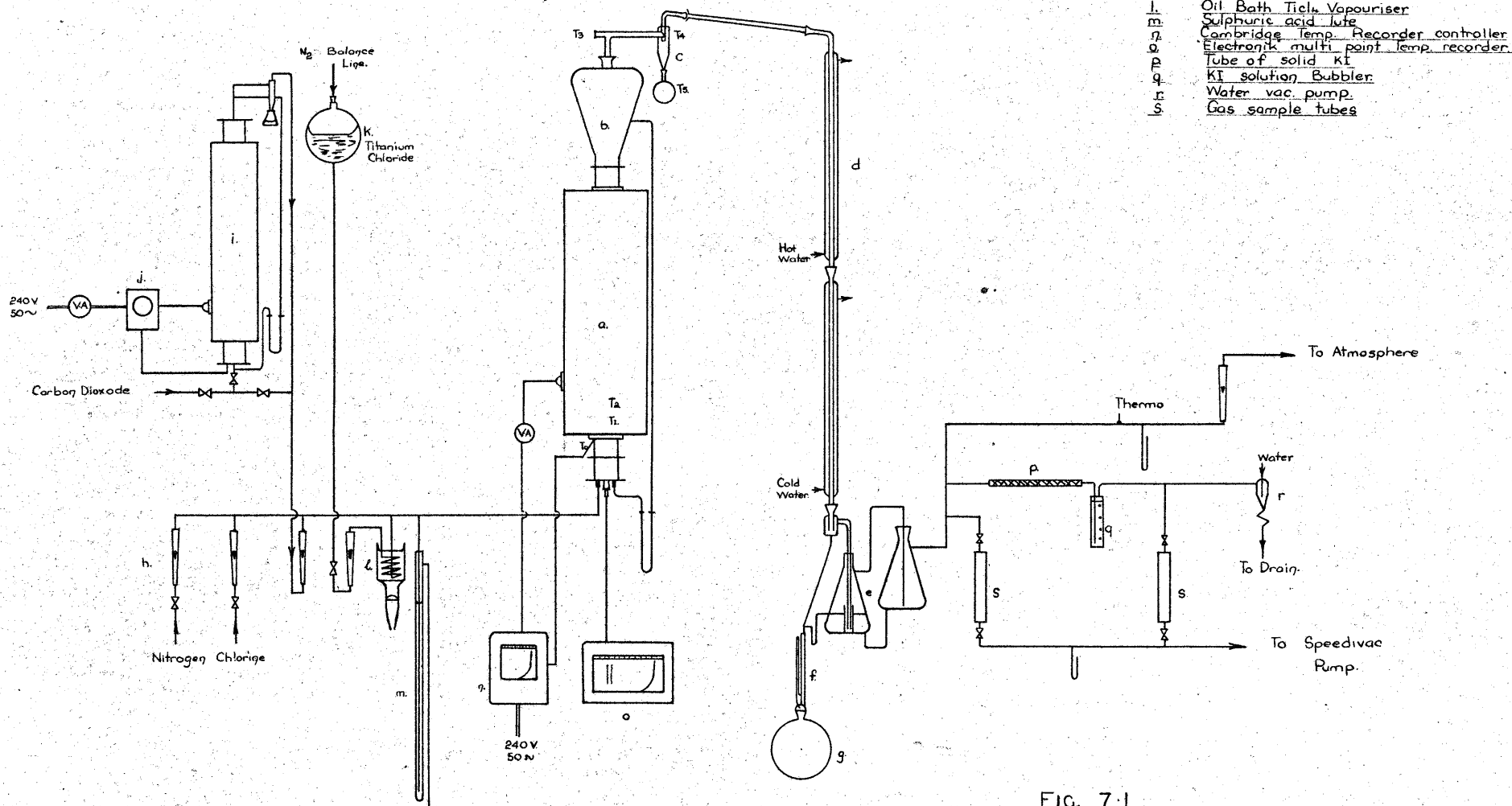


FIG. 7.1

Schematic Arrangement
of Apparatus used in the study
of
The Fluid Bed Chlorination of Rutile

Titanium Tetrachloride was supplied to the reactor as the vapour. The liquid from the reservoir was metered through a flowrator and passed into the stream of chlorine and nitrogen in the manifold, and thence through an evaporating coil immersed in oil held at 200°C. The mixture of gas and vapour then passed to the reactor.

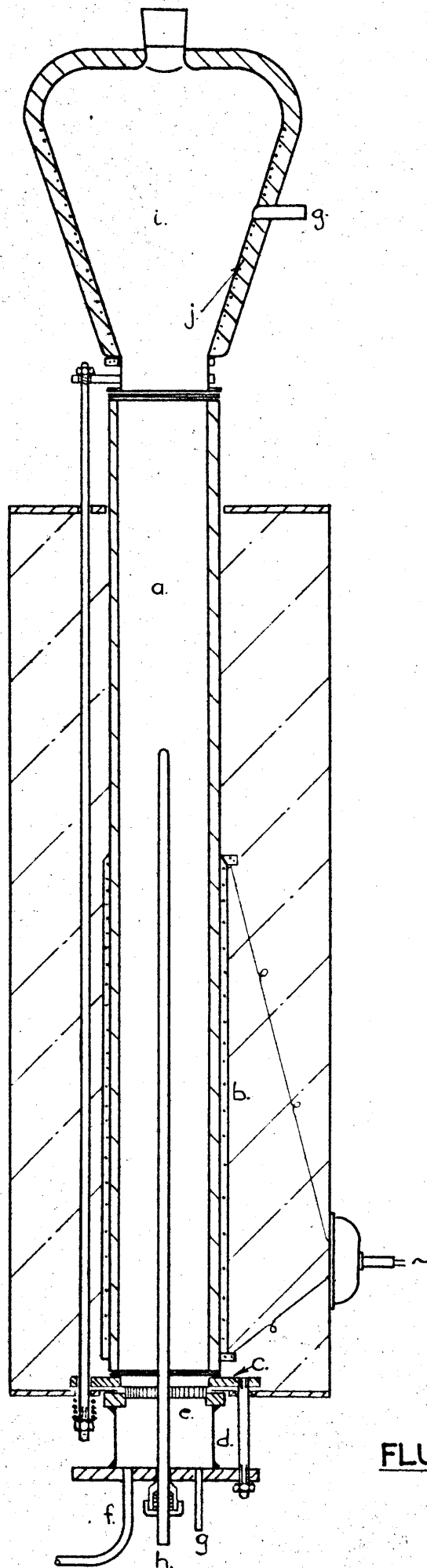
The meters used in the measurement of the gas flow rates to the reactor were Fisher and Porter 'Flowrators' calibrated for the particular gas on which they were used. These calibrations were checked from time to time, and provided the floats were kept clean no variations occurred.

Reactor

The reactor was originally set up as shown in Figure 7.2. Although alterations were made to this apparatus in the light of experimental operation, the basic design of the apparatus was not radically altered.

The reactor tube 'a' consisted of a two and one quarter inch diameter fused silica tube thirty inches long heated by means of a 1.37 kW resistance heater. The heater 'b' was wound from 22 S.W.G. Brightway C wire on the bottom twelve inches of the tube imbedded in Alfrax cement. The reactor tube was initially lagged with three inches of slag wool contained in a copper sheath. This was later changed to 'Vermiculite', an exploded micaceous material, which was found to give much better service.

The bottom of the reactor was constructed from nickle, and consisted of a bottom plate 'c' clamped to the ground end of the silica tube by means of spring loaded tie rods, and the base section 'd' which carried a porous distributor

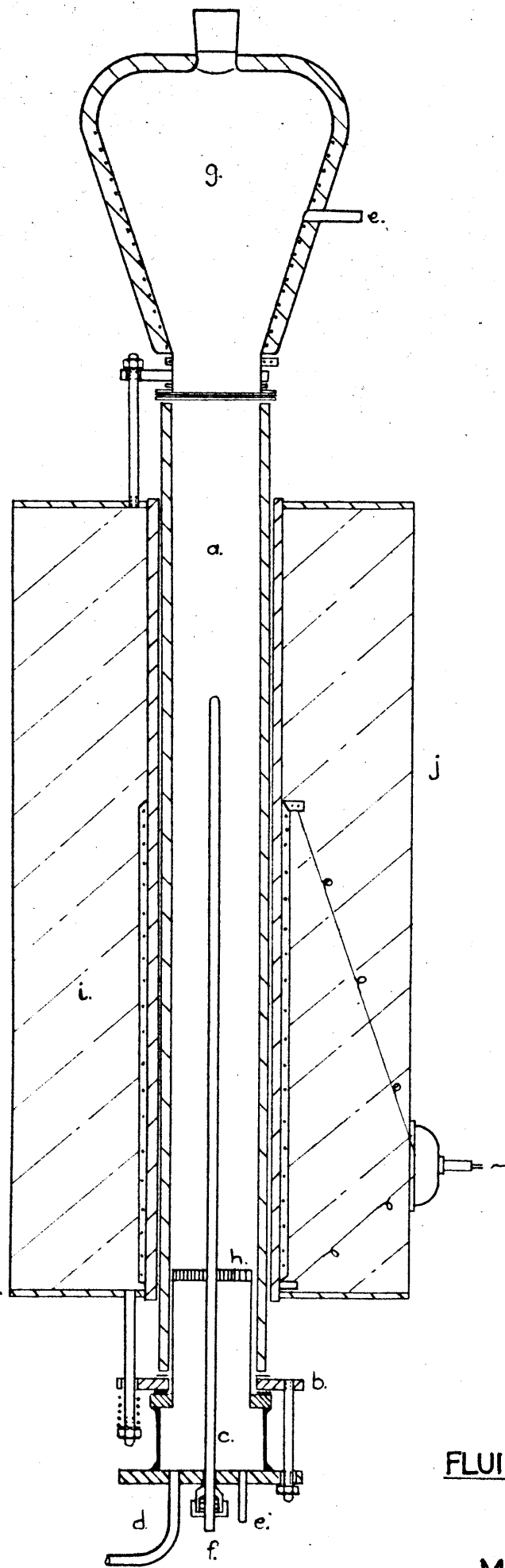


Key:-

- a. Reactor Tube
- b. Resistance Heater
- c. Bottom Plate
- d. Base Section
- e. Distributor Plate
- f. Gas Inlet
- g. Pressure Taps
- h. Thermo Sheath
- i. Knockout Drum
- j. Resistance Winding

FIG. 7-2
FLUID BED CHLORINATION
REACTOR.

Original Design.



Key:-

- a. Reactor Tube
- b. Bottom Plate
- c. Base Section
- d. Gas Tubes
- e. Pressure Taps
- f. Thermo Sheath
- g. Knockout Drum
- h. Distributor Plate
- i. Radiant Heater
- j. Lagging Sheath

FIG. 7-3

FLUID BED CHLORINATION REACTOR

Modified Design

plate 'e', a gas inlet tube 'f', a pressure tap 'g' and a silica thermocouple sheath 'h'. The gas distributing disc used was a No.46 grit carborundum grinding wheel sealed into the nickle support ring by 'Misco'lute' porcelain cement. The distributor was found to give satisfactory service under most conditions.

The knockout drum 'i' at the top of the reactor, which served to separate the larger entrained particles from the gas stream, was constructed from a two litre pyrex flask flanged at the neck to fit the silica tube. The flask was wound with a resistance winding 'j' and lagged with magnesia asbestos.

The seals of the bottom plate and the knockout drum to the silica tube were origionally made by means of one sixteenth inch asbestos mill-board impregnated with sodium silicate, but this was found to be unsatisfactory and the jointing material was changed to one thirty second 'Salamanderite' smeared with silicone grease. This gave satisfactory service.

The above reactor design gave trouble with leaks at the joint between the silica tube and the bottom nickle disc, and it was found impossible to obtain an effective seal under a chlorine and titanium tetrachloride atmosphere at temperatures in the range of 700 to 900°C.

To avoid the above difficulties and dismantling the lagging sheath to do any work on the reactor tube, the reactor and heating system were reconstructed as shown in Figure 7.3. In this design a separate radiant heater was used to heat the reactor and the base of the reactor was altered to remove the joint between the bottom plate 'c' and the reactor tube 'a' from the heated zone.

In the initial design of the reactor the temperature of the reaction zone was controlled by a Cambridge On-Off Controller operating on the power supply to the heating element, and actuated by means of a thermocouple in the centrally placed sheath. A ten amp Variac was included in the electrical circuit to provide a wider range of control than would otherwise have been possible.

In the modified apparatus the location of the control thermocouple was changed to the annular space between the reactor tube and the heater as ^{it} was found that temperature lags were too great if the couple was placed in the centre of the bed. The bed temperature was then measured at two points in the centre of the bed and recorded by means of a Brown "Elektronik" multi-point recorder. The control of the bed temperature was achieved by setting the control point of the Cambridge Controller at a value to give the desired bed temperature as indicated by the couples located in the bed. These couples were placed four inches apart the lowest being one inch above the gas distributor.

In experiments in which it was desired to vary the bed temperature during the run, the reactor was raised to the desired peak temperature and then cooled by blowing air through the annular space between the heater and the reactor tube. By control of the flow of air and the energy input to the controller accurate control of the cooling rate was obtained.

Cyclone

The cyclone for the removal of solids carried over from the reaction zone before the gasses passed to the condensation system consisted in the original apparatus of a two litre conical flask fitted with a tangential inlet. This was found inadequate, as entrained solids clogged the top of the condenser.

A size analysis of the solids carried over from the reactor showed that the largest particles were of the order of 100 microns in diameter while 12.5% by weight were below 10 microns, 8.6% below 5 microns and 2% below 1.5 microns. A well designed cyclone can be expected to give effective removal of particles down to about five microns, the above figures showed that this separation would give about 91% separation of the entrained material. Accordingly a cyclone shown in Figure 7.4 was designed to operate with an inlet velocity of approx. 50 ft./sec.

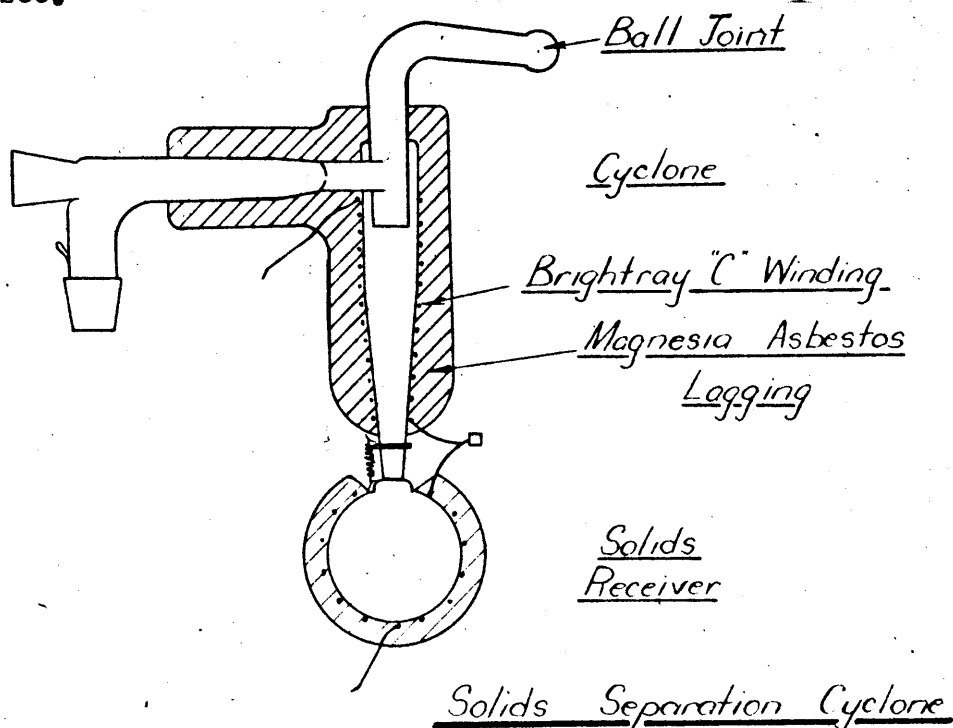


Figure 7.4

A test of the cyclone using coke as the entrained material showed that the largest particles in the exit gas were of the order of 5 microns, indicating that the cyclone reached design performance. The cyclone at all times operated satisfactorily.

As shown in Figure 7.4 the cyclone and solids receiver were heated electrically to prevent condensation of titanium tetrachloride and was connected to the condensation of system by means of glass ball and socket joint to allow flexibility on setting up the apparatus.

Condensation System

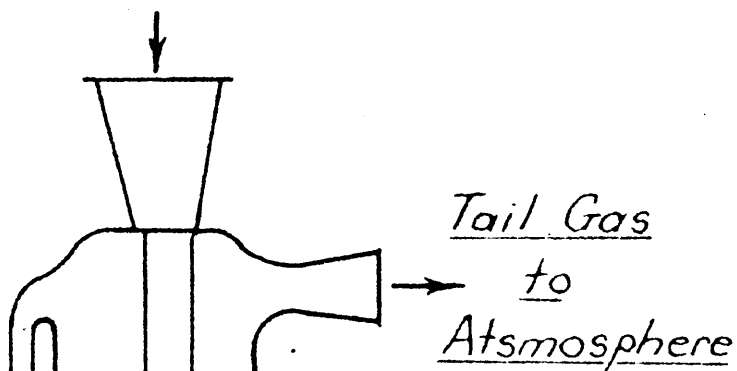
The condensation system used was simple and consisted of two condensers, a thirty inch Leibig condenser and a thirty inch Davies double wall condenser used in series. These condensers gave complete cooling of the gas and vapour mixture, as well as allowing variation in the condensation conditions.

Liquid Separation System

Figure 7.5 shows the first of several liquid separation systems tried and found to be unsatisfactory.

The gas passing to the condensation system consists of titanium tetrachloride vapour, carbon dioxide, carbon monoxide and chlorine. On cooling this gas liquid titanium tetrachloride is formed and the gas leaving the condenser is saturated with titanium tetrachloride vapour. The problem of separating the condensed liquid and the gas is complicated by a fog of titanium tetrachloride formed by the rapid cooling of the gas which has to be separated if accurate measurement of the rate of reaction was to be made. This fog also contained solid ferric chloride particles which presented difficulties due to their deposition as a sludge in sections of the separation apparatus which resulted in blockages. The operations required for the successful performance of the separation were therefore twofold; the disengaging of the liquid titanium tetrachloride from the gas stream and the separation of the titanium tetrachloride - ferric chloride fog.

Gas & Liquid
from Condenser



Liquid Separator
and
Measuring Burette

$TiCl_4$ to Receiver

Figure 7.5

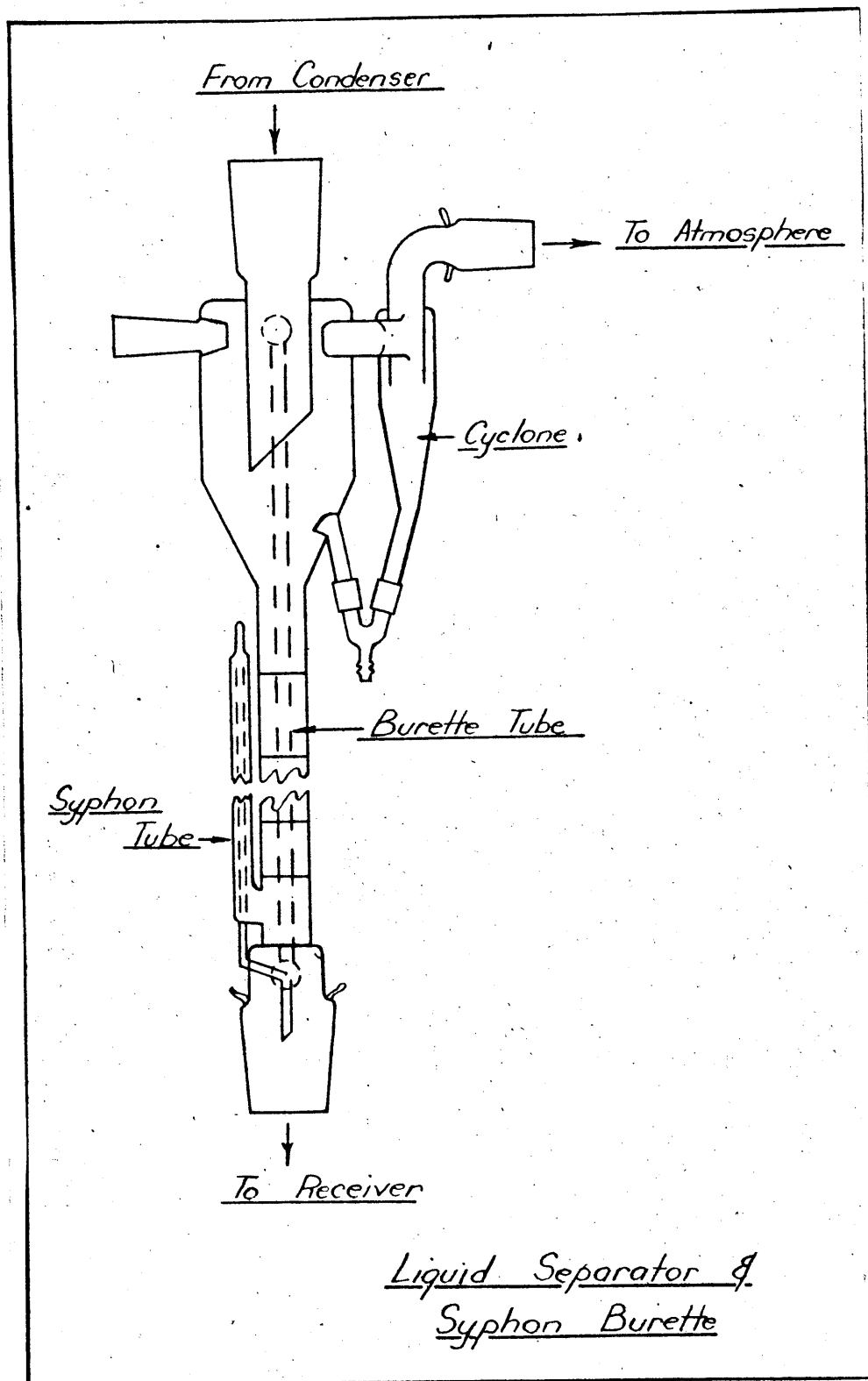


Figure 7.6

Figure 7.6 shows the first of the modifications designed to remove the fog. While this apparatus operated satisfactorily for the separation of the liquid and gas and gave some separation of the fog; the entrance of the cyclone was blocked by the formation of a plug of ferric chloride.

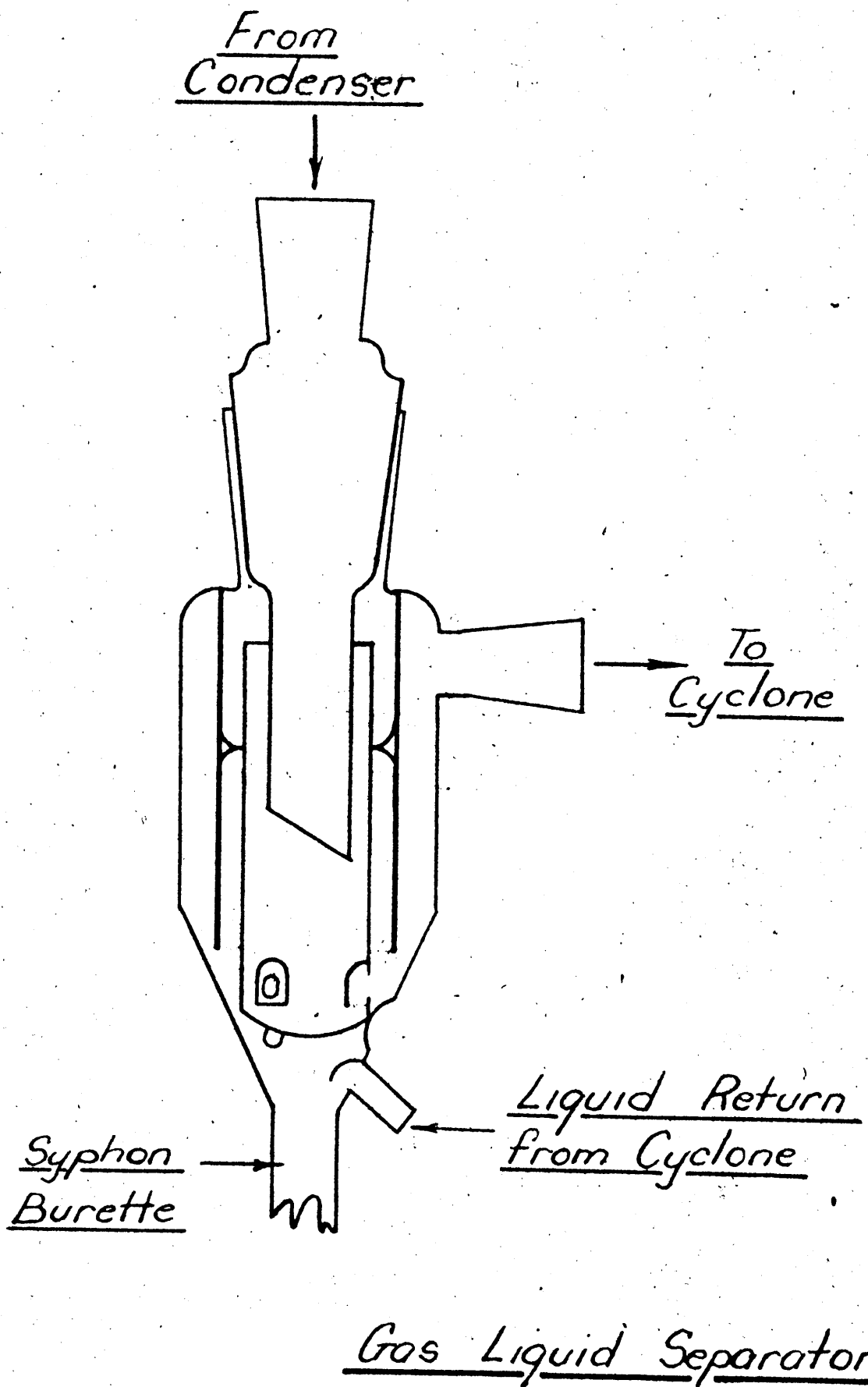


Fig. 7.7

A baffle system was introduced in the liquid separator as shown in Figure 7.7 in an effort to remove the ferric chloride, but this did not prevent the formation of blockages at the entrance to the cyclone. Placing a cyclone the same size as that used for the solids separation after the baffle section alleviated the blockages sufficiently to allow successful operation during the run.

Most of the ferric chloride collected in the first cyclone, which also removed some fog, allowing the second cyclone to operate successfully for the separation of the fog. Very little titanium tetrachloride collected in the traps placed after the small cyclone or in the gas line to the stack indicating fairly efficient removal of the fog.

Trouble again occurred with blockages of ferric chloride in the runs in which nitrogen was introduced with the chlorine feed and it was again necessary to redesign the separation system.

In the new system the gas was scrubbed with liquid titanium tetrachloride which removed both titanium tetrachloride and ferric chloride, and the equipment used for this operation is shown in Figure 7.8.

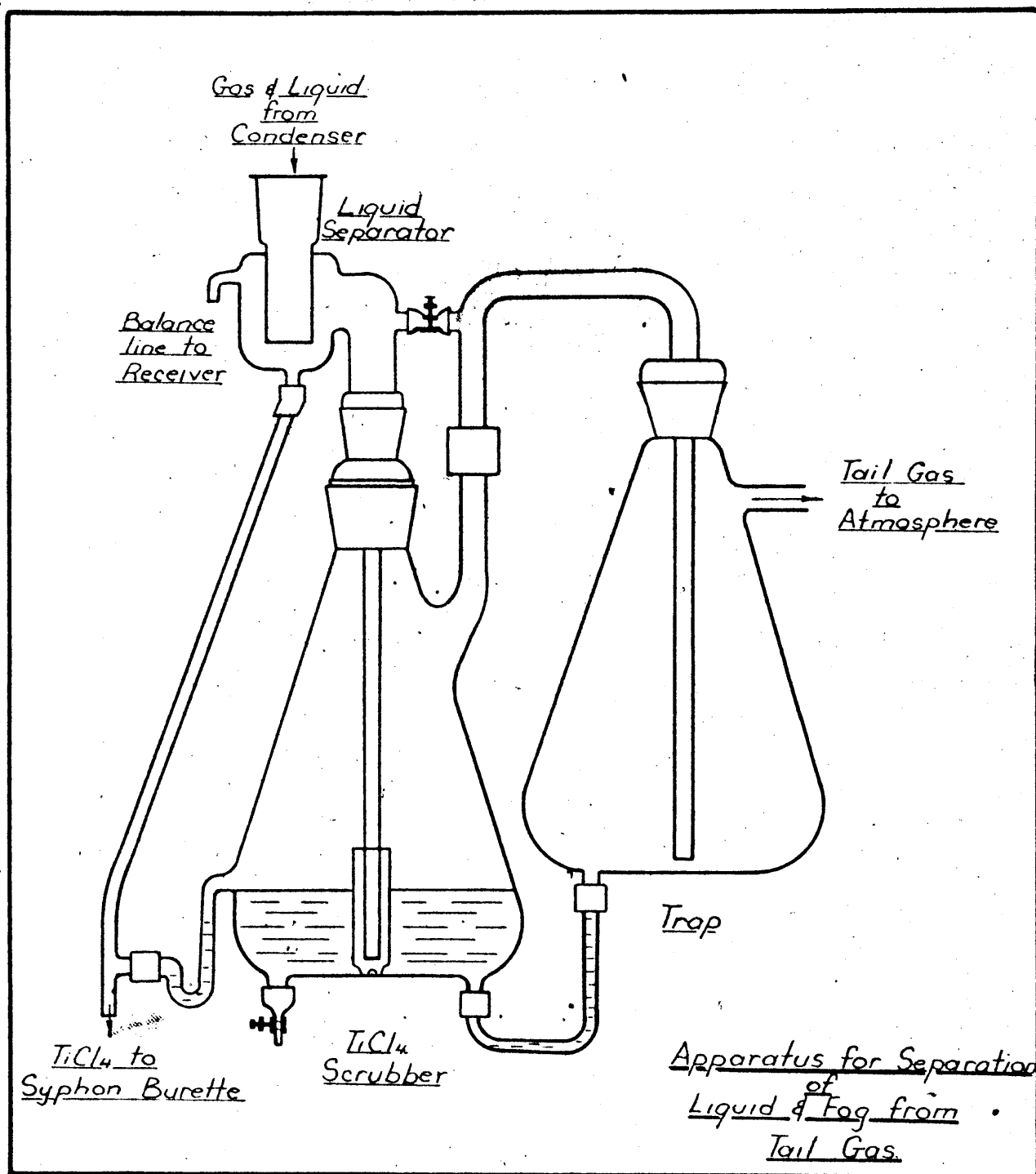


Figure 7.8

In this apparatus the scrubber and the U seal was first filled with titanium tetrachloride, and as the fog was removed the separated liquid flowed to the measuring burette. Satisfactory operation was obtained with this system.

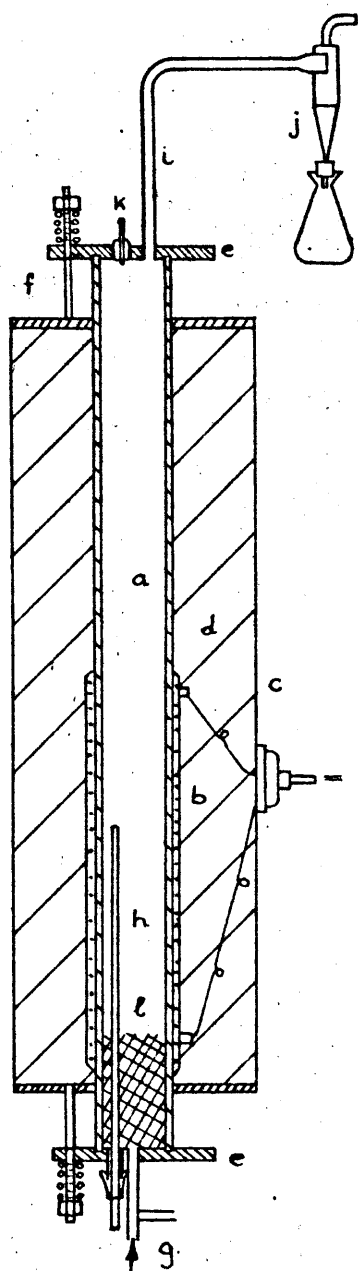
Measurement of the Rate of Reaction

The rate of reaction was determined by measuring the rate of condensation of titanium tetrachloride. The first of the systems used is shown in Figure 7.5. In this apparatus the liquid draining from the condenser was collected in the burette and the rate measured by timing the rise over a known volume. When the burette was full the liquid was drained into the receiver through the stop-cock.

This principle operated satisfactorily for the measurement of the rate, but failed due to inability to find an effective lubricant for the stop-cock.

Figure 7.6 shows the syphon burette used to give continuous operation. When the burette is full the liquid overflowed through the syphon and the cycle was repeated. A check on the accuracy of the system of various flow rates showed errors of not more than plus or minus one percent.

During the runs on variation of temperature it was found necessary to make the rate measurement automatic in order to allow one person to satisfactorily operate the apparatus and take gas samples. This was achieved by using two indentations in the burette as prisms which, as the tube filled with liquid, successively refracted a light beam away from indicating photocells. This apparatus is shown in Figure 7.9. When the burette is empty the current from the cells is balanced and the meter is in the central position. As the column of liquid rises past the bottom slit the light beam is refracted so that it does not pass to the photocell and the resultant out of balance current in the cell circuit caused the meter needle to swing against the stop. This caused a change of capacitance in the stop which was used to operate a capacity sensitive switch to cause a step to be shown on a recorder chart. As the liquid refracts the top light beam the balance in the cell circuit was restored,



- Key
- a. Silica Tube
 - b. Kanthal A winding
 - c. Lagging Sheath
 - d. Diatomaceous Earth
 - e. End Plates
 - f. Tie Rods
 - g. Co₂ inlet tube
 - h. Thermocouple Sheath
 - i. Delivery Tube
 - j. Cyclone

Fluid Bed
Carbon Monoxide
Furnace

Figure 7.10

The seals were made with Salamanderite and silicone grease. The temperature of the bed was controlled by a Cambridge on-off controller operating on a thermocouple placed in the sheath. The bottom four inches of the tube were filled with porcelain chips which acted as a gas distributor and served to remove the hot zone from the end plates.

In the production of carbon monoxide the reactor was charged with crushed "Norit" activated charcoal and brought up to the desired temperature under fluidization with nitrogen. Carbon dioxide was then admitted and the carbon monoxide formed passed through a dust filter to the titanium tetrachloride reactor.

Using a twenty four inch deep bed of carbon and a bed temperature of 1075°C it was found possible to obtain carbon monoxide containing only 0.6% of carbon dioxide at production rates of four litres per minute. At rates of six litres per minute the amount of carbon dioxide rose to 10%. Higher conversion rates could be obtained by increasing the temperature, a product containing only 0.4% carbon dioxide being obtained at rates of fourteen litres per minute and a temperature of 1250°C . It was however impracticable to run at this temperature due to crystalization and breakup of the silica tube.

Preparation of the Charge for Chlorination

The charge to the reactor unless otherwise stated consisted of a mixture of rutile and carbon in amounts to give a TiO_2 to C ratio of 3.33:1 by weight. Rutile beach sand used was supplied by National Minerals Pty.Ltd. and the carbon source was petroleum coke obtained from Glen Davis Oil Refinery. Petroleum coke was selected because of its very low ash content which simplified the materials balances and made possible the estimation of carbon in the residued by ignition.

The petroleum coke was ground in a Braund mill, size between 48 and 200 mesh by screening and elutriated with air to remove the fines. The coke was then roasted at 900°C in a bed fluidized with nitrogen to remove volatile materials. The proximate analysis of the coke after roasting was:

Volatile and Water	2.02%
Fixed Carbon	97.83%
Ash	0.15%

The rutile sand was received as a closely sized material falling in the size range of 60 to 100 mesh. This material was ground in a ball mill and air elutriated to remove fines. After grinding the rutile analysed 96.7% TiO_2 .

The charge to the reactor was prepared from these materials by mixing the required amounts in a revolving jar fitted with a set of lifting flights.

The use of air elutriation to remove the fines was decided on after initial runs had been carried out to reduce the loss of rutile and carbon from the bed due to solids carryover in the gas from the reactor. While this loss from an unelutriated charge was not great, the errors were in this way reduced to a minimum.

Operation of the Chlorination Apparatus

After the apparatus had been thoroughly dried out it was assembled and the reactor and knockout drum isolated from the remainder of the system by plugging the line to the cyclone. The mixed material was then charged to the reactor through the charging port at the top of the knockout drum, power was turned on to the heater and the temperature of the reactor raised. During the initial part of the heating period the voltage on the winding was controlled to 140V by means of the Variac. When the temperature had reached about 400°C the voltage was increased to 230V and nitrogen was introduced to the bed at a rate to give vigorous fluidization as indicated by the manometer across the bed. This served to promote heat transference, to maintain uniform temperatures through the bed and to sweep any water evolved from the charge out of the reactor. Nitrogen was selected to prevent burning of carbon while the charge was brought to temperature. During the heating period the knockout drum and

cyclone system was also brought up to operating temperature to prevent any condensation of water in these parts of the apparatus.

All moisture must be excluded from the apparatus during chlorination as it will react with titanium tetrachloride to form the hydroxide and oxychlorides which result in blockages in the gas lines.

When the bed has reached the reaction temperature the liquid separation system was filled with titanium tetrachloride and the charge port closed. Water was introduced to the condensers and the chlorine, and other gas flows where these were required, were set at the desired rates. After an interval of two or three minutes titanium tetrachloride began to condense and measurement of the condensation rate was commenced.

It was found that the temperature of the bed increased when the chlorination was commenced due to the exothermic nature of the reaction, but the correct temperature under nitrogen fluidization to give the desired reaction temperature could be judged from experience. This temperature was usually about 25°C lower than the final reaction temperature.

During the course of the reaction, (all chlorinations being carried out batchwise,) the temperature was controlled as described above, while the flow rates were controlled manually. Some indication of the course of the reaction could be obtained from the manometer across the bed, which as well as indicating the nature of the fluidization also indicated the weight of material in the bed.

Gas samples were taken periodically as described below, and the temperature and flow rate of the tail gas were measured.

When the run was complete, as shown by the negligible rate of condensation of the product and the low pressure drop across the bed, the chlorine was turned off and the reactor was allowed to cool. While the system was cooling it was purged with a slow stream of nitrogen to remove all titanium tetrachloride and chlorine. When the reactor was cool the residue of the charge was removed by pneumatically conveying it overhead through a tube introduced into the reactor through the charging port and the remainder of the system was sealed off at the entrance of the cyclone. The unchlorinated charge in the annular space between the base of the reactor and the reactor tube was removed by taking off the base section. After cleaning the base section of the reactor and remaking the joint to the base plate the reactor was again ready for use. Between runs the cyclone, condensation system and liquid separation system were kept sealed to prevent the entry of moisture.

After each run the residues from the reactor, and the annular space and the cyclone were weighed and analysed for carbon and rutile content, and the total weights of titanium tetrachloride collected and chlorine used were determined. From these values, the measured rates of reaction, and the analysis of the tail gas, materials balances were calculated and the rates of chlorine feed and titanium tetrachloride condensation checked.

CHAPTER VIII

Analytical Methods & their Development

Analysis for Titanium

The analysis of rutile was first attempted using a Jones reductor and potentiometric titration with Ceric Sulphate. This was found to be time consuming and reduction with zinc amalgam was tried as an alternative. Doubt was cast on the accuracy of this method when the reduction was followed potentiometrically, complete reduction not being obtained.

The following photometric method was then developed and gave a quick and accurate method for the analysis of rutile and titanium tetrachloride.

In this method the estimation was carried out using the yellow pertitanic acid complex formed between hydrogen peroxide and titanium. The colour of the test solution was compared photometrically with a standard containing a known amount of titanium. Comparisons were made in 5% sulphuric acid solution using a Cambridge "Uvispeck" spectrophotometer working with one centimeter cells and comparing at the peak of the titanium absorption band. (410 m μ)

Tests carried out on the interference of iron and chromium showed that iron as FeO would not interfere when present in concentrations up to 50% of the concentration of titanium dioxide and chromium showed no interference when present in amounts up to 5% of the amount of titanium dioxide in the sample.

Errors may also occur due to the formation of yellow complexes with hydrogen peroxide by the metals vanadium, molybdenum and cerium which absorb at the same band as the titanium complex. As, however, the absorption of the vanadium complex is only one quarter that of titanium at 410 m μ ., the errors

arising if vanadium is neglected is only one quarter those arising if the estimation is carried out by a redox method. In the estimation of titanium in ores containing less than 0.5% vanadium pentoxide, the final error would be less than 0.1%.

The effect of temperature on the light absorption of the complex was investigated and variation was found only above about 50°C. The complex was also found to be quite stable with time, no change taking place over several days.

The above method was checked against the conventional redox method of analysis of a number of samples of rutile as carried out by a Public Analyst and the results were found to be in good agreement. These results are given below.

<u>Sample</u>	<u>Photometric</u>	<u>Redox</u>
	% TiO ₂	% TiO ₂
1	97.2	97.0
2	91.0	90.7
3	97.5	97.3
4	91.8	92.1
Ti Metal	99.6% Ti	99.5% Ti (Gravimetric)

Analysis of the Tail Gasses

The tail gas consisted of a mixture of chlorine, titanium tetrachloride, carbon dioxide, carbon monoxide, carbonyl chloride and in some cases nitrogen. To obtain a complete materials balance on the system it was necessary to determine all components and devising a suitable system which would give satisfactory results quickly proved to be rather a difficult task.

Method 1: Figure 8.1 shows the first apparatus devised for the analysis of the tail gas.

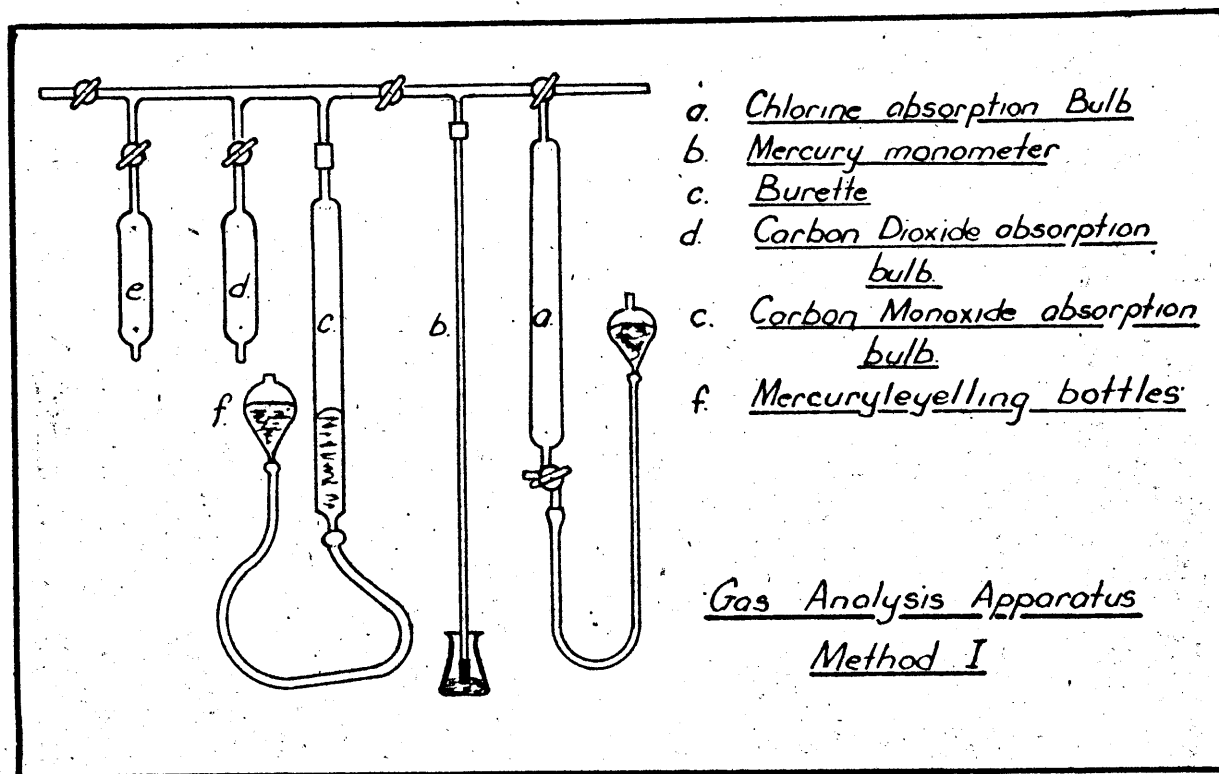


Figure 8.1

Chlorine was determined by introducing one millilitre of mercury into a burette containing the gas sample. Chlorine was absorbed to form the chlorides and the volume of chlorine removed was measured by measuring the decrease in pressure.

Carbon dioxide and carbon monoxide were determined on the gas from which chlorine had been removed by absorption in potassium hydroxide solution and acidic cuprous chloride respectively.

This system was unsatisfactory due to the great difficulty in removing the mercuric chloride from the absorption bulb.

Method 2: A sample of gas was collected in a winchester fitted with a dip tube and a dropping funnel. One hundred millilitres of 2N NaOH were introduced, shaken to absorb the gas and the contents washed out and made up to a standard volume.

Chlorine was then determined by adding potassium iodide and titrating with sodium thiosulphate. The unneutralised sodium hydroxide was determined by acid titration in the presence of barium chloride using phenolphthalein as the indicator, and the total chlorides was determined by titration with silver nitrate.

From these titrations and the volume of the sample bottle, the percentages of chlorine, carbon dioxide and titanium tetrachloride were calculated, assuming no carbonyl chloride in the tail gas. This assumption was made on the basis that at the temperature of reaction the equilibrium was such that carbonyl chloride would not be formed. Carbon monoxide was determined by difference.

This analysis was found to be unsatisfactory because of the determination of carbon monoxide by difference and some doubt as to the presence of carbonyl chloride in the gas samples taken.

Method 3: In this method chlorine was estimated by aspirating a known volume of gas through a solution of potassium iodide, chlorine being determined on the liberated iodine, and determining carbon dioxide and carbon monoxide on the aspirated gas by the orsat analysis.

When the materials balances on a number of runs were calculated the method was found to be insufficiently precise, as it appeared that the estimated values of carbon dioxide were low, probably due to the solution of the gas in

the potassium iodide solution.

Method 4: In this method the analysis was carried out on two sets of samples collected in evacuated bottles. Three samples were collected for the determination of chlorine, carbonyl chloride and titanium tetrachloride, and three for the determination of carbon dioxide, carbon monoxide and nitrogen. Figure 7.1 shows the system used for the collection of the samples.

For the analysis for chlorine, titanium tetrachloride and carbonyl chloride gas samples were collected in evacuated bottles as shown in Figure 8.2. The bottles were enclosed in a light tight bag to prevent the photocatalysed reaction,

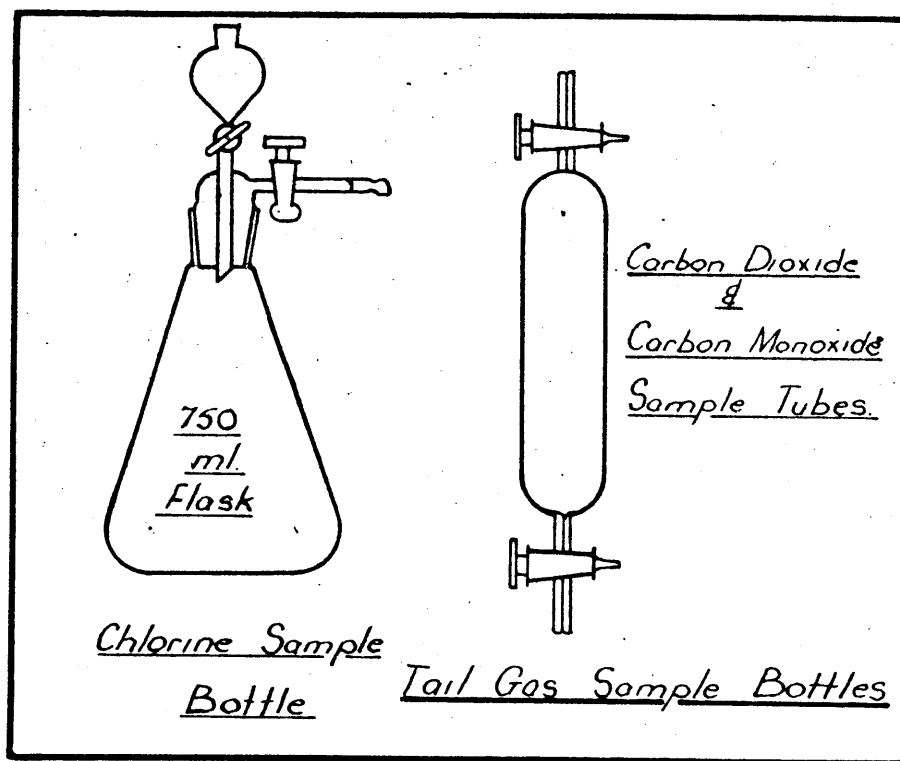


Figure 8.2



occurring in the collected sample. The pressure in the bottle prior to sampling was measured by a manometer in the line between bottle and the vacuum pump, and knowing the volume of the bottle, the volume of the collected sample

was determined.

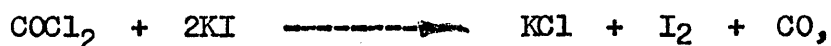
Fifty millilitres of 2N NaOH were introduced into the bottle through the funnel and the mixture allowed to stand while the gasses were absorbed to form NaOCl, NaCl, Na₂CO₃ and Ti (OH)₄. The solution was then filtered the residue was washed with a 1% solution of sodium nitrate and the filtrate made up to 250 ml. in a standard flask. The titanium hydroxide on the filter paper was washed with ammonium nitrate solution, ignited and weighed as TiO₂, from which weight the amount of TiCl₄ in the sample was calculated.

An aliquot of the filtrate was treated with potassium iodide, acidified with hydrochloric acid and the liberated iodine titrated with sodium thiosulphate which result gave the free chlorine in the sample.

A second aliquot was treated with 3% hydrogen peroxide to reduce the hypochlorite to the chloride. Nitric acid was added, the solution boiled to destroy all the hydrogen peroxide and neutralised using solid calcium carbonate. The total chlorides were then estimated by titrating with silver nitrate using potassium chromate as the indicator. Knowing the amounts of free chlorine and titanium tetrachloride in the sample the amount of carbonyl chloride was calculated.

At the completion of the runs on variation of rate with temperature, the amount of titanium tetrachloride in the tail gas as determined by the above method was checked against values determined from the temperature - vapour pressure relation ship and found to be slightly low. This was in the expected direction of any errors in the determination, and on these higher values for titanium tetrachloride in the tail gas the carbonyl chloride figures were reduced

For the analysis of the tail gas for carbon dioxide, carbon monoxide and nitrogen, the chlorine, titanium tetrachloride and carbonyl chloride were removed from the sample by passing the gas stream through a tube containing wet potassium iodide crystals and then through a solution of potassium iodide. A continuous slow stream of gas was drawn through the system to keep the potassium iodide solution in carbon dioxide equilibrium with the gas stream and so eliminate errors due to the solution of this component. The great bulk of the chlorine and titanium tetrachloride were removed in the tube packed with wet potassium iodide crystals, the solution serving mainly to remove the traces of chlorine, iodine or titanium tetrachloride carried forward from the absorption tube. Carbonyl chloride was also removed from the gas by the reaction



which, in decomposing the COCl_2 formed by the photocatalytic reaction in the tail gas after the gas leaves the reactor, gave the correct concentration of carbon monoxide for reactor conditions.

Samples so collected were analysed for carbon dioxide, oxygen, carbon monoxide and nitrogen using a modified Fisher apparatus. In this analysis small amounts of carbon monoxide were determined by absorption in acidic cuprous chloride solution, while larger concentrations were determined by explosion with oxygen and absorption of the carbon dioxide so formed in potassium hydroxide. Nitrogen was determined by difference after allowing for the small amounts of air present in the samples due to incomplete evacuation of the sample bottles and leaks in the evacuated systems. This air was determined as oxygen.

This method of analysis proved to be satisfactory, and save reliable materials balances.

CHAPTER IX

Experiments to Check the Operation of the Apparatus and the Feasibility of the Fluid Bed Chlorination

Preliminary experiments were made to test the feasibility of carrying out the chlorination of rutile in the presence of carbon in a fluid bed, to test the apparatus as shown in Figure 9.1 under operating conditions, and to check the analytical methods to be used.

It was hoped as well to obtain some idea of the reaction conditions under which further experiments should be carried out.

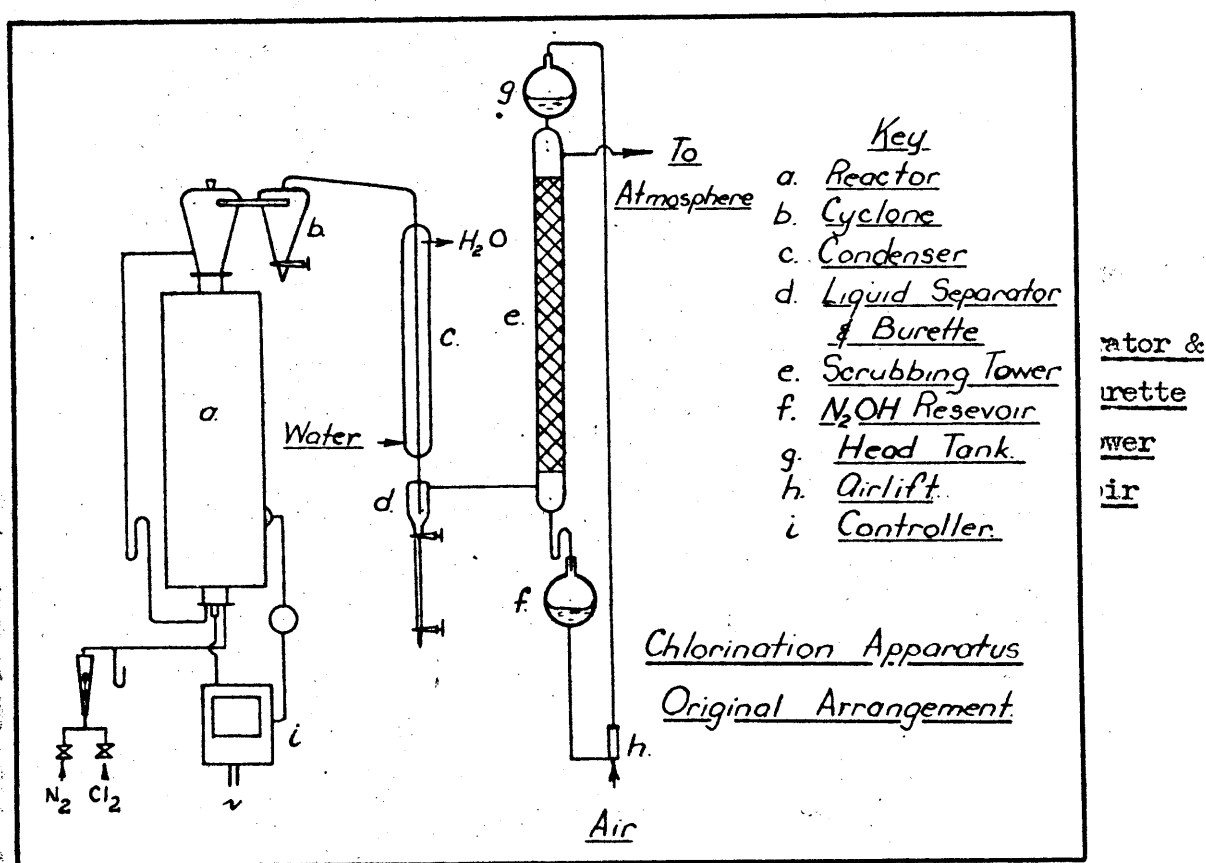


Figure 9.1

Run 1: 530 grams of ground rutile and 220 grams of ground wood charcoal were charged to the reactor and the temperature raised under nitrogen fluidization. When the temperature had reached approximately 700°C chlorine was admitted and white fumes of titanium tetrachloride observed in the liquid receiver.

It was found necessary to stop chlorination after a few minutes, a blockage forming in the receiver due to the reaction of the tetrachloride with moisture. When the apparatus was cooled it was also found that liquid titanium tetrachloride had collected in the unheated cyclone. During the chlorination large amounts of charcoal had carried from the bed into the cyclone and condensation system. A second blockage occurring during purging resulted in bursting of the cyclone.

Run 2: The apparatus was setup to include a lute in the gas line to the reactor and a resistance heater of the knockout drum and cyclone. Metallurgical coke was used in place of charcoal, as the latter gave a large percentage of fines on grinding. Chlorination was commenced at 700°C and titanium tetrachloride began to condense after about ten minutes. Approximately 200 grms of liquid was collected in eighty minutes.

Runs 3 & 4: These were carried out to further test the apparatus and it was found that the tail gas scrubber was unsatisfactory due to recurrent blockages. It was decided to vent the tail gas to atmosphere.

Run 5: Chlorine was turned on at 450°C and at 500°C white fumes of titanium tetrachloride were observed. At 750°C the reaction rate was found to be much faster than had been anticipated, requiring a larger chlorine flow meter, and the rate measuring set up used was found to be useless due to inability to lubricate the stop-cock.

Run 6: This was carried out using the syphon burette (Figure 7.6) which was found to be inoperable as it did not syphon due to a large bore syphon tube. A leak also occurred at the base of the reactor.

Run 7: The apparatus was set up using Salamanderite and sodium silicate as the jointing material. The syphon tube had been modified and found to be satisfactory. During the run blockages occurred, the base of the reactor leaked and the heating element of the reactor burned out.

Run 8: The reactor was set up with a redesigned base as shown in Figure 7.3, although at this stage in the development of the apparatus the heating element was still placed on the reactor tube. After the joint at the top of the reactor was twice remade to stop a leak chlorination was carried out at 750°C and a chloride feed rate of 9.4 gms/min. and the apparatus performed satisfactorily.

Run 9: This was carried out at 850°C and a chlorine rate of 13 gm/min. on a charge containing 700 grams of rutile and 300 grams of coke. A chlorine conversion of 80% was achieved.

After a run of fifty five minutes a blockage occurred at the top of the condenser due to solids carried through the cyclone.

Size analysis of the solids by means of settling and measurement with a microscope gave the following values.

Table 9.1Particle Size of Entrained Solids

Particle Diam. Microns	Cumulative Weight %
0.5	0.7
2.5	4.4
5.5	8.6
10.0	12.4
35.0	18.5
63.0	44.0
92.0	57.3
106.0	100.0

From these it was decided that a redesigned cyclone could be used to remove between 88 and 91% of the entrained solids.

Analysis of the residues in the reactor was carried out for carbon and rutile using a variety of methods to determine carbon, of which the semi-micro method for carbon in organic compounds was found to give the most satisfactory results. The Jones reductor was used for the determination of rutile, but as discussed above was not considered to be reliable. The materials balances calculated on these analysis were not satisfactory.

Run 10: The apparatus was set up with the modified cyclone and chlorination was carried out at a chlorine rate of 33 gm/min., at 910°C. In a run lasting twenty five minutes 675 gms of titanium tetrachloride was formed. The new cyclone and apparatus gave generally satisfactory operation at this higher feed rate, but trouble with the carryover of liquid in the form of fog resulting in liquid collecting in the tail gas line was more pronounced than in previous runs. A tail gas cyclone was made in an effort to prevent this.

In this run analysis of the tail gas was attempted by Method I but was found to be unsatisfactory. As a result of the difficulty encountered in the analysis of the chlorination residues, which were largely due to the presence of the ash from the coke, it was decided to use calcined Glen Davis petroleum coke which had a negligible ash content.

Run 11: was started to test the modifications made to the separation system after run ten but was discontinued when a chlorine leak developed at the bottom of the reactor. This was found to be due to a crack in the reactor tube, thought to be due to the direct heating of the silica tube. Accordingly the furnace was redesigned as shown in Figure 7.3 using a radiant heating furnace.

Run 12: was carried out to check the operation of the new apparatus, and apart from the control thermocouple which was relocated in the annular space between the heater and the furnace and the tail gas cyclone which developed a blockage, the equipment was satisfactory.

Run 13: This run was carried out to further check the apparatus and the chemical analysis required.

Chlorination was carried out on a charge containing 760 gms. of rutile and 240 gms. of coke at a chlorine rate of 29 gms/min., and a bed temperature of 970°C. For a run of 40 minutes 1453 gms. of titanium tetrachloride were formed analysing 99.5% of TiCl_4 and 0.052% FeCl_3 . The residue in the reactor weighed 125 gms. containing 52.5% TiO_2 while the cyclone residue was 26 gms. containing 35% TiO_2 . From these figures 84.9% of the charge was chlorinated and an overall chlorine efficiency of 85% was obtained.

Analysis of the tail gas by Method II gave Cl_2 :0.0%, CO_2 :22.6% and CO :76.8%. From the data available in the literature these values seemed satisfactory.

Towards the end of the run a blockage began to develop in the inlet to the tail gas cyclone.

Runs 14 & 15: were carried out to further check the operation of the apparatus and the analysis of the tail gas. It was found that all the apparatus except the tail gas cyclone was satisfactory; this operated effectively ^{at} the start of each run, removing most of the fog and giving figures for titanium tetrachloride in the gas in good agreement with those determined from the temperature vapour pressure data for a gas saturated at the condenser temperature, but as the run progressed a build up of ferric chloride occurred at the entrance of the tail gas cyclone resulting in bypassing of gas through the liquid seal and carryover of liquid titanium tetrachloride. Poking out this blockage during the run proved ineffective and further modifications were necessary. These were made as described under the next series of experiments.

Analysis of the tail gas carried out by Method II gave the following results:

Table 9.2Tail Gas Analysis

Run	Sample	Cl ₂ %	CO ₂ %	CO %	TiCl ₄ %
14	1	0.6	32.2	64.7	2.4
	2	14.0	36.7	46.9	2.4
	3	88.7	4.8	4.2	2.2
15	1	1.2	29.4	67.3	2.1
	2	3.9	47.7	45.2	2.2

These values seemed satisfactory although they could not be checked by materials balances due to the absence of measurements of titanium tetrachloride rate over the ends of the runs.

Discussion of the Results of Runs 1 to 15

These experiments demonstrated the feasibility of carrying out the chlorination of rutile in the presence of carbon in a fluid bed. Observations showed the reaction to commence at about 500°C, the rate increasing with temperature to 950°C which was the highest temperature reached. It was shown that high chlorine conversions could be obtained at chlorine velocities far in excess of the minimum fluidization velocity. Analysis of the tail gas from the reactor shows that the reaction takes place to form both carbon monoxide and carbon dioxide.

The apparatus as originally designed was shown during these experiments to be unsatisfactory in many respects. The reactor needed modification to

allow effective sealing of the bottom joint and was redesigned as discussed. The method of heating the reactor was altered to reduce the chance of cracking the silica tube and to allow easier dismantling of the reactor.

It was also found necessary to use a more efficient cyclone, to increase the capacity of the chlorine meter and to use a lute in the feed line to protect the apparatus in the case of blockages.

Accurate measurement of the titanium tetrachloride rate was found to be difficult due to fog formation in the condenser, which fog had to be removed. This proved difficult due to the presence of ferric chloride particles in the fog which clogged the separation cyclone, which, until these blockages occurred operated effectively. Modification of the rate measuring burette was also required.

After these alterations had been carried out the apparatus was considered sufficiently reliable for successful operation.

After runs with wood charcoal, metallurgical coke and petroleum coke the latter was found^{to}/fulfill all requirements giving simple materials balances and analysis, complete analysis of the residues for titanium being unnecessary.

The analysis of the tail gas was attempted and after the first method used was rejected the second was at the time thought to be satisfactory.

From the results of these runs it was concluded that the apparatus and analytical methods were sufficiently reliable to proceed to experiments to determine the optimum conditions for chlorination.

CHAPTER X

The Effect of Variation of Bed Depth and Chlorine Feed Rate on Reactor Operation

The effects of change in bed depth and chlorine rate was determined in one series of experiments by runs at different chlorine rates with temperature and charge held constant, measuring the rate of reaction and weight of material in the bed as the run proceeds. Correlation of the reaction rate with the weight of material in the bed for each run showed the effect of variation of the rate with bed depth, while the correlation of the separate runs showed the effects of change in the chlorine rate.

In these experiments the rate of reaction was measured by the rate of condensation of titanium tetrachloride as described, and the weight of material in the bed at any time by the pressure drop over the bed. Four gas samples were taken in each run to give an even distribution over the run. Analysis of the residues of the chlorination then allowed an overall materials balance on TiO_2 to be calculated for the run, and for chlorine at the time at which the gas samples were taken. During these runs the temperature was held at 950°C , and all runs were carried out on material prepared in bulk before the commencement of the series. In this way variations due to the charge were eliminated.

The supply of charge for the reactor for these experiments, which were designated Series Ib, was prepared as described in chapter five, and carbon and rutile were used in the ratio of one mole of titanium dioxide to two moles of carbon, that is the stiochiometric amount for the formation of carbon monoxide as the only reduction product. The materials used in the preparation of the charge had the sieve analysis shown in Table 10.1. These analysis

gave an average particle diameter of 0.00566 ins. and 0.0057 ins. for rutile and carbon respectively. The rutile prepared for the charge analysis 96.7% TiO_2 and the carbon analysed 2.02% volatiles and water, 97.8% fixed carbon and 0.15% ash. The prepared charge analysed 76.8% rutile.

Table 10.1

Sieve Analysis of Material used in Experiments Series Ib

Tyler Mesh	Rutile	Carbon
	% by weight	
* 65	0.0	8.0
100	44.5	50.0
115	72.0	70.0
150	84.3	89.1
200	93.0	93.5
- 200	100.0	100.0

The apparatus as finally developed in Runs 15 Series Ia was used in runs 1 to 4 of this series and further modifications were then made as described below. Analysis of the tail gas was carried out by Method 2 in Runs 1 & 2. In run 2 the gas samples were taken in a conical flask without provision to exclude light and chlorine and carbon monoxide in the sample reacted to form carbonyl chloride. It was decided that this method was unsatisfactory and succeeding analysis were carried out by Method 3.

Experimental Results

The results of experimental chlorinations runs 1 to 7 are shown in Tables 10.2 to 10.8.

During the first two runs the chlorine rate was found to be unsteady as the gas delivery rate from the cylinder was low. This was corrected by heating

Table 10.3Charge 750 gm. Temperature 950 - 975°CChlorine Rate 32.5Run 2

Time Run Min.	P.D. cm. CCl ₄	TiCl ₄ Rate gm./min.		TiO ₂ Removal Rate gm/min.	Weight TiO ₂ in Bed gm	Sample
		Measured	Total			
1		29.7				
4		37.8	39.0	16.4	443.5	
6	17.5	36.8	38.0	16.0	411.3	* 1
7		36.3	37.5	15.8	395.0	
8	16.2	36.5	37.7	15.9	378.8	
10.5	14.5	36.8	38.0	16.0	330.4	* 2
12		37.6	38.8	16.3	306.2	
13	13.3	36.5	37.7	15.9	290.2	
16	11.4	29.5	36.3	15.3	243.6	
18	10.7	33.1	44.3	14.5	214.6	
19		31.8	33.0	13.5	200.6	* 3
20	Blockage	occurred	&	Shut Down	for	1 minute
21	7.0	29.0	30.2	12.7	173.4	
22	6.6	26.2	27.5	11.6	149.2	
25	6.2	26.2				* 4

Gas Samples Taken

These samples were not analysed due to the reaction of the chlorine and carbon monoxide in the samples to form carbonyl chloride.

Residues

Reactor 247 gm.
Cyclone 4 gm.

Wt. TiCl₄ collected 880 gm.
Calc'd Chlorine Rate 32.8 gm/min.

Table 10.4

Charge 750 gm. Temperature 970°C Chlorine Rate 40 gm/min.

Run 3

Time Run min.	P.D. cm. CCl ₄	TiCl ₄ Rate gm./min.		TiO ₂ Remov. Rate gm/min.	Weight TiO ₂ in bed gm.	
		Measured	Total			
2		36.7	% Cl ₂	% CO ₂	% CO ₂	
4		39.6				
6		45.5	12.8	27.6	59.6	
7	17	40.6				
9	16	40.6				
13	13	35.8	21.4	30.4	48.2	
15	12	37.0				
17	12	37.8	21.4	31.0	47.6	
Reactor Residue 268 gm. 69.0% TiO ₂ Cyclone Residue 9.5 gm. Annulus Residue 81.5 gm.						

Table 10.5

Charge 750 gm. Temperature 960 gm. Chlorine Rate 42 gm/min.

Run 4

Time Run min.	P.D. cm. CCl ₄	TiCl ₄ Rate gm./min.		TiO ₂ Remov. Rate gm/min.	Weight TiO ₂ in bed gm.	Sample
		Measured	Total			
5	18.0	43.2	45.0	18.9	411	
6	17.4	42.1	43.9	18.5	393	
9	16.0	40.5	42.3	17.8	338	1
10	15.4	40.4	42.1	17.7	320	
11	14.6	39.8	41.6	17.5	303	
12	14.0	38.8	40.6	17.1	285	
14	13.2	38.8	40.5	17.0	251	
15	12.8	38.0				
Run continued for further ten minutes, but no readings taken due to blockages in the tail gas cyclone.						
1. % Cl ₂ 21.2 % CO ₂ 34.0% CO 44.8				Residues	Reactor 131gm %TiO ₂	
					Annulus 64gm %TiO ₂	
						76.8%
TiCl ₄ Collected 945 gm.					Cyclone 26gm TiO ₂	
						30.9%

Table 10.6

Charge 750 gm. Temperature 950°C Chlorine Rate 44.7 gm./min.

Run 5

Time Run min.	P.D. Cm. CCl ₄	TiCl ₄ Rate gm./min.		TiO ₂ Removal Rate gm./min.	Weight TiO ₂ in bed gm.	Sample
		Measured	Total			
4	16.5	40.7	42.8	18.0	381	1
7		43.0	45.1	19.0	323	
8	13.9	41.5	43.6	18.3	304	
9	13.6	42.0	44.1	18.5	286	
10	12.4	40.4	42.5	17.9	268	
11	11.9	39.7	41.8	17.6	250	
12	11.4	39.4	41.5	17.5	233	
14	10.4	32.4	34.5	14.5	199	2
16	9.3	34.0	36.1	15.2	166	
17	8.8	33.6	35.7	15.0	150	
19	7.9	32.0	34.1	14.4	123	
20	7.4	29.1	31.2	13.1	109	3
23	6.3	20.0	22.1	9.3	76	
25	5.6	14.1	16.2	6.8	63	
29	5.0	8.4	10.5	4.4	43	
<u>Gas Analysis</u>				<u>Residues</u>		
<u>Sample</u>	<u>%Cl₂</u>	<u>%CO₂</u>	<u>%CO</u>	Reactor 82 gm. 46.2% TiO ₂		
1	24.7	30.9	44.4	Annulus 62 gm. 76.8% TiO ₂		
2	32.1	26.5	41.4	Cyclone 26 gm. 5.6% TiO ₂		
				Wt. of TiCl ₄ Collected 968 gm.		

Table 10.7Charge 750 gm. Temperature 950°C Chlorine Rate 28 gm./min.Run 6

Time Run min.	P.D. Cm. CCl ₄	TiCl ₄ Rate gm./min.		TiO ₂ Removal Rate gm./min.	Weight TiO ₂ in bed gm.	Sample
		Measured	Total			
3	18.5	31.7	32.9	13.9	467	1
7	15.7	31.6	32.8	13.5	411	
10	13.6	32.2	33.4	14.1	370	
11	13.1	29.2	30.4	12.8	356	
13	12.7	29.5	30.7	13.0	317	
14	12.3	29.8	31.0	13.1	304	
15.5	11.7	30.8	32.0	13.5	284	
17	10.7	31.9	33.1	13.9	264	2
19	9.3	29.8	31.0	13.1	237	
22	8.4	27.3	28.5	12.0	198	
23	7.7	27.2	28.4	12.0	187	
24	7.5	26.4	27.6	11.6	177	
25.5	6.6	24.8	26.0	11.0	160	
27	6.1	24.1	25.4	10.7	144	
29	5.7	20.8	22.0	9.3	124	3
30.5	5.2	18.7	19.9	8.4	111	
32.5	4.7	14.7	15.9	6.7	95	
36.5	off					

<u>Gas Analysis</u>				<u>Residues</u>	
<u>Samples</u>	<u>%Cl₂</u>	<u>%CO₂</u>	<u>%CO</u>	Reactor	127 gm. 41.5% TiO ₂
1	9.7	29.4	60.7	Annulus	63 gm. 76.8% TiO ₂
2	12.3	31.2	56.5	Cyclone	3 gm.
3	24.8	26.2	49.0	TiCl ₄ Produced 977 gm.	

Calculated Chlorine Rate 29.0 gm./min.
--

Table 10.8

Charge 1100 gm. Temperature 950°C Chlorine Rate 42 gm/min.

Run 7

Time Run min.	P.D. Cm.CCl ₄	TiCl ₄ Rate gm/min.		TiO ₂ Remov. Rate gm/min.	Weight TiO ₂ in Bed gm.	Sample
		Measured	Total			
1	28	47.5	49.3	20.8	681	1
5	24	48.4	50.2	21.0	593	
7	23	47.5	49.3	20.8	551	
9	21	47.5	49.3	20.8	509	2
10.5	20.4	47.5	49.3	20.8	478	
11.5		48.4	50.2	21.2	457	
12	19	48.4	50.2	21.2	457	
12	19	48.4	50.2	21.2	446	
14	18	46.0	47.8	20.2	426	
15	17	46.0	47.8	20.2	406	
15.5		45.0	46.8	19.7	396	
16.5	16	44.5	46.3	19.5	377	
17.5	15.7	43.0	44.8	18.9	357	3
20.5	14	39.5	41.3	17.3	303	
21.5		39.9	41.7	17.6	285	
22.5	13.0	38.5	40.3	17.0	268	
23.5	12.3	37.5	39.3	16.6	251	
24.5	11.8	37.5	39.3	16.6	235	
25.5		36.8	38.6	16.3	219	
26.5	10.8	33.2	35.0	14.8	203	
27	10.2	33.0	34.8	14.7	182	
29	9.5	32.7	34.5	14.5	168	
30	9.0	29.1	30.9	13.0	155	
32		30.3	32.1	13.5	128	
36	6.5	23.1	24.9	10.5	83.5	
38	5.9	15.2	17.0	7.3	66	
41	5.5	10.8	12.6	5.3	45.5	
41.5	off				43	
<u>Gas Analysis</u>				<u>Residues</u>		
<u>Sample</u>	<u>%Cl₂</u>	<u>%CO₂</u>	<u>%CO</u>	Reactor	112 gm.	39.6% TiO ₂
1	9.5	40.4	50.2	Cyclone	23 gm.	36.2% TiO ₂
2	13.3	34.8	50.2	Annulus	64 gm.	76.8% TiO ₂
3	19.6	32.3	48.1	Wt. of TiCl ₄ collected 1603 gm.		
4	31.4	36.2	42.4			

Although the control of the temperature during the runs was not as precise as could be desired; this, however, was mainly due to lack of close attention to this variable. In run 1 the temperature fell to 875°C at the end of the run, while in run 4 the temperature varied as much as plus or minus twenty degrees from the control temperature.

The operation of the liquid entrainment separation system was not satisfactory due to the formation of ferric chloride blockages in the inlet to the tail gas cyclone. This resulted in interference with the measured rate and entrainment of liquid titanium tetrachloride in the tail gas. The blockages caused a shut down of one minute during run 2 while it was cleared and inability to make any rate measurement during the last ten minutes of run 4. Prior to the start of run 5 a spare cyclone made for solids separation was placed between the liquid separator and the tail gas cyclone. This removed the bulk of the ferric chloride and allowed the runs to be carried out without complete blockage of the line to the tail gas cyclone. In run 7 some irregularity in the rate measurement occurred due to a partial blockage in the tail gas cyclone.

Table 10.9 gives the results of materials balances calculated on runs 1, 4, 5, 6 and 7.

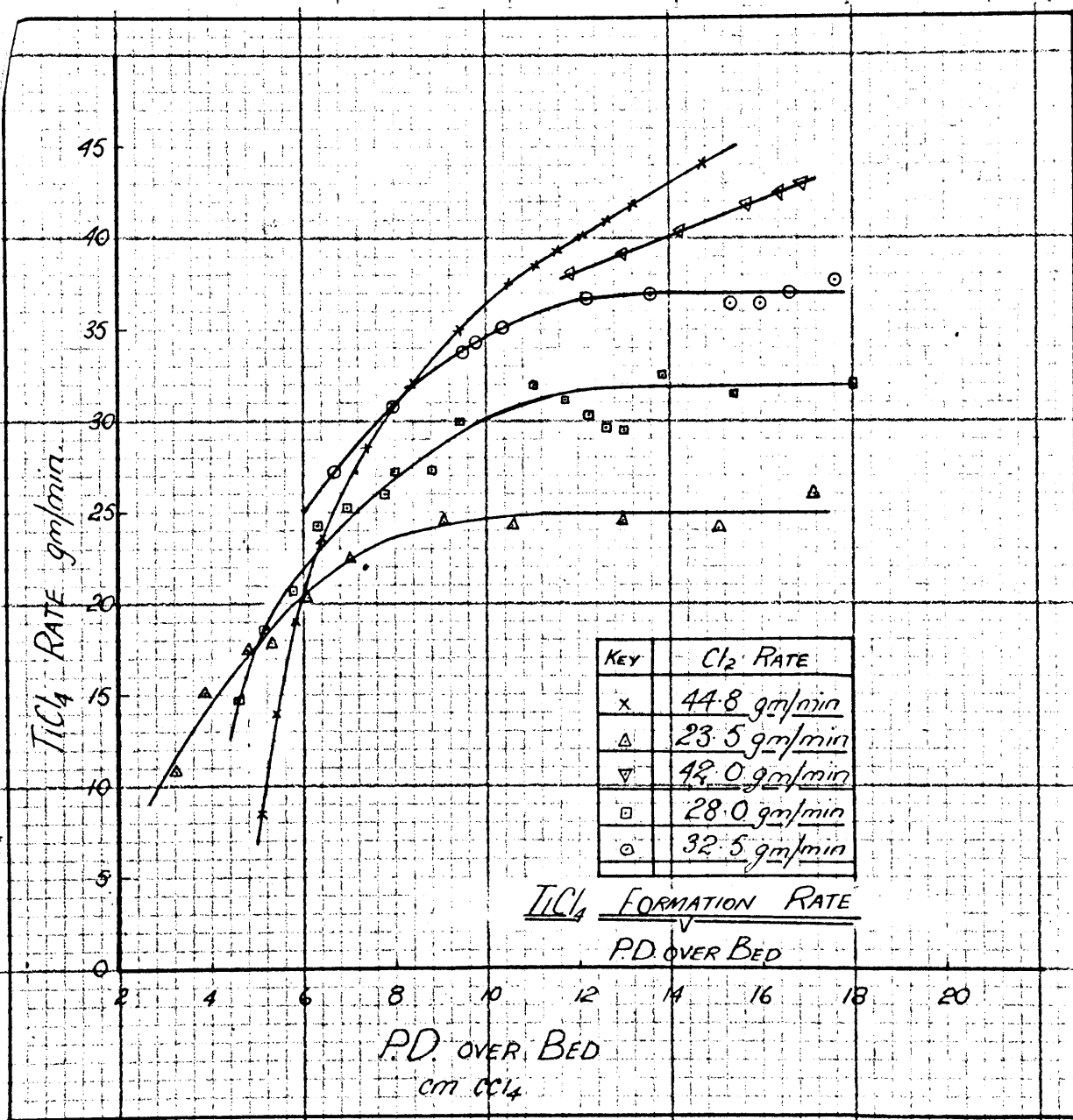


Figure 10.1

Table 10.9

Run	Materials Balances % Accounted for		
	Rutile	Carbon	Chlorine
1	97		84
4	98		87
5	92	110	95.5
			82.5
6	95	112	96
			92
			65
7	96	97	95
			97
			95

These balances confirm the accuracy of the rate measurement on titanium tetrachloride and the analysis of the residues from the experiments and show that the analysis of the tail gas for carbon and chloride was not completely reliable. The analysis for chlorine gave accurate results for low concentrations but low results where high concentrations were present. The high results for the carbon balances indicated low figures for carbon dioxide in the tail gas but these could also occur from inaccuracies in the calculation of the tail gas rates; this would be avoided by direct measurement of the tail gas rate.

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Correlation of the Reaction Rate with the Weight of
Titanium Dioxide in the Bed

The rate of reaction, as measured by the rate of production of titanium tetrachloride was initially correlated with the weight of material in the bed by plotting rate versus the pressure drop over the bed which, for a fluid bed, is equal to the bed weight. This plot indicated a general trend, as shown in Figure 10.1, but the method was not sufficiently accurate, for the weight of material at the end of the run, as calculated from pressure drop measurements, did not agree with the weight of the residues.

Figure 10.2 shows the production rate plotted against the weight of titanium dioxide in the bed. This weight was calculated from the measured rate of condensation of the tetrachloride and the weight of rutile remaining in the reactor at the end of the run. The method of calculating the weight of material in the reactor at any time and the materials balances on the system together with a sample calculation of run 7 are given in Appendix II.

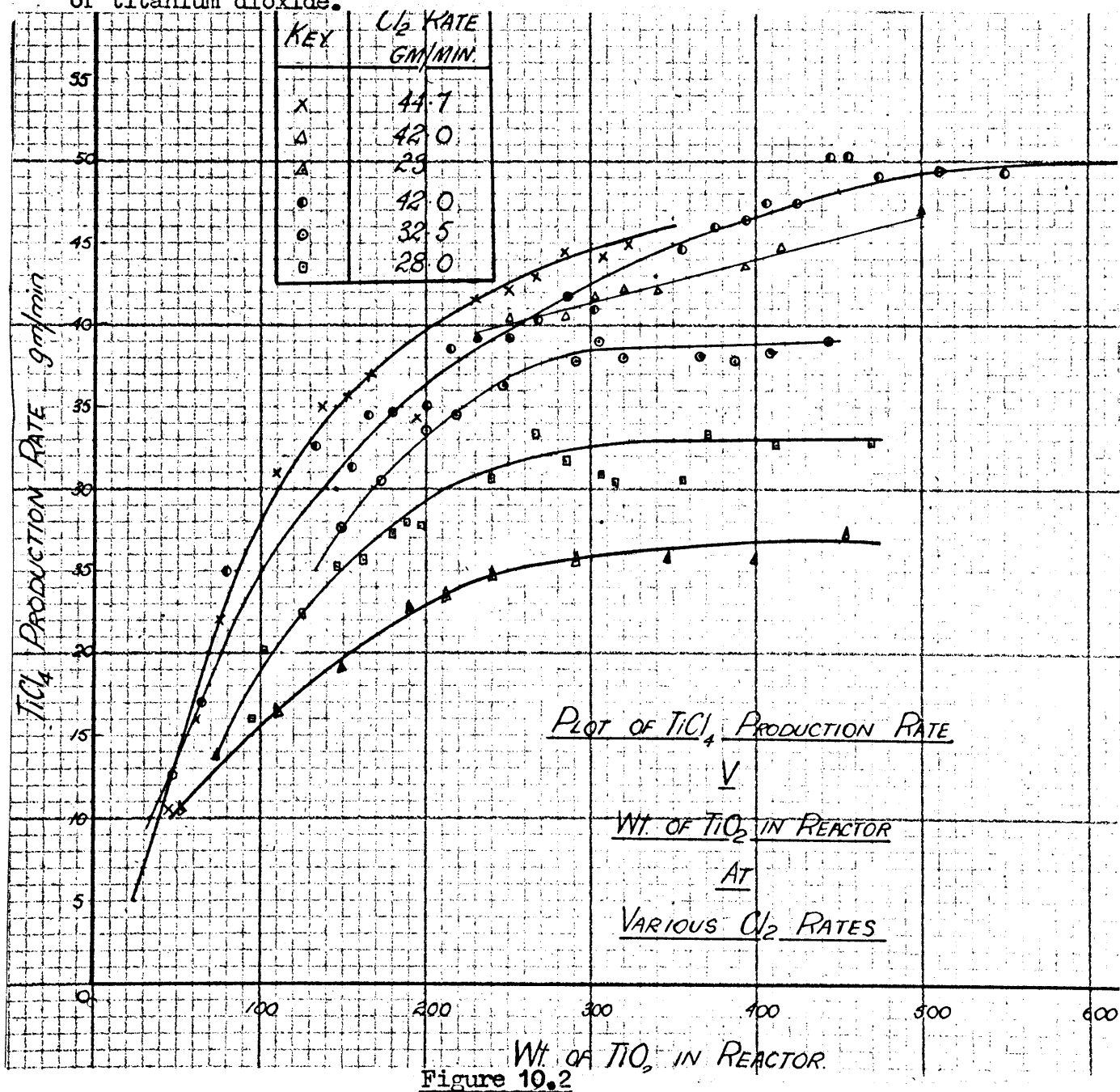
These curves show that as the weight of material in the bed increases the rate of formation first increases rapidly and then tails off as the amount of free chlorine in the gas in contact with titanium dioxide approaches zero. If these results are plotted on log - log paper, as in Figure 10.3, a straight line correlation is obtained except for the points at the top of the curve, where as the chlorine concentration approaches zero the curve becomes asymptotic to the abscissa.

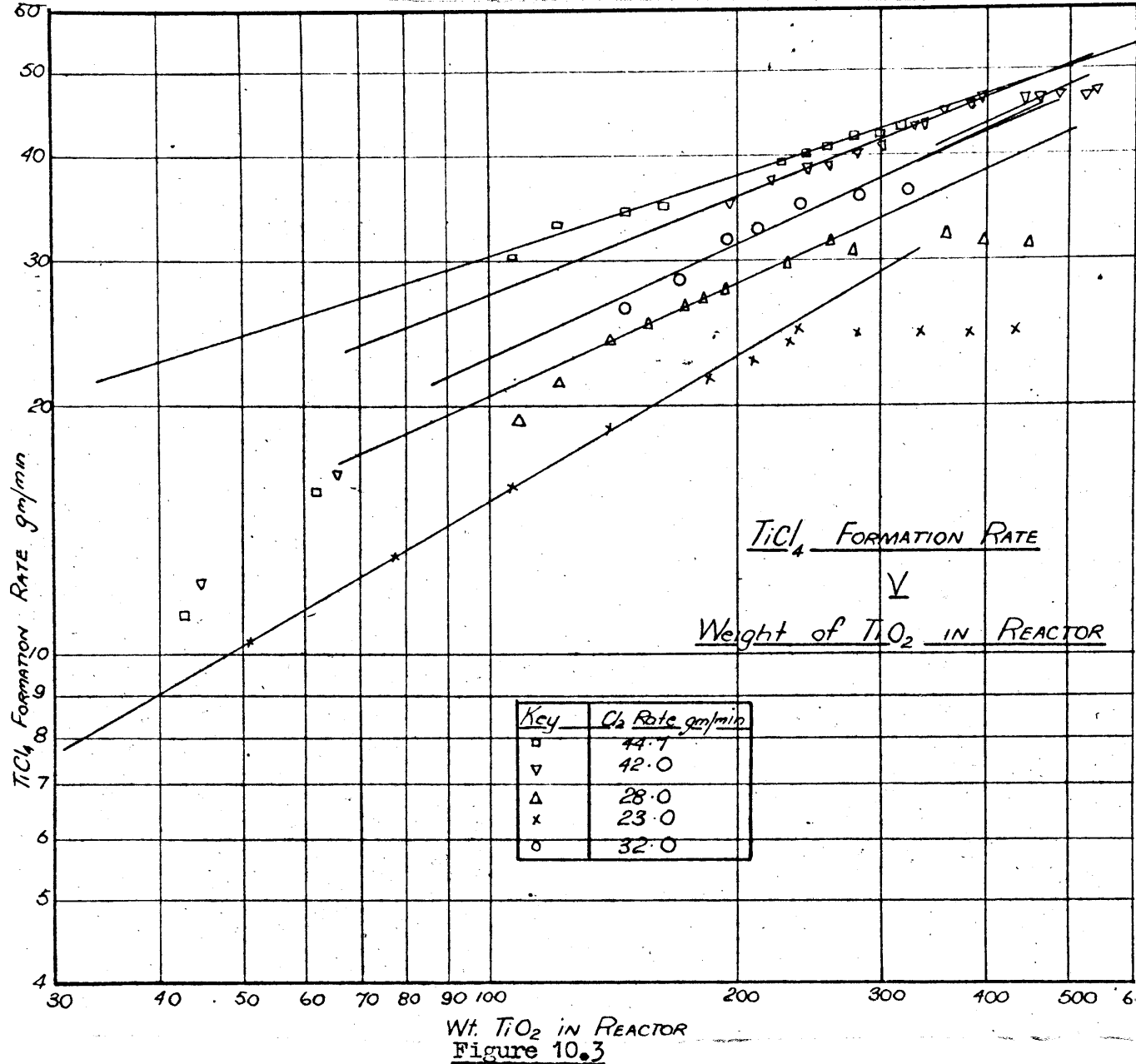
As these points represent the start of each run it is felt these values were due to a lag period before the maximum condensation rates were obtained.

This was born out in latter experiments. These results do however show that above about ninety percent conversion of chlorine the increase in conversion with increase in the weight of material in the bed is slow.

Correlation of the Reaction Rate with Chlorine Feed Rate

The variation of the reaction rate with the chlorine feed rate is shown in Figure 10.4 for a constant weight of titanium dioxide in the bed. The values plotted are taken from the curves in Figure 10.2 for a bed content of 100 gms. of titanium dioxide.





This plot shows a linear correlation, the scatter of results being attributable to variation of temperature between runs and the accumulation of errors in the determination of the weight of oxide in the bed.

Figure 10.5 shows a plot of the length to diameter ratio of the bed required to obtain 90% conversion of the chlorine feed against the chlorine rate expressed as lbs./min./ft², and shows that the L/D ratio increases gradually up to a feed rate of about 3 lbs./min./ft²., above which the increase is rapid. This means that up to this feed rate the contact efficiency between the solid and gas, decreases only slowly, but above 3 lbs./min./ft.² slugging becomes more pronounced, and bubbles of gas pass through the bed without coming

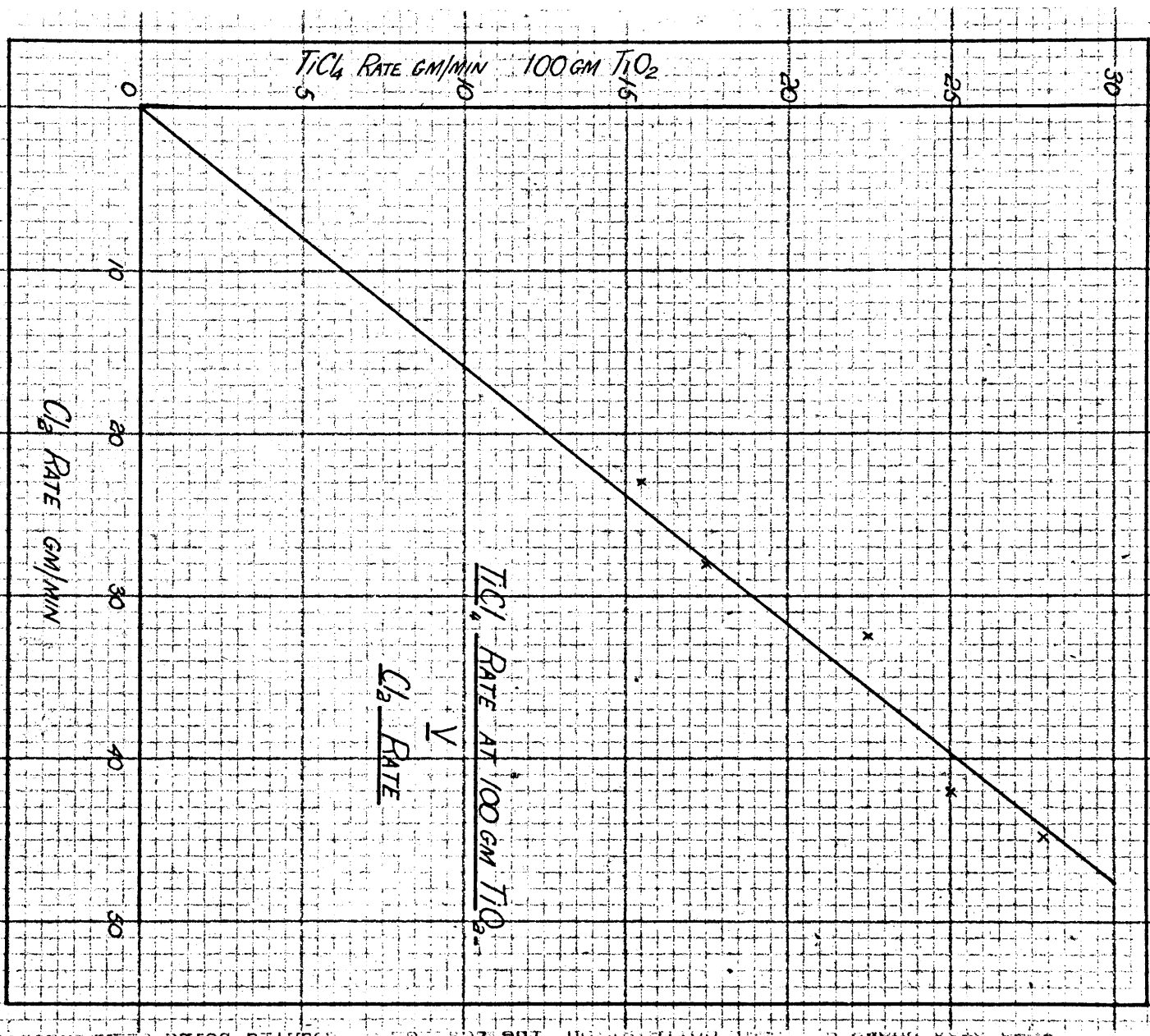


Figure 10.4

into effective contact with the bed material. For efficient operation therefore this chlorine feed rate should not be exceeded.

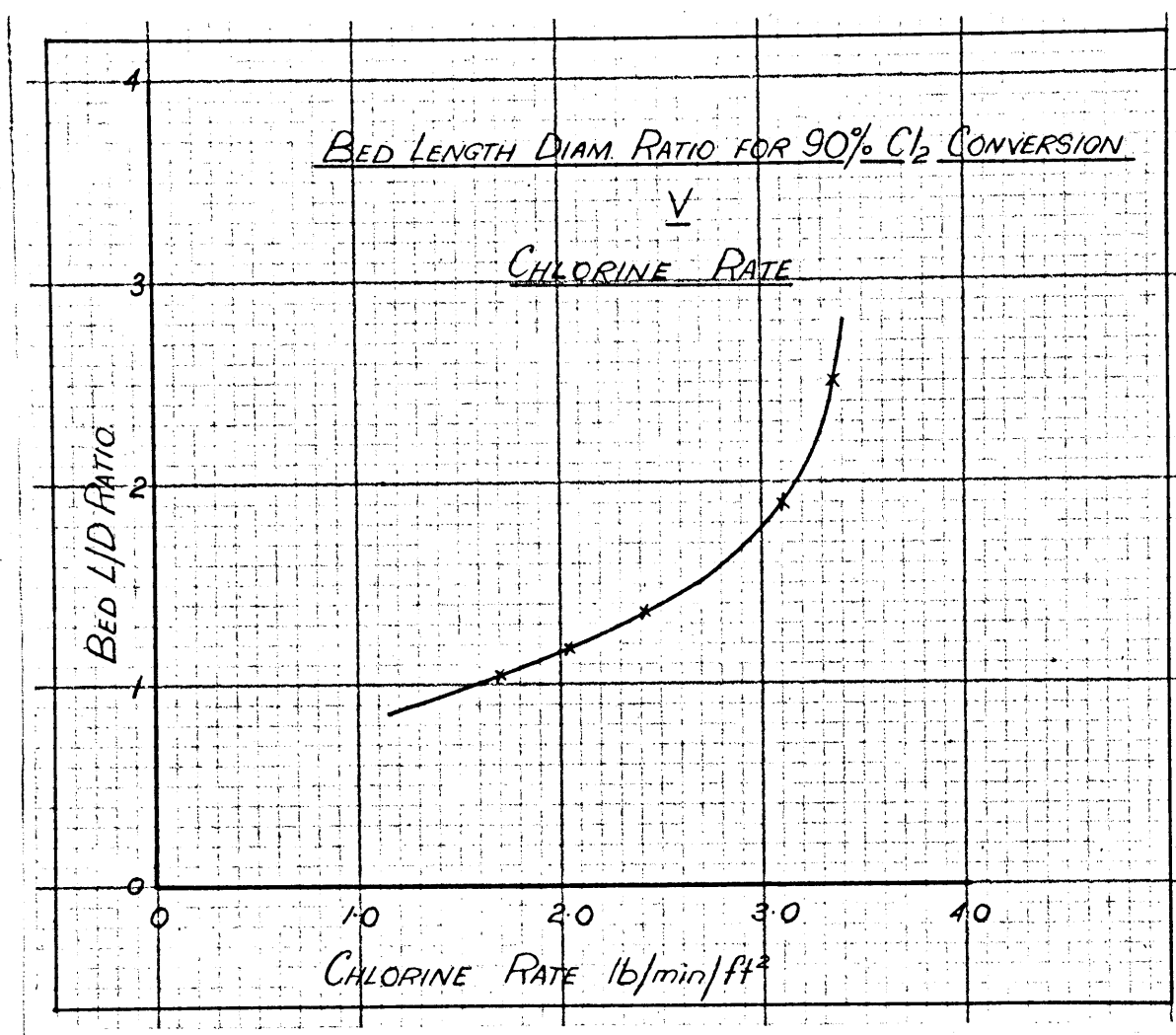


Figure 10.5

Composition of the Tail Gas

Analysis of the tail gas has shown the presence of titanium tetrachloride, chlorine, carbon dioxide and carbon monoxide. No determination of the amount of carbonyl chloride present was made, as under the conditions of the reaction the equilibrium partial pressure of this substance in the system is 9.9×10^{-8} atmosphere (Godnev and Pamfilov (45)). Some carbonyl chloride is, however, probably present in the tail gas due to the photocatalysed reaction between chloride and carbon monoxide taking place in the system after the reactor. The high values for titanium tetrachloride obtained in run 1 are almost certainly

due to the presence of carbonyl chloride.

The tail gas analysis confirmed the results of the preliminary runs that carbon dioxide is formed as one of the products of the reaction. Table 10.10 gives the analysis of the tail gas for Series Ib experiments calculated on a chlorine and titanium tetrachloride free basis.

Table 10.10

CO₂ and CO Analysis for Series Ib Experiments

Run	Sample No.	Percentage by Volume		Run	Sample No.	Percentage by Volume	
		CO ₂	CO			CO ₂	CO
1	1	35.4	64.6	5	1	41	59
	2	40.3	59.7		2	39	61
	3	42.6	57.4	6	2	32.8	67.2
	4	37.4	62.6		3	35.6	64.4
3	1	31.6	68.4		4	34.9	65.1
	2	38.6	61.8	7	1	44.6	55.4
	3	39.4	60.6		2	41.2	57.9
4	1	43.2	56.8		3	40.2	59.8
	2	40.0	60.0		4	38.2	61.8
	3	39.0	61.0				

While these analysis are consistent within themselves, the high figures obtained for the carbon balances, Table 10.0, suggest that the carbon dioxide values are low. This is consistent with the possible errors in passing the gas through a water solution of potassium iodide to remove chlorine, and using brine as the confining liquid for the analysis. These errors are not, however, of sufficient magnitude to invalidate general conclusions which may be drawn.

No variation of the composition with change in the chlorine feed rate is apparent between the runs, the ratio of the dioxide to the monoxide remaining in the order of 2:3. There is also no consistent trend in the variation of the amount of carbon dioxide in the gas with change in the weight of material in the bed. If carbon dioxide was formed as the first product of the reaction, as in the equation



an increase in the amount of carbon dioxide in the tail gas would be anticipated for shallow beds, i.e. it would increase as the run proceeds. This trend is only apparent in runs 3 and 6, while the remainder of the runs show the opposite trend. This may be accounted for by the increase in the carbon to rutile ratio in the bed as the run proceeds, due to the excess of carbon in the charge for the reaction taking place. This trend is particularly noticeable in run 7 which was carried out on a large charge, and in which the C:TiO₂ ratio altered more than in other runs.

Conclusions

The reaction rate has been shown to have a logarithmic correlation with the weight of titanium dioxide in the bed up to about 90% conversion of the chlorine in the feed, above which the rate tends to become asymptotic to a value equal to complete conversion.

The rate of formation has been shown to vary linearly with increase in the chlorine feed rate to the reactor, although feed rates in excess of 3lbs/min/ft² of cross section, should be avoided, as due to an increase in slugging the length to diameter ratio of the bed required to give 90% conversion of the chlorine feed rises sharply for rates above this figure.

While analysis of the tail gas was thought to be subject to some errors, it showed that the reaction was occurring to form both CO and CO₂ in a ratio of approximately 6:4 by volume. No marked effects in this ratio due to change in bed weight of chlorine feed rate could be traced.

CHAPTER XI

The Variation of the Reaction Rate with Change of Temperature

The experiments in the preliminary runs reported in chapter nine showed that the reaction commenced at approximately 500°C and increased with increase in temperature, marked increases occurring above 700°C; this was contrary to the findings of McTaggart.

From the results of the experiments carried out on variation of the chlorine rate to the reactor and the weight of material in the bed it was apparent that these variables could be eliminated in an investigation of the temperature effect by carrying out a series of runs at different temperatures and a constant chlorine feed rate, correlating the reaction rate with temperature at a constant weight of titanium dioxide in the bed. To avoid variations due to particle size, it would be necessary to use the same weight and particle size of material in each charge. It was decided therefore to carry out runs at 600°, 700°, 800°, 900° and 950°C using a charge of 800 gm. of material and a chlorine rate of 35 gm./min.

The reactor charge for the series of experiments was prepared as described previously, and materials with the following size analysis was used.

Table 11.1
Size Analysis of Material Used in Experiments Series II

Tyler Mesh	% by Weight	
	Rutile	Carbon
65	0.9	22.5
100	46.5	69.5
115	75.0	83.5
150	89.0	92.5
170	92.4	96.0
200	96.4	98.0
200	100.0	100.0

This gave average particle sizes for rutile and coke of 0.0057 ins. and 0.0067 ins. respectively. The rutile analysed 97.5% titanium dioxide, and the carbon analysed 2.7% volatiles, 97.1% fixed carbon and 0.2% ash. As in the previous runs the charge was made up with 76.8% rutile and 23.2% carbon, this being the stiochiometric proportions required for the reaction to give carbon monoxide as the only oxygen containing product.

Preliminary runs were carried out to obtain gas samples to check the tail gas analysis using Method Four described above. The analysis for carbon monoxide and carbon dioxide was first carried out using acidulated brine as the confining liquid, but this was unsatisfactory with large concentrations of carbon dioxide and a change was made in technique to use mercury.

During these preliminary runs it was found impossible for one person to operate the apparatus, take gas samples and measure the rate of condensation of titanium tetrachloride. An automatic rate measuring device was therefore developed to give continuous measurement of the rate of condensation. This apparatus has been described in chapter six. The trial runs carried out to test the operation of this meter showed it to be satisfactory, although the operation of the capacity switch was rather sensitive and required attention during the run.

After these runs had been carried out, and the operation of the apparatus and the analysis of the tail gas were considered to be satisfactory, the investigation of the effects of temperature on reaction rate commenced. The experimental results obtained are given in Tables 11.2 to 11.12 which cover the results of Runs 3, 4, 5, 7, 8, 9, 10, 11, 14, 15 and 16 of the experimental series II.

This series of experiments itself falls into three sections, runs 3 to 7, 8 to 11 and 14 to 16, and the results will be discussed in these groups.

Table 11.2

Charge 800 gm. Temperature 900°C Chlorine Rate 35 gm/min.

Run 3

Run Time Min.	TiCl ₄ Rate gm./min.		TiO ₂ Removal Rate gm/min.	Weight TiO ₂ in Bed gm.	Sample
	Measured	Total			
2.6	27.6	29.8	12.5	548	1a,b
4.0	36.5	38.7	16.3	518	
5.3	39.5	41.7	17.5	495	
6.4	39.5	41.7	17.5	476	
7.6	39.0	41.2	17.3	455	
8.7	45.0	47.2	17.3	436	
13.9	34.2	36.4	15.3	357	
15.2	34.2	36.4	15.3	336	
16.6	33.4	35.6	14.9	315	2a & b
17.9	33.4	35.6	14.9	295	
19.3	32.0	34.2	14.4	275	
20.7	31.5	33.7	14.2	265	
22.0	30.0	32.2	13.5	237	
23.6	28.7	30.9	13.0	215	
25.2	27.6	29.8	12.5	193	
26.8	25.1	27.3	11.5	178	
28.6	24.5	26.7	11.2	157	3a & b
30.6	22.0	24.2	10.2	136	
32.6	20.0	22.2	9.3	116	
35.0	17.5	19.7	8.25	95	
37.8	13.6	15.8	6.6	75	
<u>Gas Analysis</u>			<u>Residues</u>		
<u>Sample</u>	<u>Cl₂%</u>	<u>TiCl₄%</u>	<u>CO₂%</u>	<u>CO%</u>	
1	23.6	3.1	35.2	38.1	Reactor 84 gm. TiO ₂ % 59.3%
2	34.5	3.3	28.6	34.6	Annulus 58.8 gm. TiO ₂ 76.5% TiO ₂
3	66.0	3.2	13.2	17.5	Cyclone 12 gm. TiO ₂ 30.8%

Table 11.3Charge 800 gm. Temperature 900°C Chlorine Rate 35 gm/min.Run 4

Time Run Min.	TiCl ₄ Rate gm./min.		TiO ₂ Removal Rate gm./min.	Weight TiO ₂ in Bed gm.	Sample
	Measured	Total			
1.5	35.2	36.9	15.5	548	
2.8	33.2	34.9	14.7	528	
4.1	39.4	41.1	17.2	502	
5.3	38.9	40.6	17.1	482	
6.1	37.6	39.3	16.5	463	
7.7	35.8	37.5	15.8	442	
8.9	34.9	36.6	15.4	423	
10.3	35.2	36.9	15.6	405	
11.6	34.5	36.2	15.2	385	
12.9	34.5	36.2	15.2	365	
14.2	34.2	35.9	15.1	341	
15.5	33.6	35.3	14.9	322	
16.9	32.5	34.2	14.4	305	
18.2	32.8	34.5	14.7	282	
19.6	32.5	34.2	14.4	261	
21.0	31.8	33.7	14.2	241	
22.4	30.5	32.2	13.6	221	
24.0	28.2	29.9	12.6	200	
25.6	30.0	31.7	13.4	182	
27.2	26.5	28.2	11.9	162	
29.0	24.3	26.0	10.9	142	
30.9	22.8	24.5	10.8	122	
33.1	17.0	18.7	7.9	102	
40.0	Chlorine off				
<u>Gas Analysis</u>					<u>Residues</u>
<u>Sample</u>	<u>Cl₂</u>	<u>TiCl₂</u>	<u>CO₂</u>	<u>CO</u>	
1	20.2	3.9	35.6	48.4	Reactor 96.5 gm. 41.6% TiO ₂
2	26.5	2.4	32.7	38.4	Annulus 57.5 gm. 76.8% TiO ₂
3	58.0	2.4			Cyclone 9.0 gm. 40.2% TiO ₂

Table 11.4

Charge 800 gm. Temperature 800°C Chlorine Rate 35gm/min.

Run 5

Time Run Min.	TiCl ₄ Rate gm./min.		TiO ₂ Removal Rate gm./min.	Weight TiO ₂ in Bed gm.	Sample
	Measured	Total			
2.7	21.4	21.9	8.8	520	
4.6	22.3	22.8	9.2	502	
6.7	21.1	21.6	9.1	484	
8.8	22.5	23.0	9.3	465	
10.9	20.0	20.5	8.2	447	
13.2	19.4	19.9	7.9	429	
15.4	19.2	19.7	7.8	411	
17.7	19.4	19.9	7.9	393	
20.0	19.4	19.9	7.9	375	
22.4	18.8	19.3	7.7	356	
24.7	18.8	19.3	7.7	339	
27.1	18.5	19.0	7.6	320	
29.5	17.5	18.0	7.1	303	
32.0	16.8	17.3	6.8	285	
34.6	17.3	17.8	7.1	267	
40.0	16.2	16.7	6.6	230	
42.8	15.8	16.3	6.4	212	
45.0	C h l o r i n e o f f			198	

<u>Gas Analysis</u>						<u>Residues</u>	
<u>Sample</u>	<u>Cl₂</u>	<u>COCl₂</u>	<u>TiCl₄</u>	<u>CO₂</u>	<u>CO</u>		
1	49.0	3.5	0.6	25.2	21.7	Reactor	305.5 gm. 71.9% TiO ₂
2	67.0	3.2	0.6	16.4	12.9	Annulus	59.5 gm.
3	68.3	2.3	0.6	17.9	10.9	Cyclone	2.5 gm. 32.8% TiO ₂
						Wt. of TiCl ₄ collected 508 gm.	

Table 11.5

Charge 800 gm. Temperature 715°C Chlorine Rate 35 gm/min.

Run 7

Time Run Min.	TiCl ₄ Rate gm./min.		TiO ₂ Removal Rate gm./min.	Weight TiO ₂ in Bed gm.	Sample
	Measured	Total			
8.0	17.2	18.1	7.6	613	
10.5	17.0	17.9	7.5	594	
13.0	17.1	18.0	7.6	575	
15.0	17.2	18.1	7.6	560	
17.5	17.0	17.9	7.5	541	
20.0	17.0	17.9	7.5	522	
22.0	17.0	17.9	7.5	507	
24.5	16.7	17.6	7.4	488	
27.0	16.4	17.3	7.3	469	
29.5	16.4	17.3	7.3	451	
32.0	16.0	16.9	7.1	433	
35.0	15.5	16.4	6.9	412	
37.0	15.3	16.2	6.8	398	
39.5	15.3	16.2	6.8	382	
42.0	14.3	15.2	6.4	365	
45.0	13.5	14.4	6.1	346	
48.0	13.4	14.3	6.0	328	
51.0	13.7	14.6	6.1	316	
53.5	12.9	13.8	5.8	296	
57.0	12.1	13.0	5.5	276	
60.0	12.1	13.0	5.5	260	

Tail Gas Data

Barometer 769 mm.Hg

Time Run	Temp. °C	Rate Air Equ. ft ³ min.	Analysis %			
			Cl ₂	TiCl ₄	CO ₂	CO
*	19.5	0.64	92.0	0.6	2.4	5.0
14	19.5	0.64	76.4	0.9	15.7	6.9

Residues

Reactor 355 gm. 763.2% TiO₂
Annulus 63 gm. 76.8% TiO₂
Cyclone 5 gm. 30.5% TiO₂

Wt. of TiCl₄ collected 993 gm.

* at 620°C

Table 11.6

Charge 800 gm. Temperature - Chlorine Rate 35 gm./min.

Run 8

Time Run Min.	TiCl ₄ Rate gm./min.		Bed Temperature °C	Chlorine Balance %	Sample
	Measured	Total			
1.25	27.6	28.4	884	104.5	
3.0	33.9	34.7	885		
4.25	33.0	33.8	882		
5.5	31.5	32.3	876		
7.0	30.4	31.2	870		
8.5	29.4	30.2	862		
10.0	28.0	28.8	854		
11.5	27.1	27.9	851		
13.0	26.4	27.2	849		
14.5	25.6	26.4	846		
16.25	24.5	25.3	845		
18.0	24.5	25.3	850		
20.0	23.5	24.3	852		
21.5	23.4	24.2	850		
23.25	23.8	24.6	850		
25.0	22.6	23.4	850	102.6	
27.0	21.3	22.1	848		
29.0	20.3	21.1	847		
31.0	18.9	19.7	847		
33.0	17.7	18.5	844		
36.0	15.2	16.0	844	105.0	
39.0	11.8	12.6	844		

Tail Gas Data

Barometer 768 mm.Hg.

Time Run Min.	Temp. °C	Rate Air Eqv. ft ³ /min	Analysis %				
			Cl ₂	TiCl ₄	COCl ₂	CO	CO ₂
12	19.5	0.515	50.6	0.8	5.6	21.0	22.0
29	20.0	0.545	56.6	0.9	4.9	16.5	21.4
39	19.8	0.57	80.6	0.9	3.3	6.6	8.6

Residues

Reactor 124 gm.
Annulus 63 gm.
Cyclone 4.5 gm.

Wt. of TiCl₄ collected 1070 gm.

Table 11.7Charge 800 gm. Chlorine Rate 35gm/min.Run 9

Time Run Min.	Temp. °C	TiCl ₄ Rate gm/min.		Time Run Min.	Temp. °C	TiCl ₄ Rate gm/min.	
		Measured	Total			Measured	Total
5.0	785	21.5	22.2	33.5	705	9.4	10.1
7.0	775	21.0	21.7	38.0	702	8.9	9.6
9.0	765	19.4	20.1	43.0	700	8.4	9.1
11.0	752	17.3	18.0	52.0	660	2.8	3.5
13.5	735	14.7	15.4	64.0	675	4.1	4.8
16.5	732	13.9	14.6	70.0	727	9.4	10.1
19.0	745	15.3	16.0	74.0	745	10.0	10.7
22.0	749	15.4	16.1	78.0	757	10.5	11.2
24.5	751	15.7	16.4	82.0	765	9.6	10.3
27.0	742	14.8	15.5	86.0	765	10.7	11.4
30.0	725	12.1	12.8	91.0	758	6.4	7.1

Tail Gas Data

Barometer 767 mm.Hg.

Time Run Min.	Temp. °C	Rate Air Eq'v. ft ³ /min.	Analysis %				
			Cl ₂	TiCl ₄	COCl ₂	CO ₂	CO
6	18.0	0.51	58.6	0.8	6.7	20.0	14.0
25	18.7	0.55	76.2	1.0	3.7	12.1	7.0
30						64.5	35.5
52	19.2	0.61	90.4	0.7	3.9	3.3	1.7
71						66.0	34.0
90						58.4	41.6

Residues

Reactor 186 gm.

Cyclone 2 gm.

Annulus 60 gm.

Weight of TiCl₄ collected 869 gm.

Weight of Chlorine Used 3423 gm.

Calculated Rate = 36.5 gm./min.

Table 11.8

Charge 800 gm. Chlorine Rate 35gm./min.

Run 10

Time Run Min.	Temp. °C	TiCl ₄ Rate gm/min.		Time Run Min.	Temp. °C	TiCl ₄ Rate gm./min.	
		Measured	Total			Measured	Total
3.0	988	40.5	41.6	16.0	950	35.1	36.2
4.0	988	48.4	49.5	17.0	940	33.2	34.3
5.0	995	49.7	50.5	18.5	932	31.4	32.5
5.75	997	47.1	48.2	19.75	925	29.2	30.3
6.5	995	45.8	46.9	21.0	915	26.8	27.9
7.5	995	45.8	46.9	23.0	905	23.8	24.9
8.5	991	43.6	44.7	24.5	912	22.4	23.5
9.5	988	42.6	43.7	28.0	928	23.5	24.6
10.5	986	40.6	41.7	30.0	903	19.2	20.4
11.5	980	40.6	41.7	32.5	895	13.3	14.4
12.5	975	38.9	40.0	36.0	880	7.6	8.7
13.5	970	38.1	39.2	45.0	chlorine off		
14.75	960	36.9	38.0				

Tail Gas Data

Barometer 762 mm.Hg

Time Run Min.	Temp. °C	Rate Air Eq'v. ft ³ /min.	Analysis %				
			Cl ₂	TiCl ₄	COCl ₂	CO ₂	CO
6	20.5	0.42	7.64	1.0	4.5	36.7	50.2
15	21.0	0.45	28.8	1.16	6.1	28.1	36.6
21	21.3					46.0	54.0
27						46.0	54.0
32	22.2	0.59	73.8	1.02	6.1	8.6	10.6

Residues

Reactor 100 gm.

Cyclone 11 gm.

Annulus 60 gm.

Weight of TiCl₄ collected 1088 gm.

Weight of Chlorine Used 1643 gm.

Calculated Rate = 36.5 gm./min.

Table 11.9

Charge 1050 gm. Chlorine Rate 35 gm./min.

Run 11

Time Run Min.	Temp. °C	TiCl ₄ Rate gm./min.		Time Run Min.	Temp. °C	TiCl ₄ Rate gm./min.	
		Measured	Total			Measured	Total
2.5	960	41.5	42.6	19.0	962	40.6	41.7
3.5	962	42.5	43.6	20.0	957	43.1	44.2
4.25	968	49.0	50.1	21.0	950	39.7	40.8
5.0	972	50.3	51.4	22.0	940	38.0	39.1
6.0	975	50.3	51.4	23.25	935	35.8	36.9
7.0	985	49.0	50.1	24.5	932	33.8	34.9
7.75	994	49.0	50.1	25.5	927	34.7	35.8
8.5	1000	48.4	49.5	26.75	922	33.1	34.2
9.5	1005	47.6	48.7	28.0	915	31.9	33.0
10.5	1005	47.6	48.7	29.25	917	32.5	33.6
11.25	1005	47.6	48.7	30.5	932	31.9	33.0
12.0	1002	47.0	48.1	31.75	938	29.8	30.9
13.0	997	47.5	48.6	33.25	932	30.8	31.9
14.0	992	44.6	45.7	34.5	922	27.1	28.2
15.0	988	44.6	45.7	37.0	906	9.4	10.5
16.0	980	43.6	44.7	40.25	902	15.5	16.6
17.0	974	43.1	44.2	49.0	876	7.5	8.6
18.0	970	40.6	41.7				

Tail Gas Data

Barometer 761 mm.Hg

Time Run Min.	Temp. °C	Rate Air Eq'v. ft ³ /min.	Analysis %				
			Cl ₂	TiCl ₄	COCl ₂	CO ₂	CO
10	23.5	0.385	1.1	1.28	3.7	38.9	55.2
21						42.7	57.3
26	23.5	0.47	22.3	1.48	2.9	32.0	41.3
29						50.8	49.2
37	23.5	0.51	53.6	1.47	3.5	20.2	21.2

Residues

Reactor	114 gm.	Weight of TiCl ₄ collected	1490 gm.
Cyclone	17 gm.	Weight of Chlorine Used	1734 gm.
Annulus	62 gm.	Calculated Chlorine Rate =	37.2 gm./min.

Note: The Chlorine Rate was unsteady at the start of the run.

Table 11.10

Charge 1666 gm. Chlorine Rate 35gm./min.

Run 14

Time Run Min.	Temp. °C	TiCl ₄ Rate gm./min.		Time Run Min.	Temp. °C	TiCl ₄ Rate gm/min	
		Measured	Total			Measured	Total
2.25	907	39.7	40.7	27.25	987	44.7	45.7
3.25	907	40.6	41.6	28.0	983	44.7	45.7
4.25	905	40.6	41.6	29.0	978	41.6	42.6
5.25	908	46.1	47.1	30.0	973	44.7	45.7
6.25	912	48.3	49.3	31.0	960	42.5	43.5
7.0	909	49.6	50.6	32.0	952	40.6	41.6
8.0	907	48.1	49.1	33.0	945	38.8	39.8
9.0	913	47.7	48.7	34.0	937	38.8	39.8
9.75	920	47.7	48.7	35.25	925	37.2	38.2
11.25	924	47.7	48.7	36.25	910	35.8	36.8
13.25	931	47.7	48.7	37.25	897	35.8	36.8
14.25	940	54.2	55.2	38.75	885	33.8	34.8
15.5	947	46.1	47.1	40.0	868	30.3	31.3
16.25	953	47.7	48.7	41.5	858	28.8	29.8
17.0	955	47.7	48.7	43.0	850	27.0	28.9
19.0	967	47.7	48.7	44.5	848	27.0	28.0
19.75	973	47.7	48.7	46.0	835	24.8	25.8
20.75	978	48.3	49.3	47.75	815	22.3	23.3
21.5	985	46.1	47.1	49.75	790	17.7	18.7
22.5	987	47.7	48.7	52.0	775	18.3	19.3
23.5	987	42.6	43.6	54.5	762	13.3	14.3
24.5	987	40.6	41.6	58.0	720	9.4	10.4
25.25	987	45.7	46.7	67.0	670	2.2	3.2
26.25	987	44.7	45.7				

Tail Gas Data

Barometer 766 mm.Hg.

Time Run Min.	Temp. °C	Rate Air Eq'v. ft ³ /min.	Analysis %				
			Cl ₂	TiCl ₄	COCl ₂	CO ₂	CO
12	25.5	0.40	0.3	1.3	3.6	47.7	47.0
19						45.0	55.0
29	25.5	0.400	4.5	1.3	3.6	41.8	52.8
44						52.4	47.6
55						60.1	39.9

Table 11.10 Continued

<u>Residues</u>			
Reactor	353 gm.	Weight of TiCl_4 collected	2062 gm.
Cyclone	37 gm.	Weight of Chlorine Used	2641 gm.
Annulus	63 gm.	Calculated Chlorine Rate =	36.5 gm./min

Table 11.11

Charge 1678 gm. Chlorine Rate 35 gm./min.

Run 15

Time Run Min.	Temp. °C	TiCl ₄ Rate gm/min		Time Run Min.	Temp. °C	TiCl ₄ Rate gm/min	
		Measured	Total			Measured	Total
1.0	970	51.2	52.6	18.75	878	40.3	41.3
2.0	962	50.6	51.6	19.75	874	40.3	41.3
2.75	962	50.6	51.6	21.0	868	39.4	40.4
3.5	962	49.5	50.5	24.0	849	36.4	37.4
4.5	956	49.5	50.0	25.25	840	34.8	35.8
5.25	952	47.2	48.2	26.5	825	34.4	35.4
6.25	948	46.8	47.8	27.75	820	32.3	33.3
7.0	940	46.5	47.5	29.0	810	31.1	32.1
8.0	925	45.3	46.3	30.25	800	28.9	29.9
9.0	915	45.3	46.3	31.75	790	27.1	28.1
10.0	906	45.2	46.2	33.25	780	25.0	26.0
11.0	900	44.4	45.4	35.0	767	22.8	23.8
11.75	897	43.4	44.4	37.0	750	19.5	20.5
12.75	892	42.3	43.3	39.0	735	22.9	23.9
13.75	887	41.8	42.8	41.0	718	14.3	15.3
14.75	882	41.8	42.8	45.0	690	8.4	9.4
15.75	880	41.2	42.2	49.5	700	8.3	9.3
16.75	881	41.2	42.0	54.5	680	7.7	8.7
17.75	882	41.2	42.2	60.5	660	5.7	6.7

Tail Gas Data

Barometer 762 mm.Hg.

Time Run Min.	Temp. °C	Rate Air Eq'v. ft ³ /min.	Analysis %				
			Cl ₂	TiCl ₄	COCl ₂	CO ₂	CO
8	25.0	0.4	1.03	1.3	3.4	55.0	39.2
20	25.1					56.2	43.8
28	25.1	0.45	37.4	1.3	0.7	37.6	23.0
38	25.4	0.50	65.0	1.3	3.3	19.5	10.9
56	25.8					67.2	32.8

Residues

Reactor 520 gm.

Cyclone 37 gm.

Annulus 63 gm.

Weight of TiCl₄ collected 1944 gm.

Weight of Chlorine used 2765 gm.

Calculated Chlorine Rate = 36 gm./min.

Table 11.12

Charge 1690 gm. Chlorine Rate 36.5 gm/min.

Run 16

Time Run Min.	Temp. °C	TiCl ₄ Rate gm/min.		Time Run Min.	Temp. °C	TiCl ₄ Rate gm/min.	
		Measured	Total			Measured	Total
26.25	851	39.4	40.4	38.5	755	22.3	23.3
27.25	841	36.5	37.5	40.25	745	20.2	21.2
28.25	834	36.8	37.8	42.0	730	18.7	19.7
29.5	826	35.7	36.7	44.0	712	15.6	16.6
30.5	821	33.9	34.9	46.5	702	13.5	14.5
31.5	810	32.0	33.0	49.5	697	12.3	13.3
33.0	800	28.5	29.5	52.5	688	11.8	12.8
34.0	790	28.2	29.2	55.75	675	9.1	10.1
35.5	778	26.1	27.1	62.0	630	3.8	4.8
37.0	768	24.8	25.8				

Tail Gas Data

Barometer 764 mm.Hg.

Time Run Min.	Temp. °C	Rate Air Eq'v. ft ³ /min.	Analysis %				
			Cl ₂	TiCl ₄	COCl ₂	CO ₂	CO
5	26	0.36	0.00	1.46	3.06	50.1	46.9
30	26	0.48	34.1	1.31	0.00	24.3	60.5
40						61.2	38.8
49						72.6	27.4
52	26.5	0.67	73.1	1.42	0.4	17.1	8.1
62						69.4	30.6

Residues

Reactor 497 gm.

Weight of TiCl₄ collected 1874 gm.

Cyclone 46 gm.

Annulus 60 gm.

Note: No rate measurements were made at the start of the run as a blockage in the balancing line on the rate meter prevented satisfactory operation. The above results were obtained after this blockage had been cleared.

The runs in the first group were carried out as planned at a fixed temperature for each run. Runs 3 and 4 were carried out at 900°C, run 5 at 800°C and run 7 at 700°C. Before the results recorded for run 7 in Table 11.5 were taken, the rate of the reaction was observed at lower temperatures while the temperature of the bed was being raised. Chlorine was passed through the bed for about ten minutes at 425°C and again at 530°C. White fumes were observed at each temperature in the condenser and in air when the gas was allowed to escape from the system, more fumes occurring at 530° than at 425°, but in each case there was no condensation of liquid. Chlorine was again passed at 620°C when the reaction was sufficiently fast to give condensable amounts of titanium tetrachloride. This rate was measured at 0.9 gm/min. which, when corrected for the loss of titanium tetrachloride in the tail gas, gave a total rate of 1.4 gm/min.

During these runs the operation of the equipment was satisfactory, although the chlorine balances were still inaccurate. The balances for runs 3, 4 and 5 are shown in the following table.

Table 11.13

Run	Sample	Chlorine Balance %
3	1	100.5
4	1	82
	2	91
	3	71
5	1	67
	2	125
	3	98.4

To obtain more precise chlorine balances it was decided to measure the tail gas rate from the condenser, and from this calculate the amount of chlorine and titanium tetrachloride leaving the system. This measurement was carried out by means of a Flowrator in the tail gas line, as shown in Figure 7.1. The

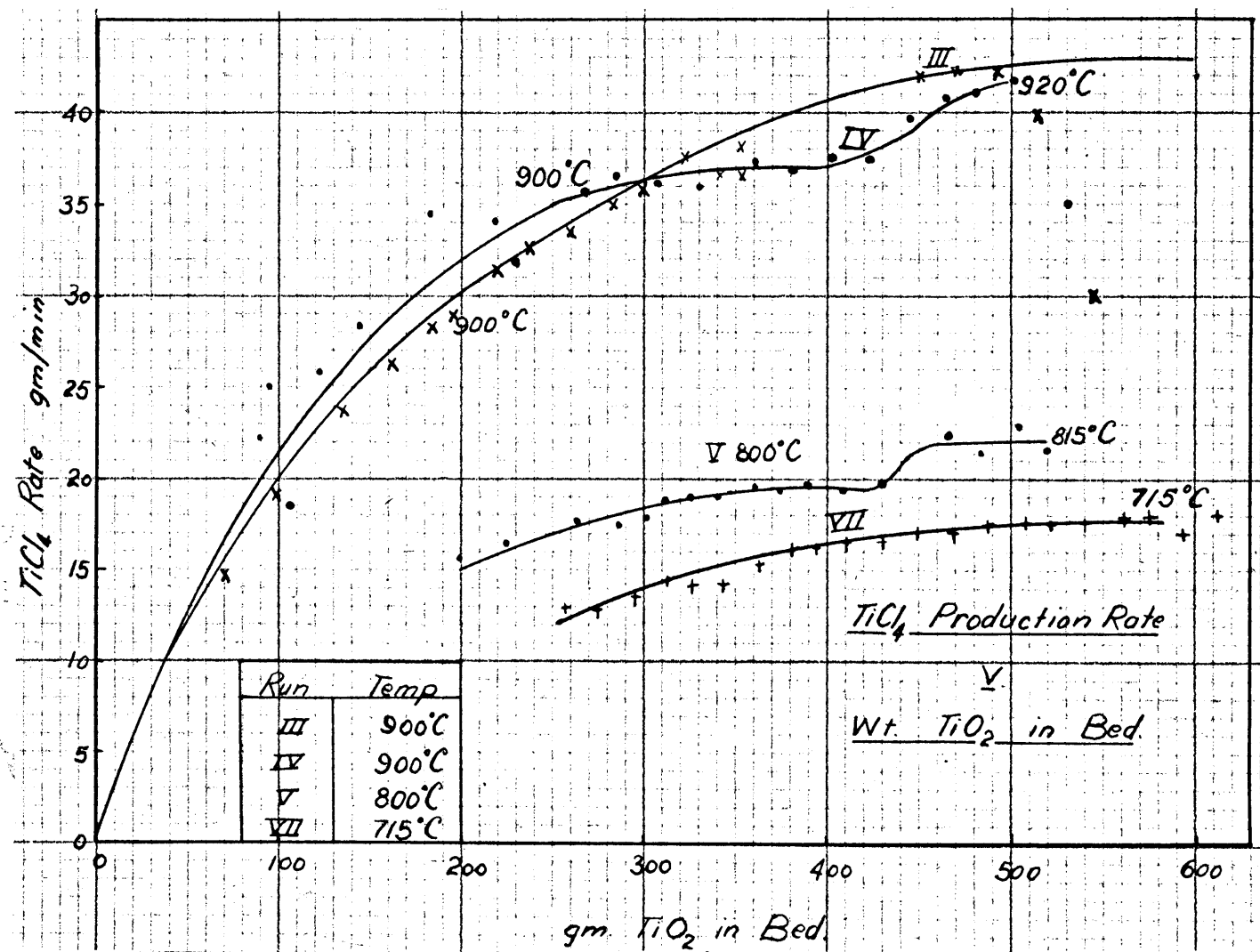


Fig. 11.1

rate was measured as an air equivalent in $\text{ft}^3/\text{min.}$ and the weight flow of tail gas in gm/min calculated using the relative density of the gas determined by analysis. Any errors due to differences of viscosity between the tail gas and air for which the meter was calibrated were small as the meter float was a viscosity stable type.

The method of calculation is shown in Appendix III.

Figure 11.1 shows the titanium tetrachloride formation rate plotted against the weight of titanium dioxide in the bed for runs 3, 4, 5 and 7. The conditions of run 3 were repeated in run 4 as a blockage in the entrance of the tail gas cyclone occurring at the start of the run resulted in a gap in the rate measurement between approximately 350 and 450 gm. of TiO_2 in the bed. The close proximity of the curves of runs 3 and 4 show the results of these experiments to be readily reproducible. In runs 3, 4 and 5 insufficient allowance was made for the rise of the bed temperature when chlorination was commenced due to the exothermic nature of the reaction, and it was found necessary to reduce the control temperature of the heating furnace to get the required temperature of the bed. This gave rise to the bumps in the curves at the start of these runs, the temperature obtaining at these times being noted on the curves.

Figure 11.2 shows the rate of formation of titanium tetrachloride for the above runs plotted against temperature.

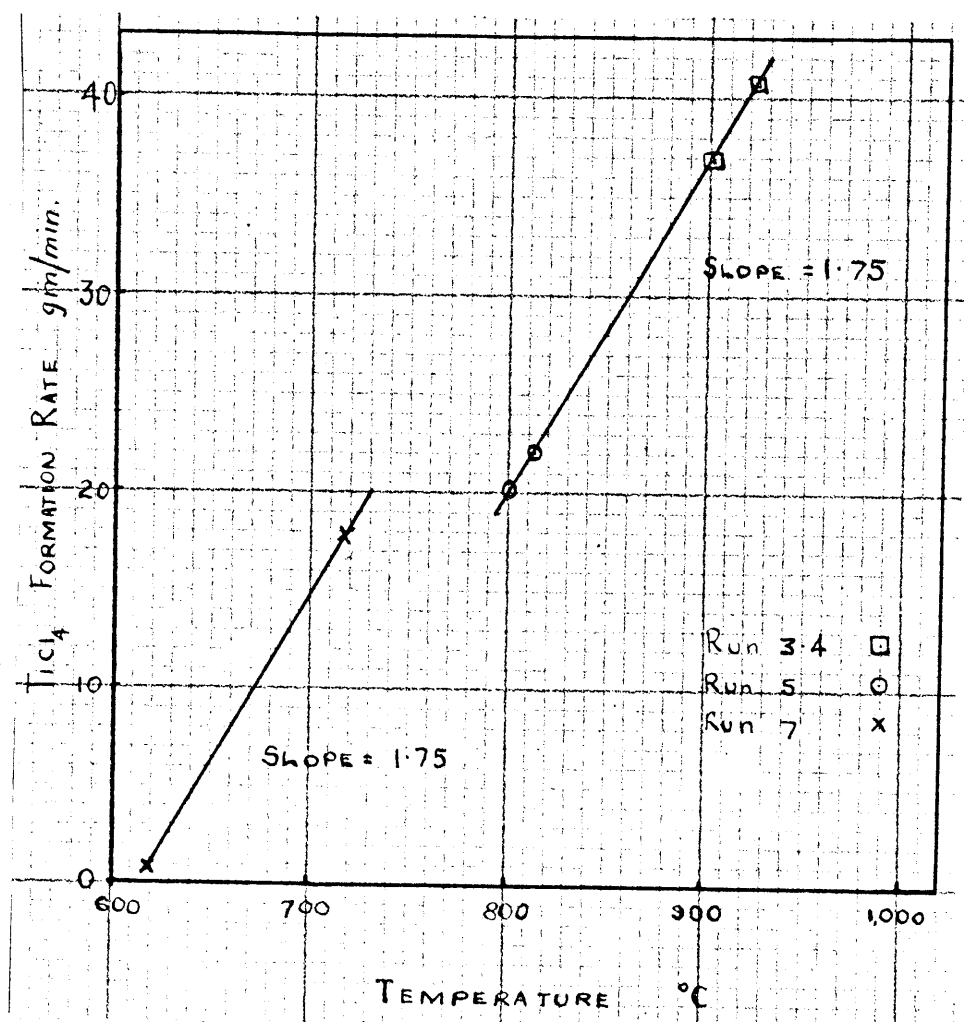


Figure 11.2

In this figure the points at 900°, 800° and 775°, which are the temperatures at which the runs were carried out, were obtained from the curves in Figure 11.1 for 400 gm. of TiO₂ in the bed. The other points were obtained from the curves for that section of the runs before the temperature of the bed was adjusted to the desired values. This plot shows that while the temperature coefficients as given by the slope of the lines, for the results of runs 3, 4, 5 and 7 were approximately the same, a between runs difference existed which increased the overall rate in run 7. The closest agreement of the points at 815° and 920°C with the line through the values at 800° and 900°C suggested that errors due to variation of the weight of TiO₂ in the bed would be small, if the weight of oxide in the bed was above that at which the formation rate is

almost constant with increase in the weight of the bed, as shown in Figure 9.2. This is supported by the result of run 7 Series Ib shown in that figure, in which an increase in the amount of oxide in the bed from 550 to 700 gm. resulted in an increase in the rate of formation of only one percent. From these results it was decided to measure the rate of formation while varying the temperature of the bed.

Run 8 was carried out commencing chlorination at 850°C, but owing to the exothermic nature of the reaction the bed temperature rose to 890° and was then controlled back to 850° at which the remainder of the run was carried out. The results of this run are given in Table 11.6, while Figure 11.3 shows the plot of rate of formation of $TiCl_4$ for the run against the time run. The temperatures shown on the curve were taken from the temperature record for the run.

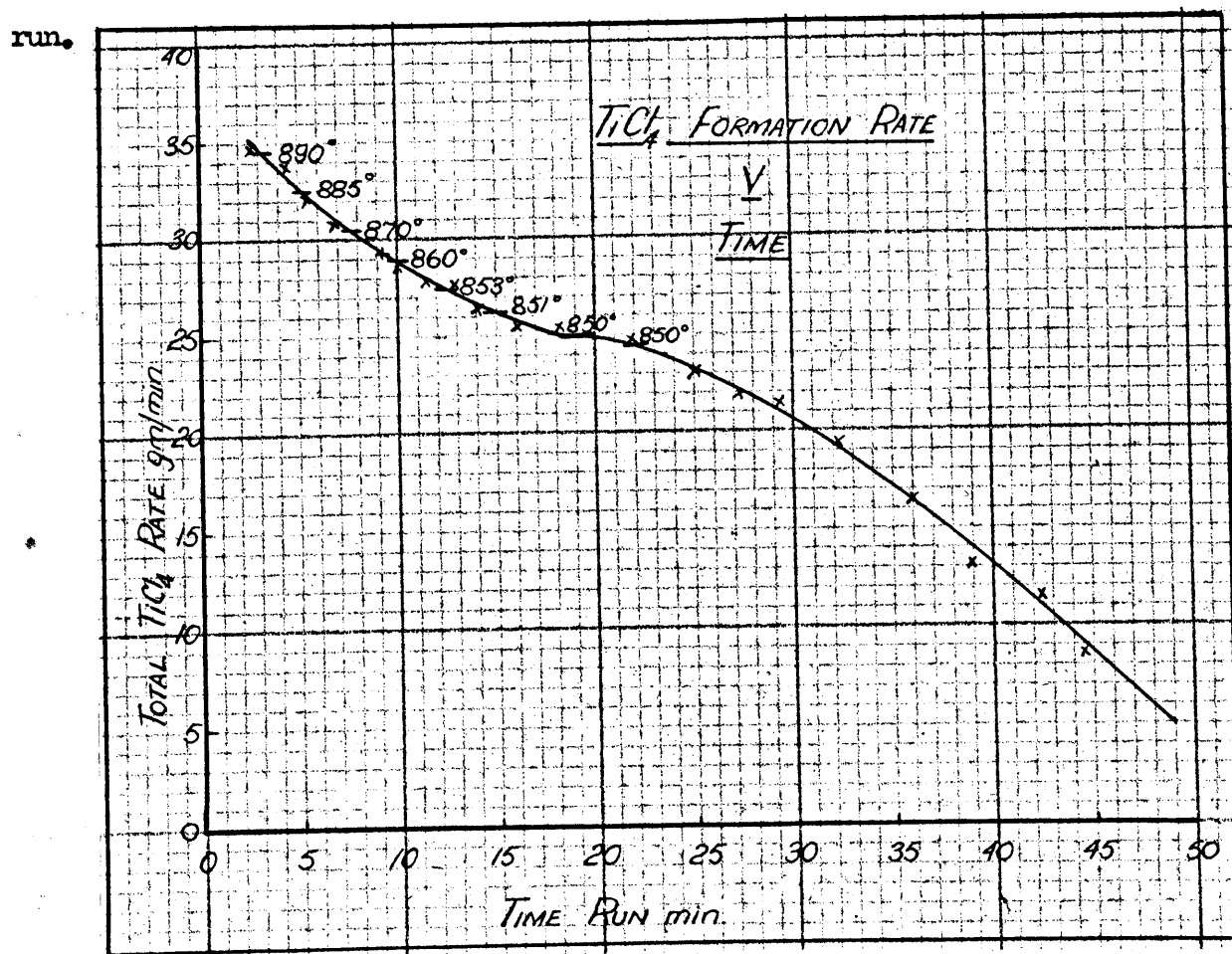


Figure 11.3

As the temperature of the bed fell there was a decrease in the rate, which flattened out as the temperature was controlled to 850°C before falling off as the weight of oxide in the bed fell below the critical amount.

The rate of formation of TiCl_4 for run eight is plotted against temperature in Figure 11.4 and the temperature coefficient determined from the data obtained in this run by variation of the bed temperature during the run shows good agreement with that obtained for fixed amount of TiO_2 in the bed from the results of runs 3, 4, 5 and 7. This confirmed the conclusions from the previous runs that data on the variation of the reaction rate with temperature could best be obtained by varying the temperature of a bed containing sufficient oxide to give only small variation in the rate with change in weight of oxide in the bed. From the results of experiments in Series Ib. the critical amount of oxide for a chlorine rate of 35 gm./min. appeared to be approximately 400 gm.

Calculation of the chlorine balances for run 8 from the measured TiCl_4 rate and tail gas rate, and the analysis of the tail gas, gave values of 104.5%, 102.6% and 99% which although higher than the theoretical value were considered to be within the range of experimental error. These values show a big improvement in precision on the values obtained in previous runs.

The results of runs 9, 10 and 11 are given in Tables 10.7, 10.8 and 10.9, and are shown in graphical form in Figure 11.4.

The results of run 9 show some agreements with the previously determined temperature coefficients; plotting the results on the same scale as the plot for runs 3, 4, 5 and 7 give slopes of 1.65 and 1.75 respectively. Towards the end of the run the temperature was increased which gave rise to the points lying below the curve. These low values were due to a deficiency of titanium

dioxide in the bed at this stage of the run.

The results of run 10 shows a rapid fall in rate as the temperature is decreased. After some fluctuation at the beginning of the run the slope of the rate-temperature curve approached that of the previous runs, but as the run proceeded the rate fell away rapidly due to the depletion of the oxide in the bed.

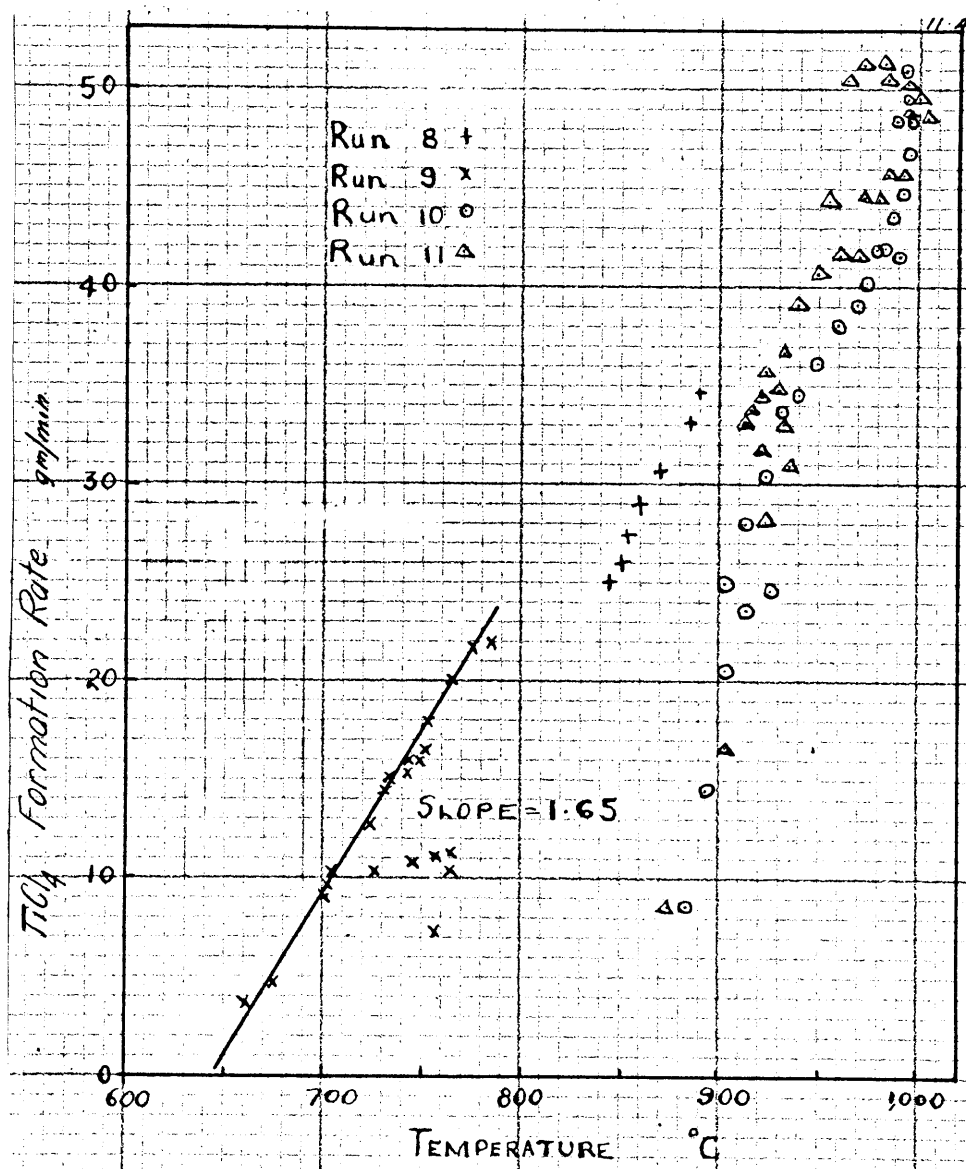


Figure 11.4

Run 11 was carried out over the same temperature range using a charge weighing 1050 gm. instead of 800 gm. as used in previous runs. In this run the temperature at the start was 960°C and during the first nine minutes was raised to 1000°C and

held there for four minutes. As the temperature was raised a TiCl_4 formation rate of 50.1 gm./min. was achieved at 968°C corresponding to 107% conversion of the chlorine feed. During the period in which the temperature was held in the range 997° to 1005°C a rate of 48.7 gm/min. was maintained, and a chlorine balance calculated during this period indicated a 105% utilisation of the chlorine feed. The reasons for these high figures for the chlorine balances is discussed below. As the temperature of the bed was reduced a few results were obtained on a curve with a slope expected from the results of previous experiments, but the formation rate soon fell away due to depletion of the oxide in the bed.

The most important result of this run was the high chlorine conversion obtained, approximating 100% of the feed. The rapid falling away of the rate of formation from the values expected from the previous temperature coefficients showed that the runs were being carried out on charges which were too small and could not support chlorination over a wide range of temperature. This feature was accentuated by the rate at which the bed temperature could be altered. In these runs this had been achieved by turning off the power to the furnace at the required maximum temperature and the heat losses from the system had then reduced the temperature of the bed. This cooling rate was, however, insufficient to cover a wide range of temperature before the titanium dioxide content of the bed was reduced below the critical amount.

In the succeeding runs the deficiency of the oxide in the bed was corrected by commencing chlorination with a charge of approximately 1650 gm. and the cooling rate accelerated by blowing cold air through the annular space between the reactor tube and the furnace. By controlling the air rate the desired rate of fall of the bed temperature could be readily obtained.

The results of runs 14 and 15 are given in Tables 11.10 and 11.11. No results were obtained from runs 12 and 13 owing to blockages occurring in the return line from the liquid separation cyclone during each run.

In run 14 formation rates corresponding to 107% conversion of the chlorine feed were again obtained. These high rates threw doubt on the accuracy of the chlorine flowmeter, which was supported by the high chlorine balances also obtained by previous runs. These chlorine balances are given in Table 11.14, and show that in almost all cases the amount of chlorine accounted for lies in the range of 102 to 107%.

Table 11.14
Chlorine Balances on Runs 8 to 15

Run	% Chlorine Accounted for					
	Measured Feed 35 gm./min.			Corrected Feed 36.5 gm/min.		
	Sample 1	Sample 2	Sample 3	Sample 1	Sample 2	Sample 3
8	105	102	99	101	98	95
9	97	101	94.	93	97	90
10	107	106	104	103	102	100
11	105	107		101	103	
14	104	106		100	102	
15	103	102	107	99	98	103

A check calibration showed the flowmeter to have been giving high flow rates due to a dirty float, the delivery rate at a meter reading equivalent to 35 gm/min. being 36.5 gm/min. Recalculation of the chlorine balances on this rate brought these into closer agreement with the theoretical figure. The meter was cleaned and recalibrated before run 16.

The results of run 16 are given in Table 11.12. This run was carried out on a charge of 1690 gm. and at a chlorine rate of 36.5 gm/min., this being the chlorine rate used in the previous runs when corrected for meter error. In this run the conditions of run 15 were repeated, chlorination being commenced at 970°C. During the first twenty six minutes of the run no results were obtained because of Maloperation of the rate meter.

Figure 11.5 shows the measured rate of formation of titanium tetrachloride for runs 14, 15 and 16 plotted against the bed temperature. The procedure of run 14 differed from runs 15 and 16 in that the chlorination was commenced at 907°C and the temperature was then raised to 987°C . It is important to note that as the temperature was raised complete conversion of the chlorine was achieved at 907°C with a bed containing 1100 gm. of rutile and continued for twenty five minutes, by which time the temperature had reached 987°C . and the oxide content of the bed had fallen to 760 gms. After this point the rate fell off although the temperature was still temporarily held at 987°C . As the temperature was reduced the rate came down also and settled onto a line having a slope of 1.66.

Runs 15 and 16 were commenced at 970°C and the temperature was then progressively reduced. In run 15 rates were obtained at the start of the run, which were in excess of the theoretical amount for the chlorine feed, but as the chlorine balances for the remainder of the run show a high order of accuracy, these results can have only been due to high chlorine rates before this was adjusted to the correct figure. For the remainder of the run the results showed little deviation from a line having a slope of 1.66. The results of run 16 are in good agreement with those of run 15, although they are in general slightly higher; at a rate of 30 gm./min. this difference being approximately five percent.

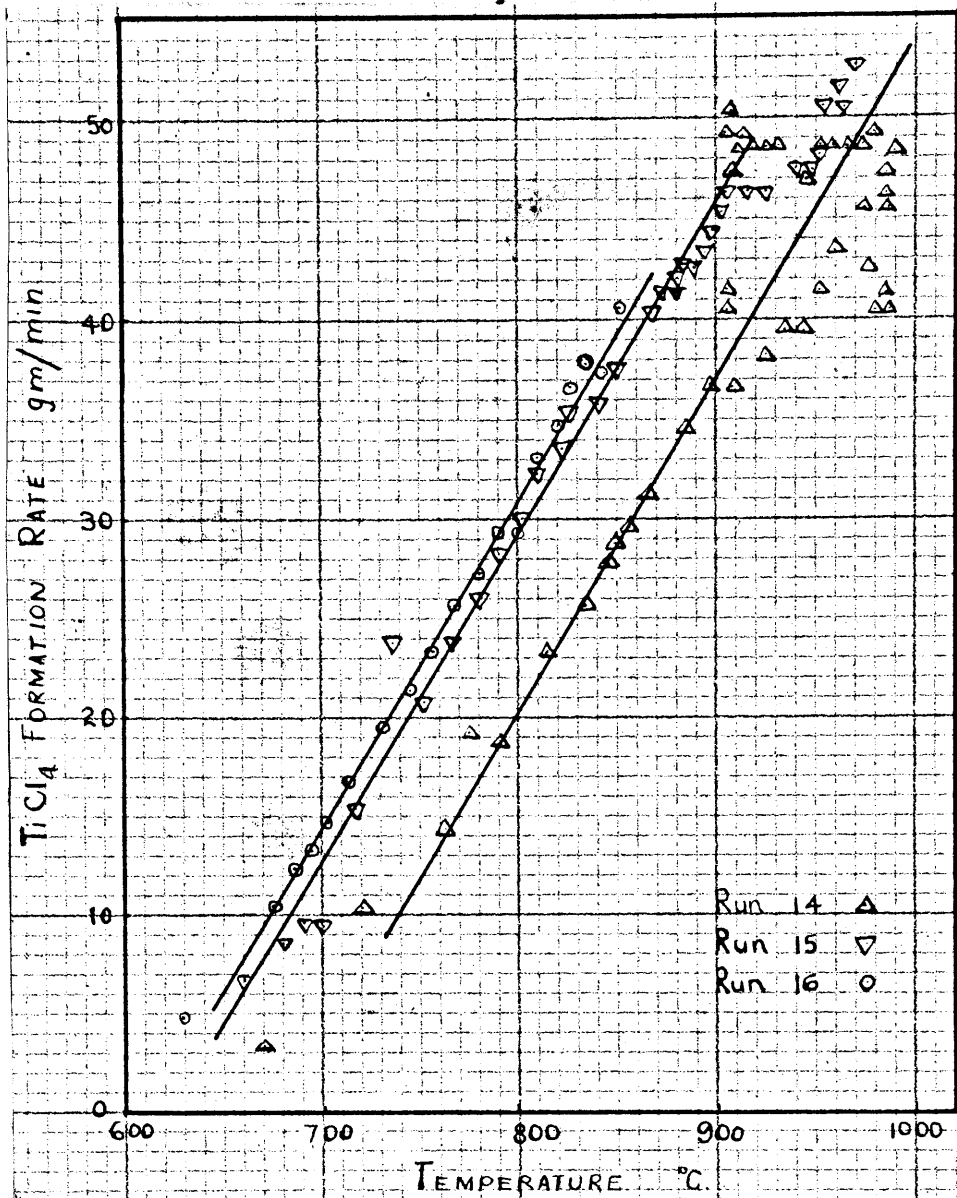
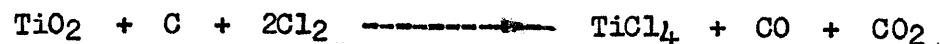


Figure
11.5

Correlation of the Variation of Reaction Rate
with Temperature

From the results obtained during the experiments carried out on Series II and described above, it may be concluded that the reaction of chlorine with rutile to form titanium tetrachloride commences at approximately 400°C and the reaction rate gradually increases yielding at about 600°C sufficient titanium tetrachloride to saturate the tail gas. From approximately 650°C the reaction rate - temperature relationship for the reaction



follows a straight line having a slope on the scales used of 1.66. This data then gives the equation

$$R_t' = 0.166\Delta T + R_t$$

Where

$R_{t'}$ = the rate of formation at $t'^{\circ}\text{C}$ (gm/min)

R_t = the determined rate at $t^{\circ}\text{C}$ (gm/min)

and $\Delta T = (t' - t)$ centigrade degrees

for the rate - temperature relationship for the reaction



from which a temperature coefficient for the reaction rate of 0.166 gm/min/ $^{\circ}\text{C}$ is obtained.

The experimental results of runs 14, 15 and 16 show that this equation holds through the range 650° to 1000°C , which was the maximum temperature obtained. The data at the top of the range does not show the same accuracy as that obtaining at lower temperatures, due to the high chlorine conversion occurring at these temperatures. Below 650°C the points show some flattening of the curve, and it may be expected that the curve would become asymptotic to the temperature axis.

The data does not show ^{the} flattening out of the rate which was obtained by McTaggart, who found no increase in the rate above 700°C . This would seem to indicate that the rates obtained by this worker above 700°C were controlled by either the chlorine feed to the reactor or the weight of oxide in the bed.

The results of runs 11 and 14 have shown that it is possible to obtain complete conversion of the chlorine feed to the reactor. Run 14 shows that complete conversion for a chlorine rate of 36.5 gm/min. and a bed containing 1100 gm. of titanium dioxide could be achieved at 907°C and was maintained at a temperature of 987°C for a bed containing 760 gm. of oxide.

As the rate of the reaction decreases with temperature, a deeper bed would be required to achieve this high degree of conversion.

Composition of the Gas leaving the Condenser

Analysis of the tail gas from the condenser was carried out for chlorine, titanium tetrachloride, carbonyl chloride, carbon monoxide and carbon dioxide, and showed the presence of each of these compounds.

The amount of chlorine in the tail gas depends on the conversion being obtained in the reactor at the time at which a sample was taken, and, as has been discussed, would vary with the temperature and the amount of material in the bed.

As in any system in which a liquid is condensed from a mixture of gas and vapour, the amount of titanium tetrachloride in the tail gas is a function of the temperature at which the gas leaves the condenser, and a comparison of the amount of titanium tetrachloride in the tail gas determined from the chemical analysis and the amounts calculated for saturation at the gas temperature, Table 11.15, shows that the gas contains very little, if any, titanium tetrachloride entrained in the form of liquid drops.

Table 11.15

Run	TiCl ₄ loss in TG.gm/min.	
	Analysis	For Saturation
8	0.9	1.12
9	1.0	1.10
10	1.16	1.39
11	1.48	1.50
14	1.30	1.69
16	1.31	1.70

These results show that the results obtained by chemical analysis are low, as superheating could not occur in the apparatus used. The analytical figures, if in error, would be likely to ere on the low side, as, owing to the construction of the absorption bottles, some difficutly was found in completely removing the hydroxide for ignition and weighing. The values for saturation are therefor considered to be the more accurate, although the errors which would result from use of the analytical values are not large. These higher figures would also result in lower values for the carbonyl chloride, as these were calculated from the total chlorides present.

Small amounts of carbonyl chloride were found in the samples of gas collected, but is considered to have been formed by the reaction of chlorine and carbon monoxide under the influence of light after the gas had left the reactor, as the figures of Godnev and Pamfilov (45) for the equilibrium partial pressure of carbonyl chloride in the range of 400° to 1000°C show that this compound would not be formed at the reaction temperature.

The analysis have shown that both carbon monoxide and carbon dioxide are formed during the reaction. Examination of the composition of the tail gas for runs 3 to 16 on a chlorine and chloride free basis (Table11.16) shows that

reaction temperature is one factor determining the amount of carbon monoxide formed in the bed, an increase in the temperature increasing the amount of carbon monoxide in the tail gas. Other variables are, however, also apparent in which the amount of carbon monoxide in the gas varies although the temperature of the bed remains fairly constant.

In a system in which carbon dioxide, carbon monoxide and solid carbon are present the composition of the gas leaving the bed will be influenced by the reaction,



in which the equilibrium (constant $k_p = \frac{p_{\text{CO}}^2}{p_{\text{CO}_2}}$) will be altered by change in temperature, and the attainment of equilibrium, and consequently the ratio of monoxide to dioxide by the time of contact of the gas mixture with the solid carbon. This would change with change in the weight of the bed and the ratio of carbon to rutile in the bed. The ratio of carbon to rutile in the bed increases in each run as the run proceeds as the beds used initially contained sufficient carbon to maintain the reaction in which carbon monoxide is formed as the only oxygen containing product.

The effect of the increased carbon content of the bed is seen in the results of run 3 in which the temperature was held at 920° to 900°C and the carbon monoxide content rose from 52 to 56%. A similar trend is seen in the results of runs 4 and 6, although in run 7 an opposite trend can be seen. In each of these runs the reduction of the total weight of the bed would tend to decrease the amount of carbon monoxide by lowering the reaction time, although the total pressure of carbon dioxide and monoxide is also lowered by the reduced conversion of chlorine, and it is impossible to completely separate the effects of these three variables.

Table 11.16

Tail Gas Analysis for CO & CO₂ : Chlorine & Chloride free basis

Run and Sample	Bed Temp. °C	CO ₂ %	CO %	Run and Sample	Bed Temp. °C	CO ₂ %	CO%
3 1	820	47.8	52.2	4 1	915	46.8	53.2
2	910	46.2	53.8	2	907	46.1	53.9
3	900	43.2	56.2				
5 1	825	53.6	46.4	6 1	710	61.9	38.2
2	800	56.4	43.6	2	740	63.2	36.8
3	800	62.2	37.8	3	725	66.8	33.2
4	805	62.2	37.8	4	725	62.4	37.6
7 1	615	59.5	40.5	8 1	855	51.3	48.7
4	725	67.2	32.8	2	850	56.8	43.2
5	725	65.0	35.0	3	850	55.8	44.2
6	725	69.6	30.4	4	840	56.2	43.8
9 1	758	59.2	40.8	10 1	988	42.2	57.8
2	750	61.7	38.3	2	987	42.0	58.0
3	725	64.6	35.4	3	915	45.7	54.3
4	690	67.0	33.0	4	928	46.9	54.0
5	735	66.2	33.8	5	895	44.4	55.6
6	765	58.4	41.6				
11 1	975	42.4	57.6	12 1	924	49.7	50.3
2	997	41.3	58.7	2	967	45.0	55.0
3	940	43.5	56.5	3	978	44.2	55.8
4	917	50.7	49.3	4	848	52.4	47.6
5	906	48.6	51.2	5	750	60.1	39.9
6	875	45.8	54.2				
15 1	905	58.4	41.6	16 1	945	51.6	48.4
2	874	56.2	43.8	2	826	54.3	45.7
3	835	62.0	38.0	3	745	61.2	38.8
4	735	64.7	35.3	4	698	72.6	27.4
5	670	67.2	32.8	5	688	67.6	32.4
				6	615	69.4	30.6

In these runs in which the temperature was held constant, or was not varied uniformly throughout the run, the effect of temperature on the composition of the tail gas is best shown by plotting the analysis for carbon monoxide on samples taken at the beginning of each run against temperature. By using the samples taken at the beginning of the run the changes due to the other variables discussed above are reduced to a minimum.

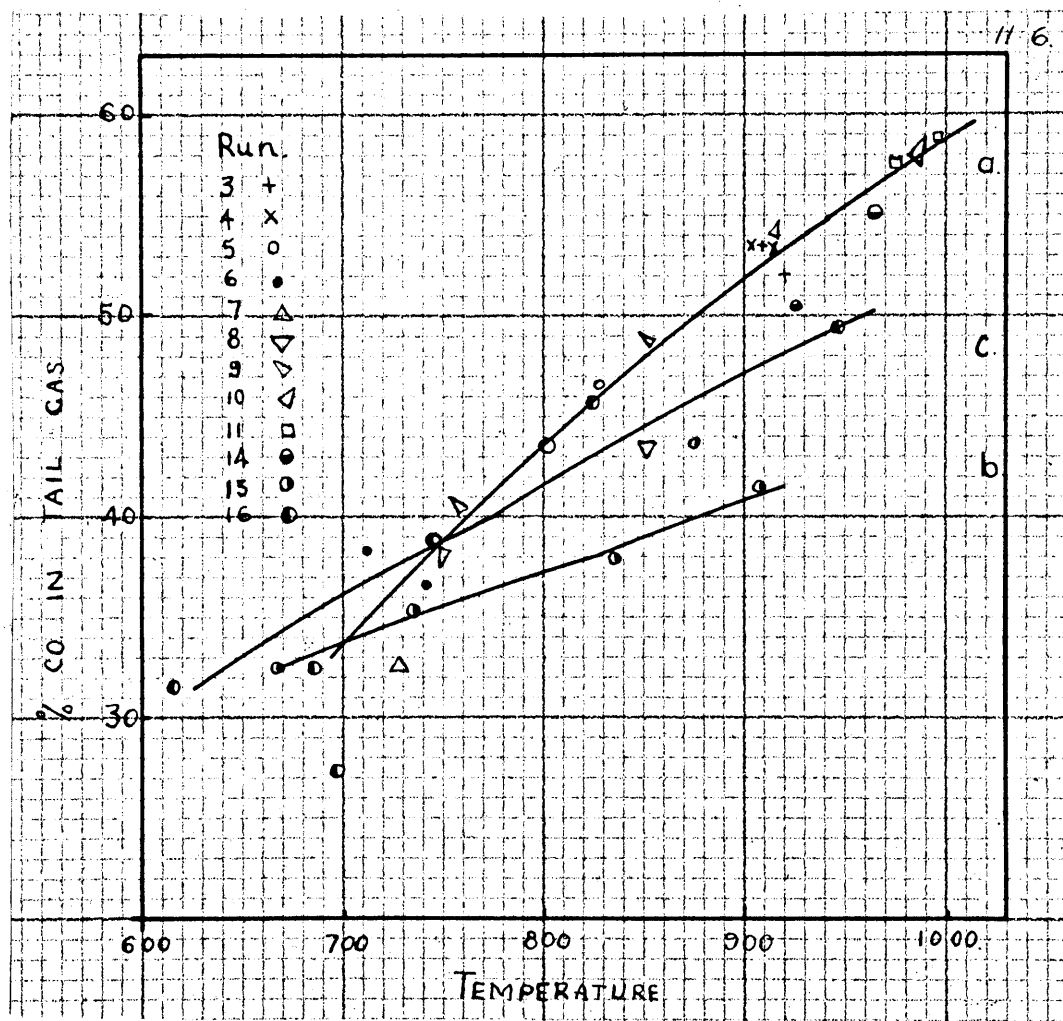


Figure 11.6

Figure 11.6 shows the amount of carbon monoxide in the tail gas, expressed as a percentage on a chlorine and chloride free basis, plotted against the temperature of the bed from which the samples were taken. Three curves are shown; curve 'a' is the plot for the first two samples from each of runs 3 to 14, while curves 'b' and 'c' are the plots for the gas analysis taken during runs 15 and 16 respectively

Although the results plotted for curve 'a' show some scatter, the variation of the percentage of carbon monoxide in the tail gas with the change in temperature can be clearly seen, an increase in temperature from 700° to 1000°C increasing the amount of carbon monoxide formed from approximately 32 to 58%. Similar trends are apparent in curves 'b' and 'c' although in each case the amount of carbon monoxide formed at high temperatures is lower than the amounts formed at similar difference exists for the results of runs 15 and 16 although these runs were carried out under identical chlorination conditions. It is thought that the difference between the carbon monoxide formation for runs 15 and 16 can perhaps be explained by differences in the initial reactivity of the carbon, caused by different heating rates used to bring the bed up to temperature, and the time the bed was held at temperature before chlorination was commenced.

The increased formation of carbon monoxide with increase in temperature would be expected for a system containing carbon monoxide, carbon dioxide and solid carbon, although the theoretical equilibrium (Figure 3.1 Appendix I) is at no time obtained.

These results show the existence of a marked difference between the chlorination of briquettes and the chlorination in a fluid bed. In the chlorination of briquettes the product of the reaction is almost entirely carbon monoxide, while as seen from the above data chlorination in a fluid bed yields between forty and seventy percent carbon dioxide depending on the temperature at which the reaction is carried out. The most obvious explanation of the higher amounts of carbon monoxide obtained in the chlorination of briquettes is the smaller carbon particle size used, the greater intimacy of contact achieved between rutile and carbon, and the lower reactor velocities used, each of which factors would allow a closer approach of the theoretical equilibrium.

McTaggart reported that the chlorination of briquettes at 700°C yielded almost entirely carbon monoxide as the oxygen containing product of the reaction, which is above the theoretical equilibrium (Stansfield -49-) of 59% carbon monoxide for this temperature. This measured temperature is, however, open to question as the true temperature of the reaction, as in the briquette process the measured temperature is that around the briquette, not of the point at which reaction occurs. As the overall reaction taking place is exothermic, the temperature in the briquette could be higher than that measured, which could account for the formation of the larger amounts of carbon monoxide. In the fluid bed process the characteristics of the bed would preclude the existence of such temperature differences.

The high concentrations of carbon dioxide in the tail gas shows it to be one of the basic products of the reaction, as the concentration of carbon monoxide is at all temperatures below the equilibrium concentration, for the

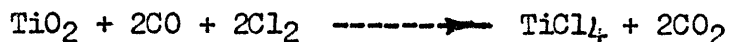
C - CO - CO₂ system

which rules out the possibility of formation of carbon monoxide as the product of reaction followed by decomposition to form carbon dioxide and carbon.

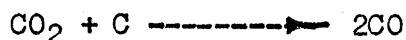
CHAPTER XII

Study of the Mechanism of the Chlorination of Rutile in the Presence of Carbon

As discussed in Chapter III, the theoretical consideration of heterogeneous reactions and the literature on the reaction of chlorine with carbon-rutile mixtures lead to the conclusions that the most likely mechanism for the reaction of chlorine with rutile in the presence of carbon was the adsorption of chlorine and carbon monoxide on the titanium dioxide surface and reaction there to form titanium tetrachloride and carbon dioxide,



followed by the reaction of carbon dioxide with the carbon in the bed to form the carbon monoxide required for the reaction of chlorine with titanium dioxide



The data gained from the experiments on the effects of chlorine velocity, bed depth and temperature on the rate of the reaction offered some support for this mechanism, as these results showed clearly that the reaction formed both carbon dioxide and carbon monoxide, and that the ratio of monoxide to dioxide was governed by the temperature of the bed. As the above mechanism suggested that carbon was not directly involved in the first reaction step it was decided not to investigate the effect of variation of the amount of carbon in the bed on the reaction rate until the chlorination using carbon monoxide instead of carbon had been investigated.

The mechanism of the reaction is, as discussed in Chapter III, best investigated using a flow system in which a stream of gas is passed through the bed, fluidizing the charge and reacting to form titanium tetrachloride and the oxides of carbon.

The order of the reaction with respect to the reactants was investigated by varying the partial pressure of the reactants in the feed, while the effect of the products on the reaction was determined by adding the product to the feed to the reactor and varying its partial pressure by altering the rate of flow of the component to the reactor and adjusting the flow of an inactive carried gas (nitrogen) to maintain a constant total rate of flow. The total pressure of the system was maintained at atmospheric, and the partial pressure of the component in atmospheres was then its fraction of the total flow. For a constant total flow the residence time of the gas in the reactor is constant and for fluid beds the characteristics of the fluidization does not alter greatly.

The order of the reaction with respect to chlorine was investigated by varying the partial pressure of chlorine in the feed to the reactor. For each partial pressure used, a batch chlorination was carried out and the rate of formation of titanium tetrachloride at a known weight of oxide in the bed determined from a plot of the reaction rate versus the instantaneous weight of oxide in the bed. The rates of reaction at a constant weight of oxide in the bed were then plotted against the partial pressure of chlorine, and an order of reaction determined from the curve so obtained. This order of reaction is an apparent order only, the relationship of the true and apparent orders depending on the percentage conversion of the feed at which the rates are measured, as well as the mechanism of the reaction itself.

The products of the reaction could be expected to effect the rate of the reaction in two ways. If the products are not readily desorbed from the surface at which the reaction is taking place, the reaction may be retarded by increase in the concentration of the products in the gas phase which would result in increase in the proportion of the free surface covered by the product;

should the reaction be autocatalysed, the reaction rate would be increased by an increase in the concentration of the product. The reaction mechanism which had been postulated however, precluded this latter possibility, and if there was to be any effect on the rate due to the products, the postulated mechanism suggested that this should be retardation due to the slow desorption of either carbon dioxide or titanium tetrachloride.

The role of the products in the reaction was determined by varying the partial pressure of the product introduced into the feed to the reactor, using the technique described above, plotting the rate of formation of titanium tetrachloride against the partial pressure of the product in the feed. If the rate falls with increase in the partial pressure of the product, the reaction rate is retarded by that product.

The order of reaction with respect to carbon monoxide was determined by holding the chlorine rate constant and varying the feed rates of carbon monoxide and nitrogen to alter the partial pressure of carbon monoxide in the feed, and maintain the total rate of flow constant. The relationship of the rate of formation to the partial pressure of carbon monoxide was then determined as outlined above for chlorine.

In drawing up a detailed programme for investigating the reaction mechanism it was decided to adopt a total rate of flow to the reactor of twelve litres per minute, that is 35.5 gm/min. of chlorine for a chlorine partial pressure of one atmosphere, which rate had been proved in previous runs to give the most satisfactory operation of the experimental apparatus. A temperature of 900°C was selected for the runs as a temperature which gave a high rate of reaction, and which could be readily obtained and controlled during the whole of the batch chlorination. Table 12.1 gives the gas flow

rates and partial pressures for the investigation of the orders of the reaction with respect to chlorine and carbon monoxide, and the effect of the reaction products on the rate of the reaction.

In drawing up this programme it was decided to determine four points on the rate-partial pressure curve for chlorine which with the origin made a total of five points on the curve, and three points on the rate-partial pressure curves for carbon dioxide, carbon monoxide and titanium tetrachloride, making with the origin a total of four points on each curve. If these results showed a marked scatter it would then be possible to do additional runs to fill in the data where needed.

Table 12.1

Flow rates for experiments varying the Partial Pressures of Chlorine, Carbon Dioxide, Titanium Tetrachloride and Carbon Monoxide.

Run	Chlorine		Nitrogen		Carbon Dioxide		Titanium Tetrachloride		Carbon Monoxide	
	PCl ₂ ats.	Feed Rate 1/min.	PN ₂ ats.	Feed Rate 1/min.	PCO ₂ ats.	Feed Rate 1/min.	PTiCl ₄ ats.	Feed Rate 1/min.	PCO ats.	Feed Rate 1/min.
Cl ₂										
1	1.0	12.0	0	0						
2	0.75	9.0	0.25	3.0						
3	0.5	6.0	0.5	6.0						
4	0.25	3.0	0.75	9.0						
CO ₂										
5	0.5	6.0	0	0	0.5	6.0				
6	0.5	6.0	0.2	2.4	0.3	3.6				
7	0.5	6.0	0.35	4.2	0.15	1.8				
TiCl ₄										
8	0.5	6.0	0	0			0.5	6.0		
9	0.5	6.0	0.2	2.4			0.3	3.6		
10	0.5	6.0	0.35	4.2			0.15	1.8		
CO										
11	0.5	6.0	0	0					0.5	6.0
12	0.5	6.0	0.2	2.4					0.3	3.6
13	0.5	6.0	0.35	4.2					0.15	1.8

In this scheme run 3 was common to each correlation.

To eliminate variations due to the particle size of the charge, it was necessary that each run be carried out on rutile and carbon prepared in the same batches. The bulk materials were prepared as described above, but were not mixed until immediately before each run. The materials used had the size analysis shown in Table 12.2.

Table 12.2
Size Analysis of Materials used
in Experimental Series III

Tyler Mesh	% by Weight	
	Rutile	Carbon
65	0.5	14.5
100	32.5	52.0
150	71.5	75.0
200	85.5	89.5
-200	100.0	100.0

which gave average particle sizes of 0.0053 ins. and 0.0058 ins. for rutile and carbon respectively. The rutile, as in the previous batches, analysed 97.5% titanium dioxide, while the petroleum coke analysed 2.3% volatiles, 97.5% fixed carbon and 0.2% ash.

As in the previous runs the charge was prepared with the stiochiometric amount of carbon for the conversion of all the oxygen in the rutile to carbon monoxide, and for these runs a charge weight of 700 gms. was selected. As it is necessary to determine the rate of formation of titanium tetrachloride for small conversion of the chlorine feed this required that the rate be determined at the end of the run when surface area of the material in the bed available for reaction was small. As the particle size of the material in the bed changes as the run proceeds this means that the rates must be determined for each run at the same weight of oxide in the bed, and that each runs must start

from the same weight and particle size of charge. Under these conditions equal amounts of oxide would be removed from the bed resulting in similar changes in the particle size for each run.

In the preliminary runs carried out before the determinations were commenced it was found that increased tail gas rates due to the addition of nitrogen to the system resulted in the carryover of too much ferric chloride, blockages of the fog separation system and inaccurate rate measurement, and it was once again necessary to modify the equipment to correct this fault. The apparatus used for this purpose is shown in Figure 7.8 in Chapter VII.

The Effect of Chlorine on the Reaction

The results of the runs carried out to investigate the order of the reaction with respect of chlorine are given in Tables 12.3 to 12.7. Run 3 (Table 12.5) was repeated in Table 12.6 due to the low values obtained for the chlorine balances which were thought to be caused by low chlorine rates resulting from bad control of the chlorine flow to the reactor.

Table 12.3

Run 1

Time Run Min.	TiCl ₄ Rate gm/min.		TiO ₂ Remov. Rate gm/min.	Weight TiO ₂ in Bed gm.	
	Measured	Total			
3.0	37.5	38.9	16.4	476	
4.5	37.5	38.9	16.4	452	
7.0	36.5	37.9	16.0	412	
8.0	33.6	35.0	14.8	396	
9.0	34.8	36.2	15.3	381	
10.0	35.0	36.4	15.3	365	
11.5	33.6	35.0	14.8	343	
13.0	35.2	36.6	15.4	320	
14.0	33.6	35.0	14.8	306	
15.0	29.4	30.8	13.0	291	<u>Charge:</u> 700 gm.
16.5	32.4	33.8	14.3	267	<u>Temp.:</u> 900°C
18.0	31.8	33.2	14.0	249	<u>PCl₂</u> : 1.0 ats.
19.5	29.2	30.6	12.9	229	<u>Cl₂ Rate:</u> 12.0 l/min. 35.5 gm/min.
21.0	27.8	29.2	12.3	210	
22.0	27.8	29.2	12.3	197	<u>PN₂</u> : 0.0 ats.
24.0	28.0	29.4	12.4	174	
25.0	25.8	27.2	11.5	162	<u>Residues:-</u>
27.0	22.9	24.3	10.3	141	Reactor: 140 gm.
29.0	20.6	22.0	9.3	121	Annulus: 140 gm.
31.0	18.6	20.0	8.4	103	Cyclone: 4 gm.
33.0	17.2	18.6	7.8	87	
34.0	17.3	18.7	7.9	79	<u>Chlorine Balance</u>
35.0	15.4	16.8	7.1	72	Time % Accounted
36.0	14.0	15.4	6.5	65	Run
38.0	11.4	12.8	5.4	53	Min.
40.0	10.6	12.0	5.1	43	13 97.5
42.0	7.9	9.3	3.9	34	23 93.0
					33 96.0

Tail Gas Data

Barometer 761 mm.Hg.

Time Run Min.	Temp. °C	Rate gm/min.	Analysis %				
			Cl ₂	TiCl ₄	CO ₂	CO	N ₂
13	26.5	20.2	24.3	1.64	40.6	33.6	
23	26.5	22.5	32.8	1.64	33.1	32.5	
33	27.0	26.4	65.6	1.71	14.8	18.0	

Table 12.4.

Run 2

Time Run Min.	TiCl ₄ Rate gm/min.		TiO ₂ Remov. Rate gm/min.	Weight TiO ₂ in Bed gm.	
	Measured	Total			
11.0	28.8	30.8	13.0	387	
12.5	28.8	30.8	13.0	368	
13.0	27.4	29.4	12.4	362	
14.0	27.8	29.8	12.4	350	
14.5	27.8	29.8	12.4	350	
14.5	26.1	28.1	11.8	344	
15.5	25.8	27.8	11.7	332	
16.0	25.1	27.1	11.4	326	
17.0	25.9	27.9	11.8	314	
17.75	24.3	26.3	11.1	306	
18.75	24.4	26.4	11.1	295	
19.5	26.6	28.6	12.1	287	
20.5	23.9	25.9	10.9	276	
21.0	23.6	25.6	10.8	270	
22.0	23.9	25.9	10.9	260	
23.0	22.6	24.6	10.4	249	
24.0	21.8	23.8	10.0	239	
24.75	21.4	23.4	9.9	231	
25.75	23.0	25.1	10.6	221	
26.5	21.5	23.6	10.9	215	
27.5	21.8	23.9	11.1	206	
28.5	20.6	22.7	9.6	196	
29.5	20.8	22.9	9.6	187	
30.0	20.8	22.9	9.6	187	
30.5	18.8	20.9	8.8	177	
31.75	19.0	21.1	8.9	166	
32.5	18.0	20.1	8.5	160	
34.0	17.9	20.1	8.5	146	
35.0	16.4	18.6	7.8	137	
36.25	18.4	20.6	8.7	127	
37.25	15.1	17.3	7.3	120	
38.75	15.0	17.3	7.3	108	

Charge: 700 gm.

Temp.: 900°C

PCl₂: 0.75 ats.

Cl₂: Rate 91/min.
- 26.6 gm/min.

PN₂: 0.35 ats.

N₂ Rate: 3 l/min.
= 3.5 gm/min.

Residues:

Reactor 153 gm.

Annulus 153 gm.

Cyclone 9 gm.

Chlorine Balance:

Time Run Min.	% Accounted
19	97.5
29	98.0
39	104.0

Table 12.4. Continued

Time Run Min.	TiCl ₄ Rate gm/min.		TiO ₂ Remov. Rate gm/min.	Weight TiO ₂ in bed gm.			
	Measured	Total					
40.0	14.7	17.0	7.2	99			
41.5	14.1	16.4	6.9	89			
43.0	12.3	14.6	6.2	79			
45.0	10.3	12.6	5.3	68			
47.0	8.7	11.0	4.6	58			
Tail Gas Data							
Barometer 752 mm.Hg.							
Time Run Min.	Temp. °C	Rate gm/min.	Analysis % by Volume				
			Cl ₂	TiCl ₄	CO ₂	CO	N ₂
19	32.5	19.3	19.9	2.47	23.3	22.1	37.8
29	32.5	21.3	28.6	2.47	16.9	17.5	33.3
39	32.3	24.7	41.1	2.47	11.5	13.8	31.4

Table 12.5

Run 3

Time Run Min.	TiCl ₄ Rate gm/min.		TiO ₂ Remov. Rate gm/min.	Weight TiO ₂ in Bed gm.	
	Measured	Total			
6.0	11.8	13.5	5.7	462	
7.0	15.1	16.8	7.1	456	
8.5	16.0	17.7	7.45	439	
9.75	16.1	17.8	7.5	430	
11.0	15.0	16.7	7.0	421	
12.5	14.4	16.1	6.8	410	
14.0	15.3	17.0	7.2	400	
15.0	15.2	16.9	7.1	393	<u>Charge:</u> 700 gm.
16.5	14.0	15.7	6.6	382	<u>Temp.:</u> 900°C
18.0	14.5	16.2	6.8	372	<u>Partial Pressure:</u>
19.5	14.4	16.1	6.8	361	Cl ₂ : 0.5 ats.
20.5	15.0	16.7	7.0	355	N ₂ : 0.5 ats.
22.0	13.8	15.5	6.5	344	<u>Flows to React.:</u>
23.5	14.3	16.0	6.7	334	Cl ₂ : 6 l/min.
25.0	14.2	15.9	6.7	324	17.75 gm/min.
26.0	14.2	15.9	6.7	318	N ₂ : 6 l/min.
28.0	13.5	15.2	6.4	305	7 gm/min.
29.5	13.9	15.6	6.6	295	<u>Residues:</u>
31.0	13.6	15.3	6.4	285	Reactor: 137.5 gm.
32.0	12.9	14.6	6.1	279	60.6% TiO ₂
34.0	12.9	14.6	6.1	267	Cyclone: 7.5 gm.
35.5	11.9	13.6	5.7	258	10.3% TiO ₂
37.0	13.5	15.2	6.4	248	
38.5	12.6	14.3	6.0	239	
40.5	12.1	13.8	5.8	228	
42.0	11.9	13.6	5.7	219	
44.0	12.2	13.9	5.9	208	
45.0	11.6	13.3	5.6	202	
47.0	12.2	13.9	5.9	191	
49.0	11.5	13.2	5.6	180	
51.0	10.2	11.9	5.0	169	

Table 12.5 Continued

Time Run Min.	TiCl ₄ Rate gm/min.		TiO ₂ Remov. Rate gm/min.	Weight TiO ₂ in Bed gm.	<div>Chlorine Balances:</div> <table><tr><th>Time Run Min.</th><th>% Accounted</th></tr><tr><td>15</td><td>92.5</td></tr><tr><td>31</td><td>90.0</td></tr><tr><td>50</td><td>96.0</td></tr></table>	Time Run Min.	% Accounted	15	92.5	31	90.0	50	96.0
	Time Run Min.	% Accounted											
15	92.5												
31	90.0												
50	96.0												
Measured	Total												
54.0	10.4	12.1	5.1	154									
56.0	10.0	11.7	4.9	143									
58.5	10.2	11.9	5.0	131									
60.0	9.5	11.2	4.7	123									
62.0	9.9	11.6	4.9	114									
64.0	9.2	10.9	4.6	104									
66.5	8.1	9.8	4.1	93									
69.0	8.6	10.3	4.3	82									
71.0	8.6	10.3	4.3	74									
73.5	7.7	9.4	4.0	64									
77.0	6.4	8.1	3.4	51									
79.5	6.0	7.7	3.2	42									

Tail Gas Data			Barometer 763 mm.Hg.				
Time Run Min.	Temp. °C	Rate gm./min.	Analysis % by volume				
			Cl ₂	TiCl ₄	CO ₂	CO	N ₂
15	29	17.0	12.0	2.04	14.0	15.7	57.2
31	29	17.3	14.5	2.04	10.5	14.0	59.0
50	29	18.2	18.6	2.04	9.9	11.5	57.2

Table 12.6

Run 3A

Time Run Min.	TiCl ₄ Rate gm/min.		TiO ₂ Remov. Rate gm/min.	Weight TiO ₂ in Bed gm.	
	Measured	Total			
5.5	13.8	15.7	6.6	463	
6.75	15.3	17.2	7.2	454	
8.0	16.9	18.8	7.9	445	
9.0	17.7	19.6	8.3	437	
10.25	18.5	20.4	8.6	426	
11.25	17.7	19.6	8.3	416	
12.5	18.8	20.7	8.7	406	
15.0	18.0	19.9	8.4	384	<u>Charge:</u> 700 gm.
16.0	18.1	20.0	8.4	376	<u>Temp.:</u> 900°C
17.0	17.7	19.6	8.3	368	<u>Partial Pressure:</u>
18.0	17.3	19.2	8.1	359	Cl ₂ : 0.5 ats.
19.5	17.3	19.2	8.1	359	N ₂ : 0.5 ats.
19.5	17.6	19.5	8.2	347	<u>Flows to Reactor:</u>
20.5	17.5	19.4	8.2	339	Cl ₂ : 6 l./min.
22.0	17.0	18.9	8.0	327	17.75 gm/min.
23.0	16.8	18.7	7.9	319	N ₂ : 6 l./min.
24.25	16.1	18.0	7.6	310	7 gm./min.
25.5	16.2	18.1	7.6	300	<u>Residues:</u>
28.0	16.7	18.6	7.8	281	<u>Reactor</u> 121 gm.
29.25	16.3	18.2	7.7	272	51.8% TiO ₂
30.25	16.0	17.9	7.5	265	<u>Cyclone</u> 11 gm.
32.0	14.7	16.6	7.0	252	18.2% TiO ₂
33.0	14.4	16.3	6.9	245	
34.5	14.5	16.4	6.9	235	
36.0	14.0	15.9	6.7	225	
37.5	13.7	15.6	6.6	215	
39.0	13.3	15.2	6.4	205	
40.5	13.2	15.1	6.4	197	
42.0	12.5	14.4	6.1	186	
43.75	12.6	14.5	6.1	178	
45.0	12.2	14.1	5.9	168	
47.0	12.5	14.4	6.1	156	
48.5	11.1	13.4	5.5	147	

Table 12.6 Continued

Time Run Min.	TiCl ₄ Rate gm/min.		TiO ₂ Remov. Rate gm/min.	Weight TiO ₂ in Bed gm.			
	Measured	Total					
50.25	11.5	13.4	5.6	138	<u>Chlorine Balances:</u> Time Run Min. % Accounted 20 103.0 40 95.0 60 96.0		
52.0	11.9	13.8	5.8	128			
54.0	10.3	12.2	5.1	118			
55.5	10.1	12.0	5.1	111			
57.75	9.5	11.7	4.9	99			
59.5	9.1	11.0	4.6	90			
62.0	9.4	11.3	4.8	78			
63.5	9.3	11.2	4.7	74			
66.5	8.4	10.3	4.3	59			
68.5	8.3	10.2	4.3	51			
71.25	7.2	9.1	3.8	40			
74.0	5.3	7.2	3.0	30			
80.0	1.9	3.8	1.6	18			
Tail Gas Data					Barometer 759 mm.Hg.		
Time Run Min.	Temp. °C	Rate gm/min.	Analysis % by Volume				
			Cl ₂	TiCl ₄	CO ₂	CO	N ₂
20	29.5	16.9	12.1	2.10	15.0	13.6	57.5
40	30.0	18.5	17.2	2.17	11.5	11.9	57.6
60	30.5	20.6	24.7	2.24	8.2	9.3	55.7

Table 12.7

Run 4

Time Run Min.	TiCl ₄ Rate gm/min.		TiO ₂ Remov. Rate gm/min.	Weight TiO ₂ in Bed gm.	
	Measured	Total			
7.5	7.3	9.4	4.0		
10.0	8.6	10.7	4.5	434	
12.0	8.8	10.9	4.6	425	
14.0	8.7	10.8	4.5	416	
16.5	8.7	10.8	4.5	404	
18.5	8.3	10.4	4.4	395	
21.0	9.6	11.7	4.9	384	
23.0	10.4	12.5	5.3	375	<u>Charge:</u> 700 gm.
26.0	8.8	10.9	4.6	362	<u>Temp.:</u> 900°C
28.0	8.2	10.3	4.3	351	<u>Partial Pressure:</u>
30.5	7.9	10.0	4.2	342	Cl ₂ : 0.25 ats.
33.0	8.3	10.4	4.4	332	N ₂ : 0.75 ats.
35.5	7.3	9.4	4.0	321	<u>Flows to Reactor:</u>
38.0	7.5	9.6	4.0	311	Cl ₂ : 3.0 l./min.
40.5	7.5	9.6	4.0	300	8.88 gm/min.
43.0	8.2	10.3	4.3	289	N ₂ : 9.0 l./min.
45.0	8.9	11.0	4.6	282	10.5 gm/min.
47.5	7.6	9.7	4.1	272	<u>Residues:</u>
50.5	7.2	9.3	3.9	260	Reactor: 170 gm.
53.0	7.2	9.3	3.9	250	67.6% TiO ₂
56.0	7.3	9.4	4.0	238	Cyclone: 11.5 gm.
58.5	7.2	9.3	3.9	228	19.6% TiO ₂
61.5	7.0	9.1	3.8	217	
64.0	6.8	8.9	3.7	207	
67.0	7.6	9.7	4.1	196	
70.0	6.3	8.4	3.5	186	
73.5	5.9	8.0	3.4	173	
76.5	5.7	7.8	3.3	165	
80.0	5.7	7.8	3.3	152	

Table 12.7 Continued

Time Run Min.	TiCl ₄ Rate gm/min.		TiO ₂ Remov. Rate gm/min.	Weight TiO ₂ in Bed gm.	<u>Chlorine Balances:</u>		
	Measured	Total					
83.5	5.4	7.5	3.2	140	Time Run Min.	% Accounted	
87.5	5.8	7.9	3.3	123			
90.5	5.1	7.2	3.0	119			
95.0	4.5	6.6	2.8	106			
99.0	4.4	6.5	2.7	95			
104.0	4.1	5.2	2.6	82			
Tail Gas Data					Barometer 760 mm.Hg.		
Time Run Min.	Temp. °C	Rate gm/min.	Analysis % by Volume				
			Cl ₂	TiCl ₄	CO ₂	CO	N ₂
29	30.0	17.1	3.2	2.17	7.4	8.6	78.7
59	29.5	17.5	6.7	2.11	5.8	6.8	78.5
79	29.5	18.6	8.8	2.11	5.7	7.5	75.0

Table 12.8 shows the titanium dioxide balances, the bed temperature at the top thermocouple and the temperature difference between the thermocouples for the bed containing 100 gm. of TiO_2 for the runs.

Table 12.8

Run	TiO_2 Balance %	Bed Temp. $^{\circ}\text{C}$	Temp. Diff. $^{\circ}\text{C}$
1	106	895	5
2	98	894	4
3R	102	897	5
4	97.5	898	10

These results together with the chlorine balances given in tables 12.3 to 12.7 show that a high accuracy was obtained in the control of the temperature chlorine rate and the measurement of the titanium tetrachloride rate, and hence errors resulting from these sources are small.

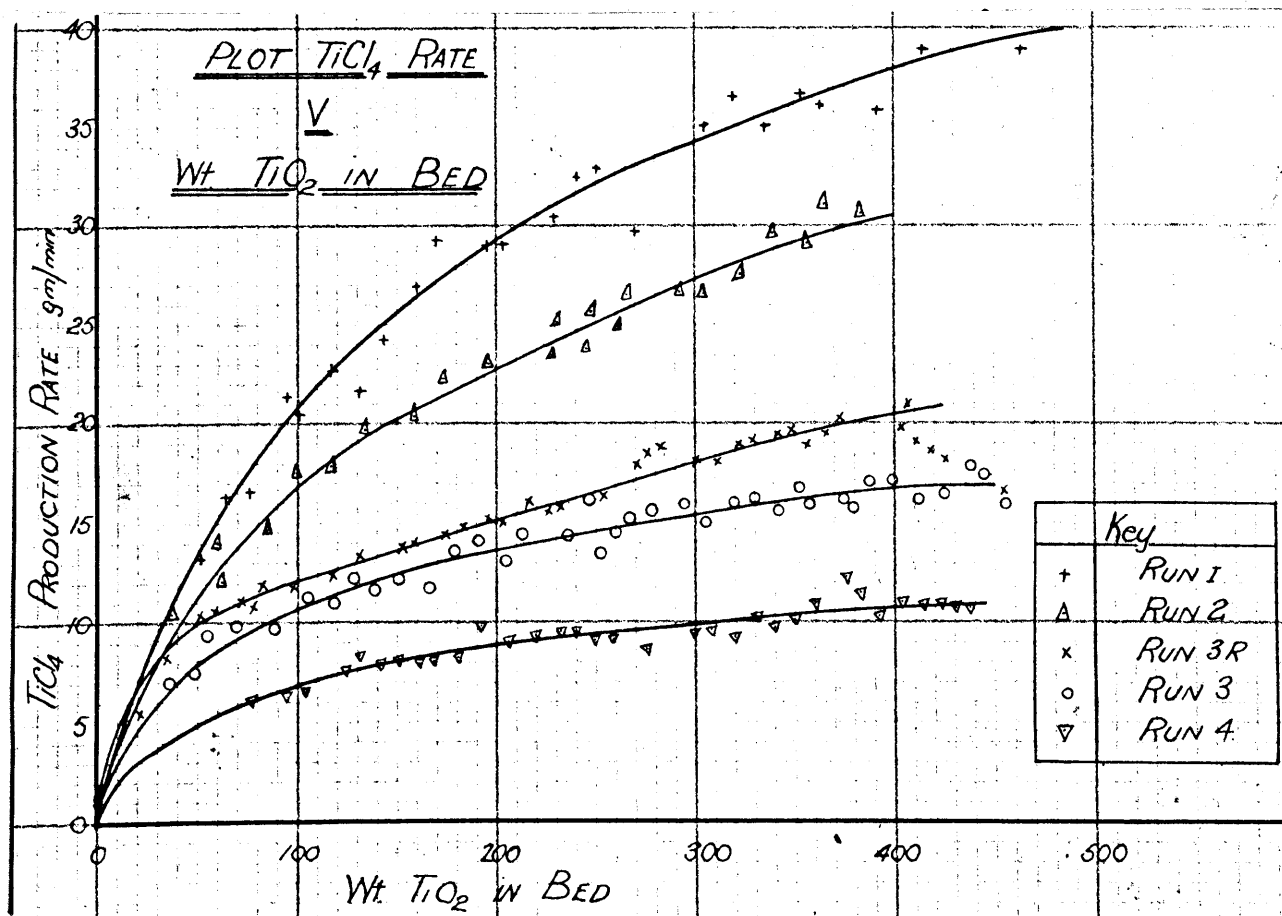
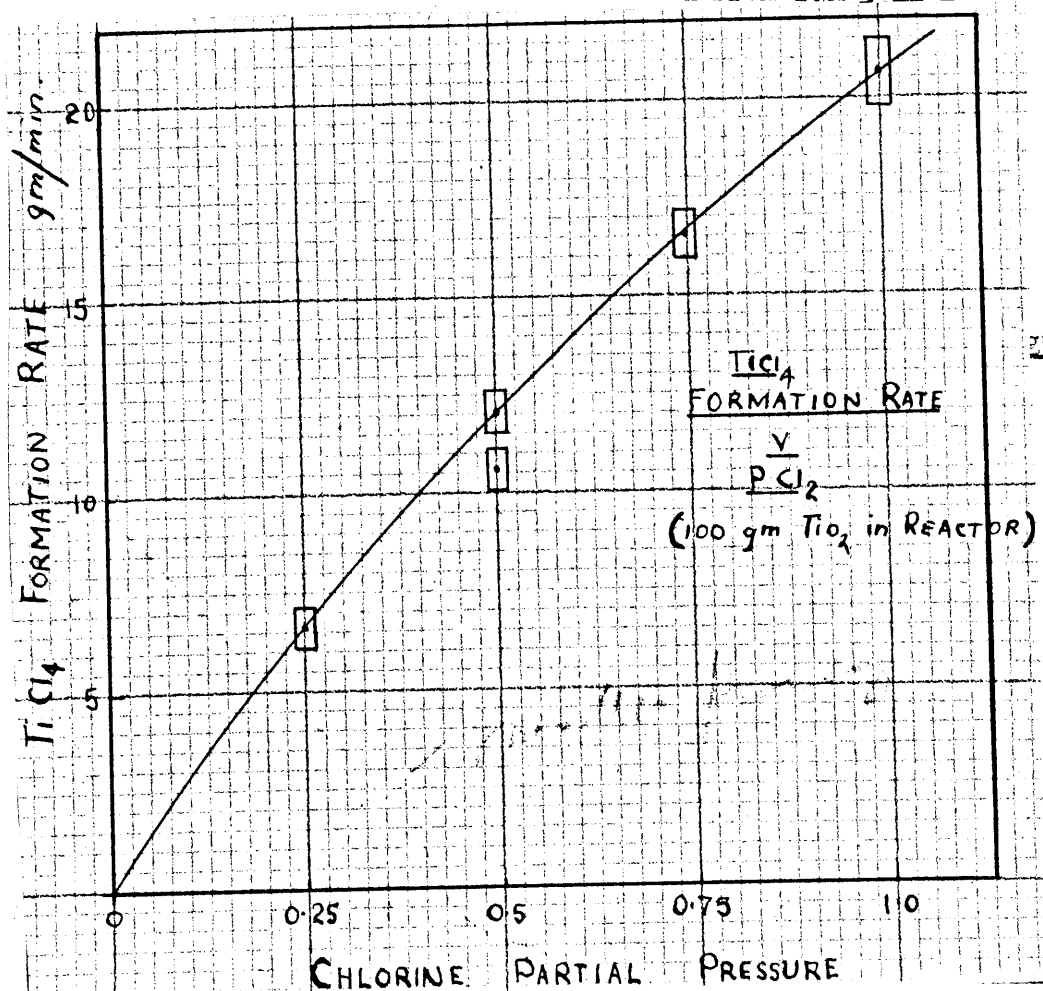


Figure 12.1

The results of these runs are plotted in Figure 12.1, which shows a plot of the titanium tetrachloride formation rate versus the weight of oxide in the bed. These results, as the results for the correlation of the runs in series I experiments, follow a smooth logarithmic curve. Those points which fall away from the curve during the main part of the run can usually be correlated with variation in the chloride rate, while the low rates at the end of the runs can be correlated with low bed temperatures due to poor temperature control in shallow beds. This was a limitation of the apparatus.

Figure 12.2 shows the plot of the rate of formation of titanium tetrachloride for beds containing 100 gms. of titanium dioxide against the chlorine partial pressure in the gas to the reactor for the respective runs. The results for runs 1, 2, 3R and 4 fall on a smooth curve, while as anticipated from the chlorine balances the results obtained from run 3 is low.



The chlorine conversion for the four runs at 100 gms. of titanium dioxide in the bed is plotted against the partial pressure of chlorine in the feed to the reactor in Figure 12.3, showing that the conversion decreases with increase in the partial pressure, falling between 44 and 59%, which values are too high to allow any useful determination of the order of the reaction.

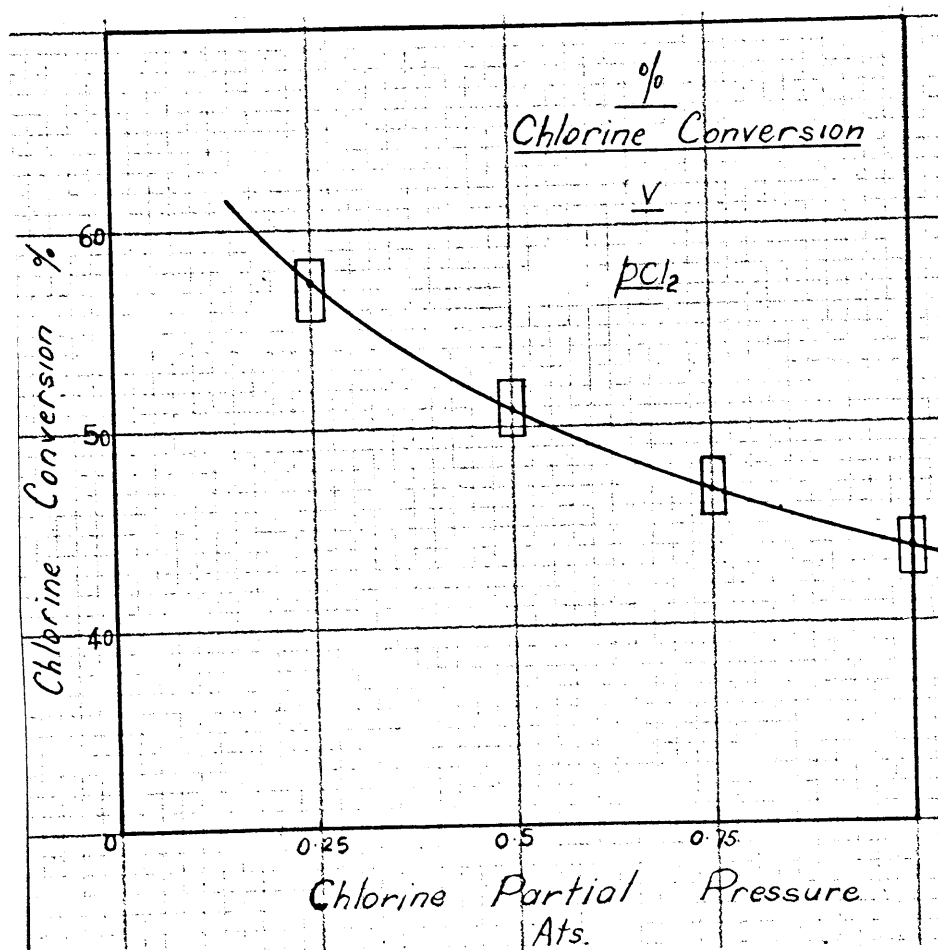


Figure 12.3

Inspection of the curves for the plot of rate of formation of titanium tetrachloride against the weight of oxide in the bed show that values for lower conversion cannot with accuracy be taken from this plot, due to the inaccuracy which was inherent in the apparatus in the control of the temperature for shallow beds, but a plot of the results on logarithmic coordinates gave a straight line correlation which could be safely extrapolated. This plot for the results of runs 1,2,3R and 4 are shown in Figure 12.4. The results of runs 2,3R and 4 all show good linear correlations between 80 and 400 gms. of rutile in the bed although there is some

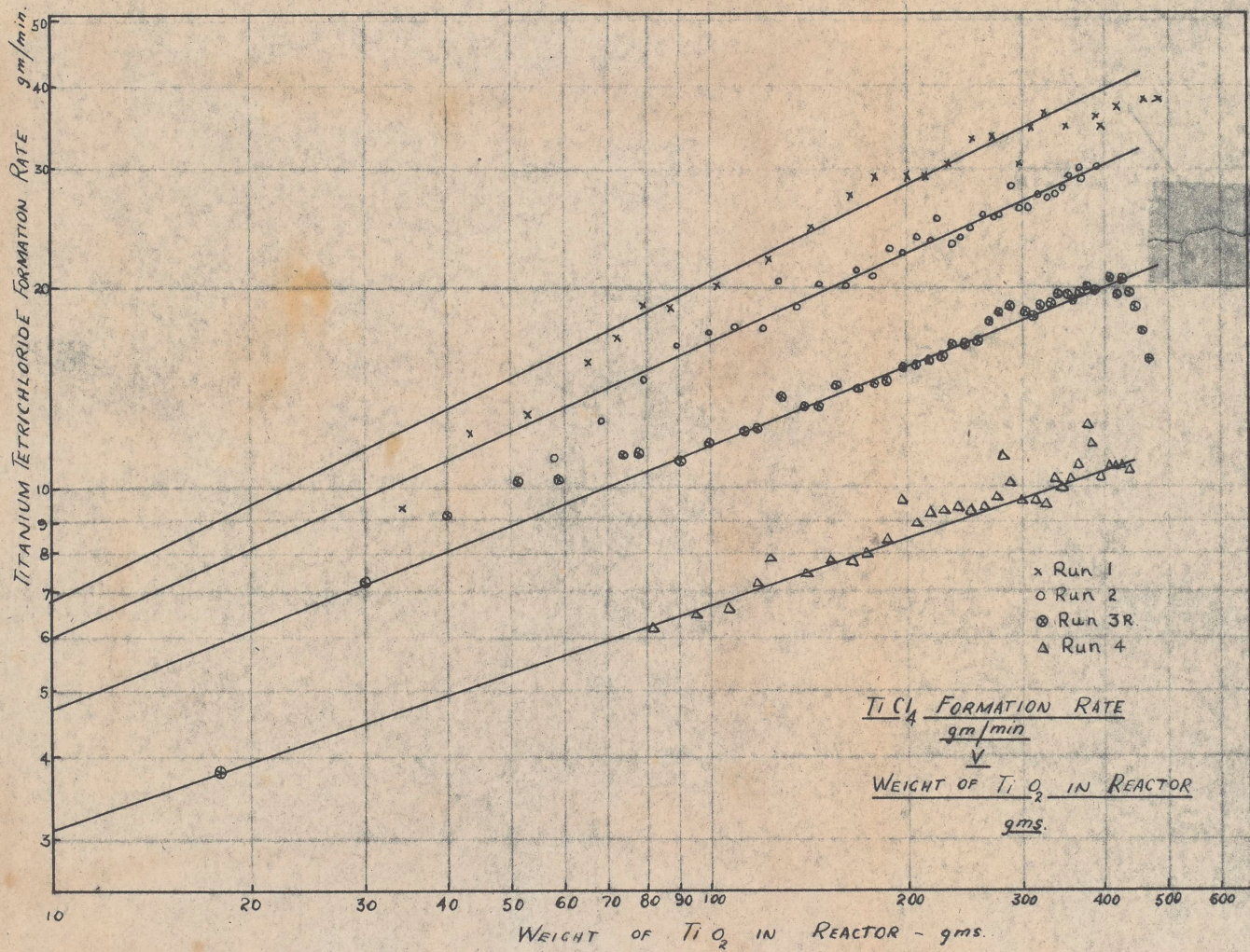


Figure 12.5 shows the plot of the titanium tetrachloride formation rate at 10 gms. of oxide in the bed taken from the extrapolated curves of Figure 12.4 plotted against the partial pressures of chlorine in the feed to the reactor on linear coordinates. These results fall on a smooth curve. Replotting of the results of logarithmic coordinates, Figure 12.6, yields a straight line with an equation

$$\frac{dx}{dt} = 7.0 p^{0.595}$$

where $\frac{dx}{dt}$ = the rate of formation of titanium tetrachloride in gms. per minute
and p = the partial pressure of chlorine in atmospheres.

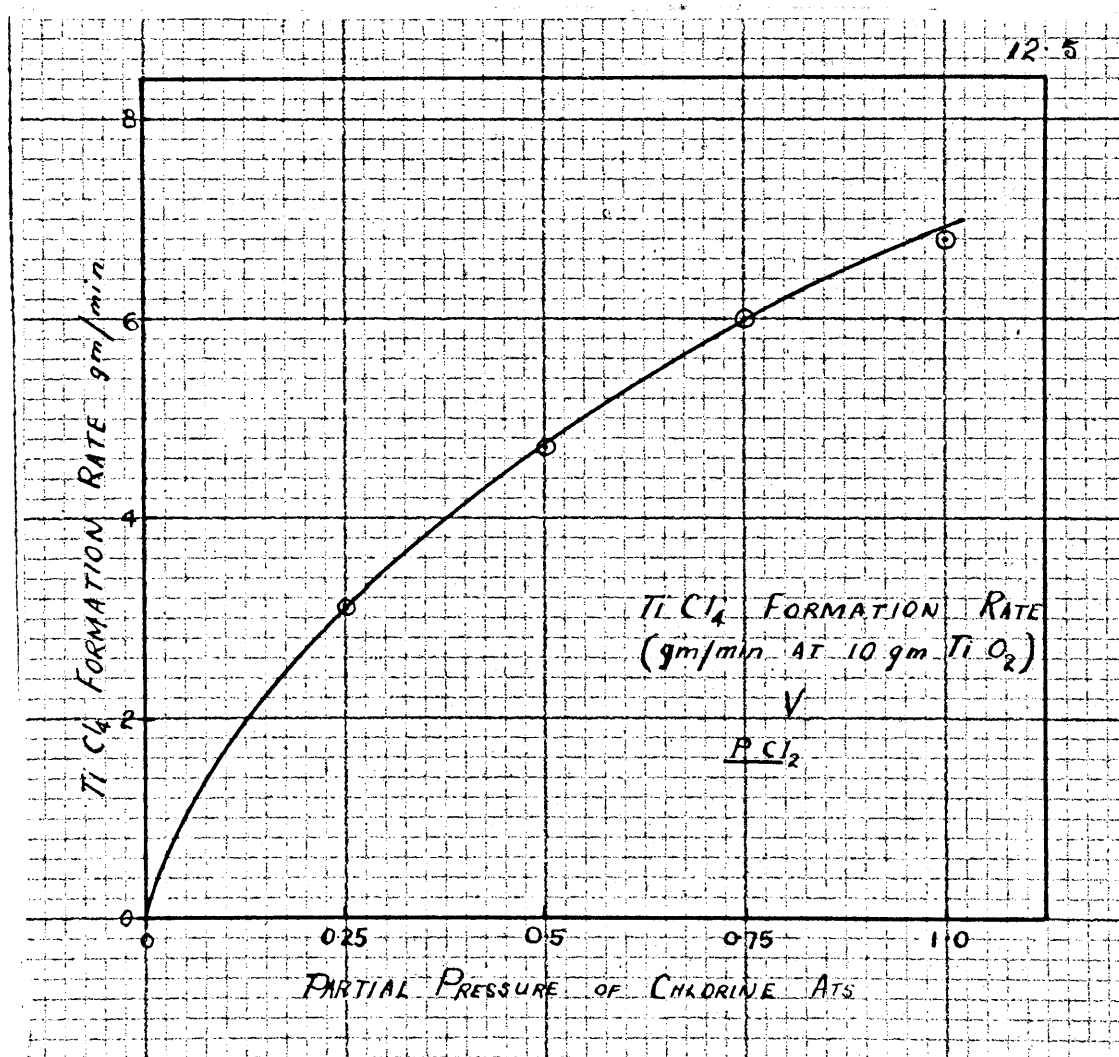


Figure 12.5

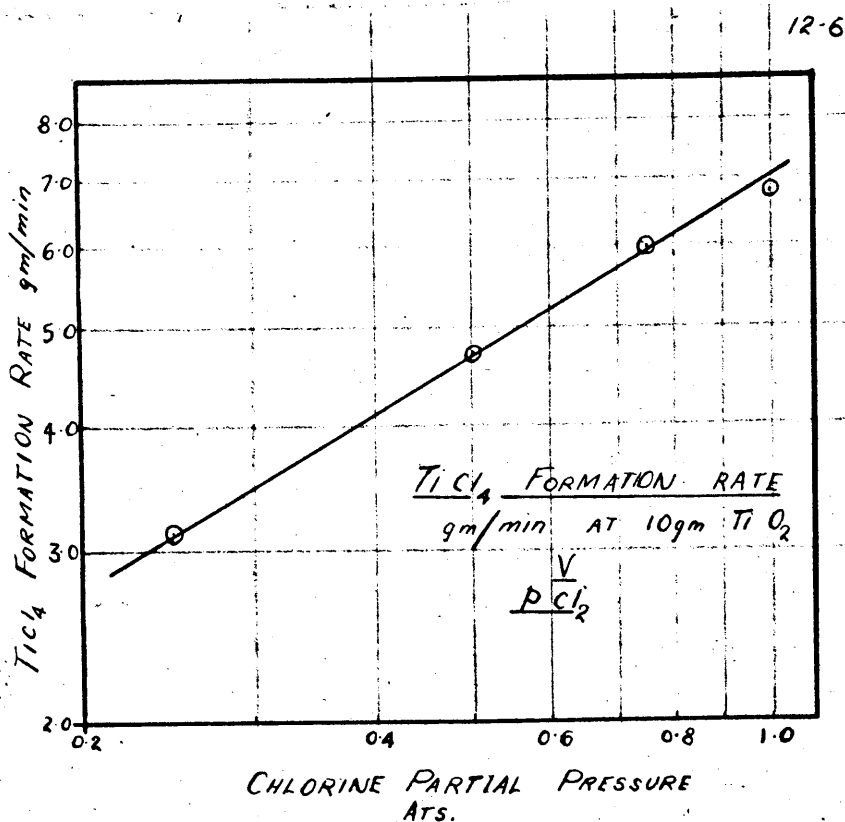


Figure 12.6

These results show that the reaction is of a fractional apparent order (0.6) with respect to chlorine. This order of reaction is determined for chlorine conversions between 14.3 and 26.9%.

The effect of Carbon Dioxide on the Reaction

The effect of carbon dioxide on the reaction was investigated by adding the gas to the feed to vary the partial pressure of carbon dioxide in the reactor. The flow rate of chlorine was kept constant at six litres per minute while the carbon dioxide rate was varied and the nitrogen rate adjusted to maintain a total flow of twelve litres per minute in all experiments, thus holding the chlorine partial pressure at 0.5 ats. while the partial pressure of carbon dioxide was varied between zero and 0.5 ats. as shown in Table 12.1. These experiments were carried out in runs 5, 6 and 7 in the manner previously described, the carbon dioxide and nitrogen rates being set before the chlorine feed was commenced.

The results of these runs are tabulated in Tables 12.9 to 12.11 and plotted in Figures 12.7 to 12.9, which show the titanium tetrachloride production rate plotted against the weight of oxide in the bed.

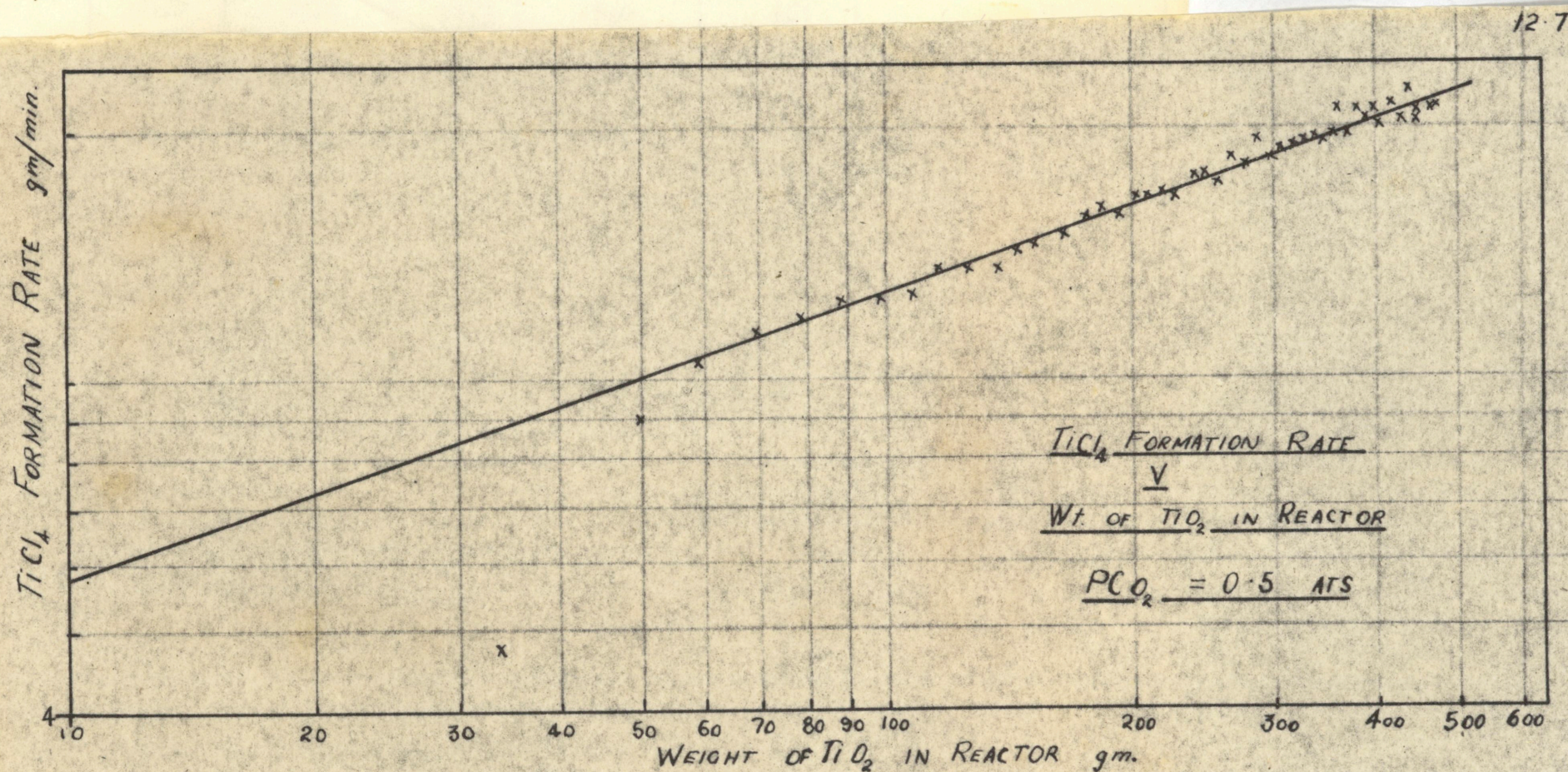


Figure 12.7

Table 12.9

Run 5

Time Run Min.	TiCl ₄ Rate gm/min.		TiO ₂ Remov. Rate gm/min.	Weight TiO ₂ in Bed gm.	
	Measured	Total			
5.0	20.2	21.7	9.2	470	
6.0	19.8	21.3	9.0	461	
7.5	19.8	21.3	9.0	447	
8.0	19.4	20.9	8.8	442	
9.5	21.0	22.5	9.4	433	
10.5	19.4	20.9	8.8	424	<u>Charge:</u> 700 gm.
11.5	20.2	21.7	9.2	413	<u>Temp.:</u> 900°C
12.5	18.8	20.3	8.6	404	<u>Partial Pressure:</u>
13.5	19.6	21.1	8.9	395	Cl ₂ : 0.5 ats.
14.5	19.4	20.9	8.8	386	CO ₂ : 0.5 ats.
15.5	19.6	21.1	8.9	377	N ₂ : 0.0 ats.
16.5	18.4	19.9	8.4	368	<u>Flows to React.</u>
18.0	19.8	21.3	9.0	355	Cl ₂ : 61./min.
18.75	18.4	19.9	8.4	350	17.75 gm/min.
20.0	17.8	19.3	8.1	340	CO ₂ : 6 1./min.
21.0	18.2	19.7	8.3	331	11.0 gm./min.
22.25	18.0	19.5	8.2	321	N ₂ : 0.0 1./min.
23.25	17.6	19.1	8.0	313	<u>Residues:</u>
24.5	17.5	19.0	8.0	303	Reactor: 132 gm.
25.5	17.0	18.5	7.8	295	58.7% TiO ₂
26.75	18.0	19.5	8.2	285	Cyclone: 14.5 gm.
28.0	16.5	18.0	7.6	275	16.2% TiO ₂
29.25	17.1	18.6	7.8	265	
30.25	15.7	17.2	7.3	258	
31.25	16.2	17.7	7.5	246	
32.75	16.3	17.8	7.8	239	
34.5	15.1	16.6	7.0	226	
35.5	15.3	16.9	7.1	219	
37.0	15.0	16.5	7.0	208	
38.0	15.1	16.6	7.0	201	
39.5	14.4	15.9	6.7	191	
40.75	14.6	16.1	6.8	183	

Table 12.9 Continued

Time Run Min.	TiCl ₄ Rate gm./min.		TiO ₂ Remov. Rate gm./min.	Weight TiO ₂ in Bed gm.				
	Measured	Total						
42.0	14.3	15.8	6.7	174	<u>Chlorine Balances:</u> Time Run Min. % Accounted 18 92.5 34 94.0 49 95.5			
43.5	13.5	15.0	6.4	165				
45.5	13.2	14.7	6.2	152				
46.75	12.7	14.2	6.0	145				
48.5	12.2	13.7	5.8	134				
49.75	12.2	13.7	5.8	127				
51.75	12.1	13.6	5.7	115				
53.0	11.2	12.7	5.4	108				
55.0	11.1	12.6	5.3	98				
56.75	10.9	12.4	5.2	88				
58.75	10.3	11.8	5.0	78				
60.5	10.0	11.5	4.9	69				
62.75	8.9	10.4	4.4	59				
65.0	7.4	8.9	3.8	50				
70.75	3.2	4.7	2.0	34				
Tail Gas Data							Barometer 766 mm.Hg.	
Time Run Min.	Temp. °C	Rate gm/min.	Analysis % by Volume					
			Cl ₂	TiCl ₄	CO ₂	CO	N ₂	
18	25.5	19.6	8.6	1.76	77.5	12.2	-	
34	27.0	20.4	12.8	1.89	70.0	15.5	-	
49	27.2	22.6	20.8	1.89	64.5	13.2	-	

Table 12.10

Run 6

Time Run Min.	TiCl ₄ Rate gm./min.		TiO ₂ Remov. Rate gm./min.	Weight TiO ₂ in Bed gm.	
	Measured	Total			
5	15.1	16.7	7.1	460	
6½	16.4	18.0	7.6	449	
7½	16.6	18.2	7.7	442	
8¾	16.7	18.3	7.7	432	
10	16.1	17.7	7.5	423	
11¼	17.6	19.3	8.2	413	
12¼	16.9	18.6	7.9	405	
13¼	18.1	19.7	8.3	396	
14½	18.6	20.2	8.5	386	
15¾	18.2	19.8	8.4	375	
16½	18.6	20.2	8.5	369	
18	18.3	19.9	8.4	356	
18¾	17.9	19.5	8.2	350	
20¼	17.6	19.2	8.1	337	
21	17.8	19.4	8.2	331	
22¼	18.6	20.2	8.5	321	
23¼	17.0	18.6	7.9	313	
25½	16.2	17.8	7.5	295	
27	16.8	18.4	7.8	284	
28	15.3	16.9	7.1	277	
29.5	15.5	17.1	7.2	265	
30¾	15.6	17.2	7.3	256	
32	15.4	17.0	7.2	248	
33	15.6	17.2	7.3	241	
34.5	16.0	17.6	7.4	230	
35¾	14.6	16.2	6.8	221	
37¼	14.8	16.4	6.9	210	
38½	14.8	16.4	6.9	202	
41¼	14.5	16.4	6.9	183	
43¾	13.7	15.3	6.5	167	
44¼	13.9	15.5	6.6	164	
46	13.0	14.6	6.2	152	

Charge: 700 gm.

Temp.: 900°C

Partial Pressure:

Cl₂: 0.5 ats.

CO₂: 0.3 ats.

N₂: 0.2 ats.

Flows to React.:

Cl₂: 6 l./min.

CO₂: 3.6 l./min.

N₂: 2.4 l./min.

Residues:

Reactor: 117.5 gm.

59.3% TiO₂

Cyclone: 14.5 gm.

18.5% TiO₂

Chlorine Balances:

Run Time Min.	% Accounted
16	98.0
31	95.6
50	92.0

Table 12.10 Continued

Time Run Min.	TiCl ₄ Rate gm./min.		TiO ₂ Removal Rate gm/min.	Weight TiO ₂ in gm/min.			
	Measured	Total					
49	12.6	14.2	6.0	134			
50½	12.3	13.9	5.9	126			
52½	11.5	13.1	5.5	114			
54	10.9	12.5	5.3	106			
56	10.6	12.2	5.2	95			
57¾	11.1	12.7	5.4	85			
59¾	10.5	12.1	5.1	75			
61½	9.3	10.9	4.6	66			
63¾	9.3	10.9	4.6	56			
65¾	8.6	10.2	4.3	47			
68¼	7.7	9.3	3.9	36			
71¼	5.8	7.4	3.1	26			
Tail Gas Data					Barometer 763 mm.Hg.		
Time Run Min.	Temp. °C	Rate gm./min.	Analysis % by Volume				
			Cl ₂	TiCl ₄	CO ₂	CO	N ₂
16	27.0	18.7	8.3	1.83	50.6	13.5	26.4
31	27.2	19.7	12.0	1.83	46.2	14.4	25.1
50	28.0	20.7	19.0	1.96	41.9	11.9	25.2

Table 12.11

Run 7

Time Run Min.	TiCl ₄ Rate gm./min.		TiO ₂ Remov. Rate gm/min.	Weight TiO ₂ in Bed gm.	
	Measured	Total			
3.25	16.6	17.9	7.6	421	
4.25	16.3	17.6	7.4	414	
5.75	16.5	17.8	7.5	402	Charge: 700 gm.
6.75	17.1	18.4	7.8	395	Temp.: 900°C
8.0	18.4	19.7	8.3	384	Partial Pressure:
9.0	17.9	19.2	8.1	377	Cl ₂ : 0.5 ats.
10.75	18.7	20.0	8.4	366	CO ₂ : 0.15 ats.
11.25	17.3	18.6	7.9	358	N ₂ : 0.35 ats.
12.5	18.0	19.3	8.2	348	Flows to Reactor:
13.5	17.5	18.8	7.9	340	Cl ₂ : 6 l./min.
14.5	17.9	19.2	8.1	332	17.75 gm/min.
17.0	18.0	19.3	8.3	329	CO ₂ : 1.8 l./min
18.0	16.7	18.0	7.6	322	3.3 gm/min.
19.25	17.2	18.5	7.8	312	N ₂ : 4.2 l./min.
20.5	16.3	17.6	7.4	302	4.5 gm/min.
21.75	16.7	18.0	7.6	293	Residues:
22.75	15.9	17.2	7.3	286	Reactor: 115 gm.
24.25	15.9	17.2	7.3	275	53.1% TiO ₂
25.25	15.6	16.9	7.1	267	Cyclone: 11 gm.
26.75	14.4	15.7	6.6	257	14.7% TiO ₂
28.0	15.3	16.5	7.0	248	Chlorine Balances:
29.5	14.3	16.1	6.8	238	Time
30.5	14.6	15.9	6.7	231	Run
32.25	15.0	16.3	6.9	219	Min.
33.5	16.6	17.9	7.6	211	%
34.75	16.1	17.4	7.4	202	Accounted
36.0	14.1	15.4	6.5	194	18.5 99.5
37.75	14.1	15.4	6.5	183	37.5 94.5
39.25	12.1	13.4	5.7	174	57.5 95.0
41.0	11.8	13.1	5.5	163	
42.5	12.2	13.5	5.7	154	
44.25	13.0	14.3	6.0	144	

Table 12.11 Continued

Time Run Min.	TiCl ₄ Rate gm/min.		TiO ₂ Remov. Rate gm/min.	Weight TiO ₂ in Bed gm.			
	Measured	Total					
45.5	11.7	13.0	5.5	137			
47.5	12.7	14.0	5.9	126			
49.0	10.9	12.2	5.2	118			
51.0	10.9	12.2	5.2	108			
53.0	10.0	11.3	4.8	99			
57.0	9.5	10.8	4.6	79			
59.25	8.9	10.2	4.3	68			
61.25	8.7	10.0	4.2	60			
64.0	8.5	9.8	4.1	48			
66.0	8.1	9.4	4.0	40			
68.75	6.8	8.1	3.4	32			
72.5	3.5	4.8	2.0	20			
Tail Gas Data					Barometer 765 mm.Hg.		
Time Run Min.	Temp. °C	Rate gm/min.	Analysis % by Volume				
			Cl ₂	TiCl ₄	CO ₂	CO	N ₂
18.5	18	18.2	12.5	1.52	29.7	12.9	43.7
37.5	23	19.2	16.5	1.52	26.9	12.1	43.1
57.5	29	21.4	26.2	1.57	22.8	8.8	40.7

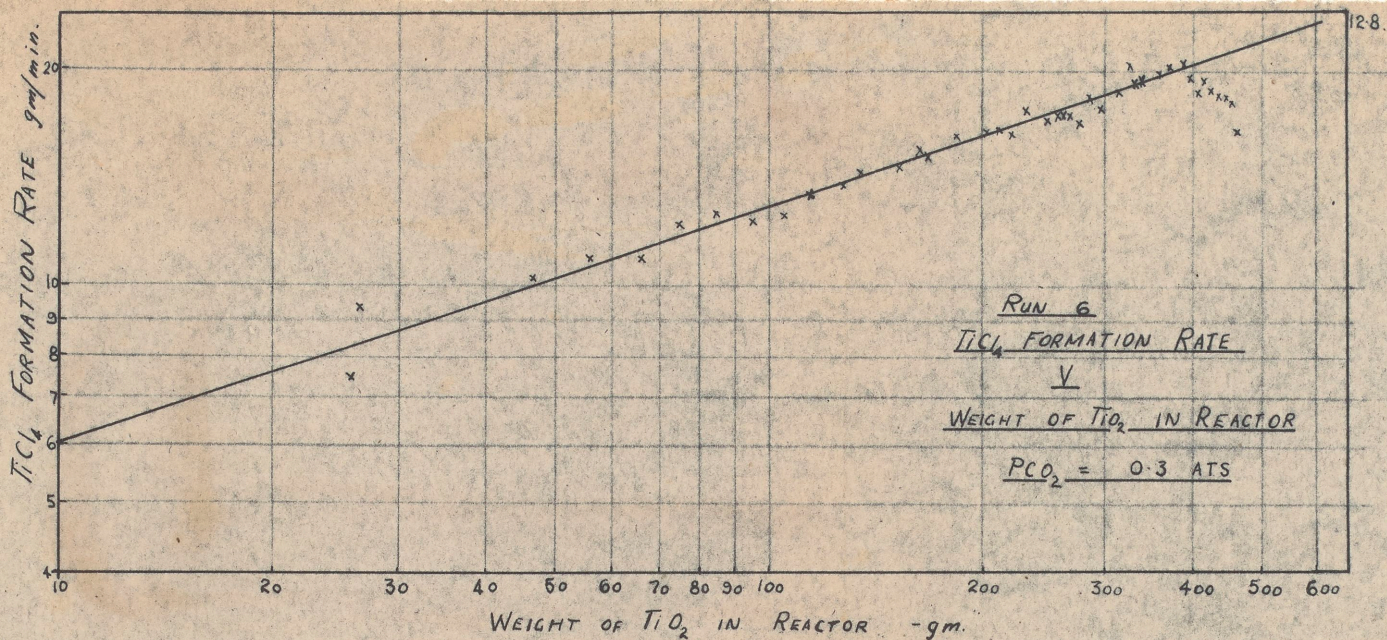
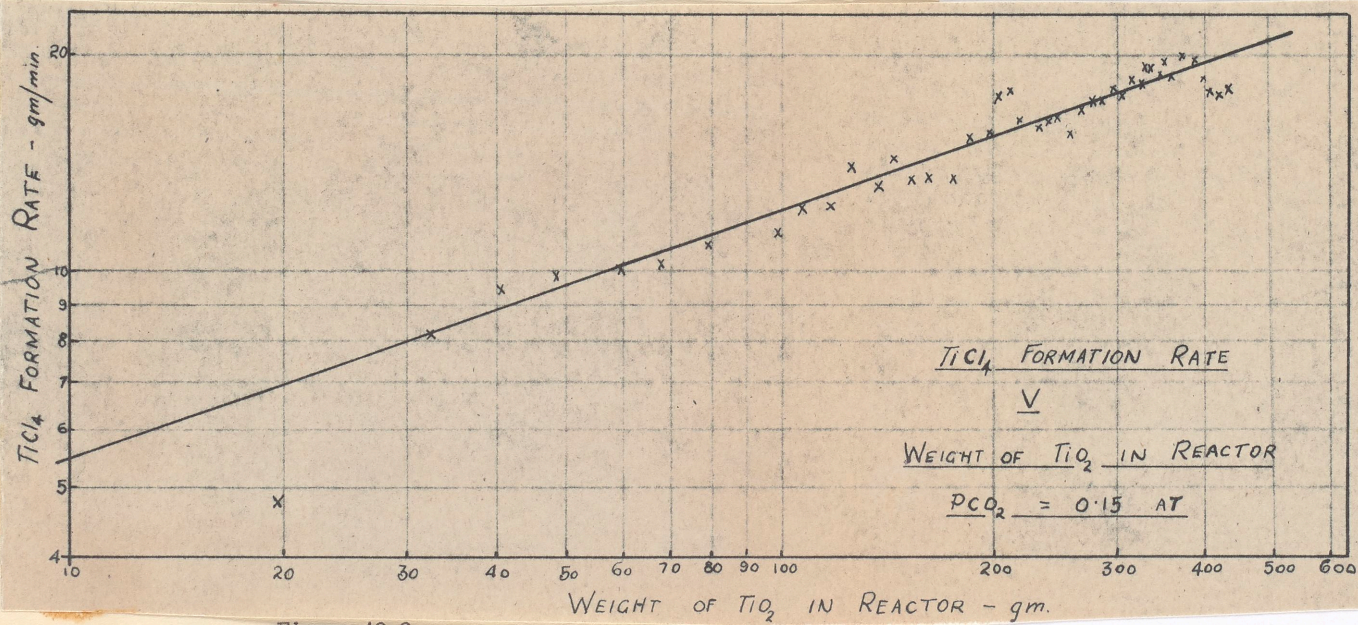


Figure 12.8



The experimental results plotted in Figures 12.7 to 12.9 have been extrapolated to a ten grams of titanium dioxide in the bed, and the titanium tetrachloride formation rate at this point has been plotted in Figure 12.10 against the partial pressure at which the run was carried out.

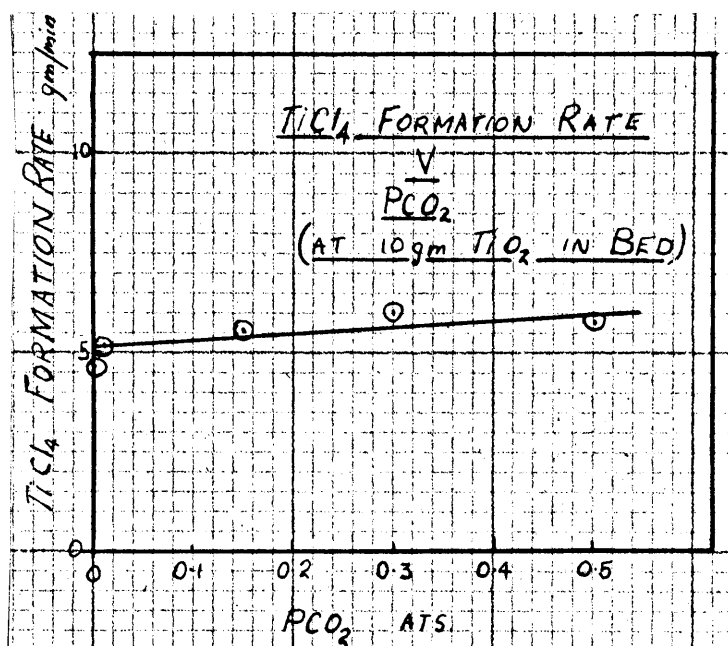


Figure 12.10

This plot shows a very slight increase in the rate with increase in the partial pressure of carbon dioxide in the feed. The magnitude of the change, and the estimated experimental error of 5% lead to the conclusion that carbon dioxide exerts no effect on the rate of the reaction. There is certainly no retarding effect which may have been expected from the reaction mechanism postulated in Chapter 3, the full range of the partial pressure change allowing for the dioxide formed in the reaction being 0.04 to 0.54 atm.

The Effect of Titanium Tetrachloride on the Reaction

The effect of titanium tetrachloride on the rate of the reaction was investigated by introducing titanium tetrachloride vapour into the feed to the reactor, and adjusting the nitrogen rate to keep the total flow constant. The partial pressure of chlorine was held at 0.5 ats. as in the runs to determine the effect of carbon dioxide.

The feed of titanium tetrachloride to the reactor was carried out in the apparatus, shown schematically in Figure 7.1, by running titanium tetrachloride liquid into the stream of mixed nitrogen and chlorine at the inlet of a coil of $\frac{3}{8}$ " diameter copper tube immersed in an oil bath heated to 200 to 220°C. The stream of gas carried the liquid down through the coil in which it was vapourised, and the mixed gas and vapour were then fed through a lagged line into the reactor. It was found that if the oil bath was brought to temperature about half an hour before the commencement of the titanium tetrachloride feed while nitrogen or nitrogen and chlorine was passing through the coil, the line was sufficiently preheated to prevent any condensation of titanium tetrachloride.

The rate of the titanium tetrachloride feed was measured by means of a laboratory test kit Flowrator in the liquid line to the vapouriser, and regulated by means of a screw clip on a section of plasticised PVC tubing in the liquid line. As the adjustment of the screw clip for any rate was very sensitive and the rate tended to wander during the run, some scatter of results was obtained.

In carrying out the runs on the variation of the partial pressure of titanium tetrachloride it was found to be impracticable to use partial pressures up to 0.5 ats. as planned, because the feed rate for this partial pressure was twice the possible production rate of titanium tetrachloride. This could

have resulted in large errors in the measurement of this rate. Accordingly the maximum partial pressure used was 0.227 ats; one run was carried out at 0.076 ats. and two at each of 0.146 ats. and 0.227 ats.

In runs 8, 9 and 10, the results for which are given in Tables and Figures 12.22, 12.12, and 12.13 the addition of titanium tetrachloride to the feed of the reactor was not commenced until the titanium dioxide content of the charge had been reduced to 150 - 200 gms. by chlorination using an equipartial pressure mixture of chlorine and nitrogen at a total flow rate of twelve litres per minute. When the titanium tetrachloride feed was commenced the nitrogen flow rate was reduced to maintain the total flow constant.

The results of these runs showed that the addition of titanium tetrachloride to the feed to the reactor increased the rate of the reaction, an increase being apparent at the point at which the titanium tetrachloride was introduced to the reactor. These results were not however completely satisfactory, as a low chlorine balance was obtained for run 9 during the addition of titanium tetrachloride and the results of both runs 9 and 10 show groups of values below the curves, due in run 9 to a blocked separator, and in run 10 to bad control of the titanium tetrachloride rate. It was decided therefore to carry out additional runs ^{to} check the results obtained and to commence the addition of titanium tetrachloride at the start of the run to spread the results over a wider range of bed weights.

Before it was possible to commence these runs it was necessary to grind additional rutile, and run 11 was carried out without titanium tetrachloride addition to obtain a base value for the new material. The results of this run is given in Table and Figure 12.14 and show little variation from those of run 3 repeat which was carried out under similar conditions, the increase in rate being

due to the slightly smaller particle size of the rutile in the new batch.

In runs 12 and 13 which were carried out at titanium tetrachloride feed partial pressures of 0.227 and 0.146 ats. respectively, titanium tetrachloride and nitrogen were passed through the reactor until a steady condensation rate was obtained, and chlorination was then commenced. The results of these runs are given in Tables and Figures 12.15 and 12.16 and, although the results show some scatter due to difficulty in controlling the titanium tetrachloride feed rate accurately the materials balances for chlorine and titanium dioxide are within the limits of the experimental error and ^{as} the measured titanium tetrachloride feed rates are in good agreement with those calculated from the total weight used, it is readily possible to draw lines of best fit through the data.

In each of these runs 8 to 13 the experimental values obtained for beds containing less than 80 gms. of titanium dioxide are, as in previous runs, subject to error due to the poor temperature control characteristics of shallow beds.

Table 12.11

Run 8

Time Run Min.	TiCl ₄ Rate gm/min.		TiO ₂ Remov. Rate gm/min.	Weight TiO ₂ in Bed gm.	
	Measured	Total			
5.0	13.4	14.4	6.1	419	
6.5	14.6	15.6	6.6	392	
7.5	16.1	17.1	7.2	385	
9.0	16.2	17.2	7.2	372	
10.0	15.2	16.2	6.8	367	
11.75	15.0	16.0	6.7	356	
12.5	17.7	18.7	7.9	349	
14.0	16.1	17.1	7.2	338	
15.0	16.0	17.0	7.1	327	
16.5	16.4	17.4	7.3	320	
18.0	15.8	16.8	7.1	313	
19.0	16.4	17.4	7.3	300	
20.0	15.0	16.0	6.7	293	
22.0	15.0	16.0	6.7	286	
23.0	14.9	15.9	7.4	279	
24.0	16.5	17.5	7.4	276	
25.5	14.7	15.7	6.6	266	
27.0	15.1	16.1	6.8	259	
28.0	16.2	17.2	7.3	249	
29.5	15.0	16.0	6.7	245	
30.25	14.9	15.9	6.7	242	
33.5	12.9	13.9	5.9	220	
35.0	13.5	14.5	6.1	213	
36.0 *	19.3	20.3 *	8.7	206 *	
37.0	9.8	10.8	4.5	200	
38.0	10.5	11.5	4.8	194	
39.0	12.2	13.2	5.6	187	
39.5	12.2	13.2	5.6	184	
40.25	13.6	14.6	6.1	180	
41.0	13.6	14.6	6.1	175	
42.0	13.1	14.1	5.9	169	
42.5	13.3	14.3	6.0	166	

Charge: 700 gm.

Temp.: 900°C

Partial Pressure:

Cl₂ 0.5 ats.

TiCl₄ 0.146 ats.

N₂ 0.354 ats.

Flows to React.

Cl₂ 6 l./min.

TiCl₄ 1.74 l./min.

13.82 gm/min.

N₂ 4.2551 l./min.

Residues:

Reactor 129 gm.

52.6% TiO₂

Cyclone 100 gm.

11.0% TiO₂

Table 12.11 Continued

Time Run Min.	TiCl ₃ Rate gm./min.		TiO ₂ Remov. Rate gm./min.	Weight TiO ₂ in Bed gm.	
	Measured	Total			
43½	13.4	14.4	6.1	160	
44½	12.2	13.2	5.6	154	
45	13.1	14.1	5.9	151	
45½	13.0	14.0	5.9	148	
46½	11.9	12.9	5.4	142	
47	12.6	13.6	5.7	140	
48	13.8	14.8	6.2	134	
48¾	14.4	15.4	6.5	130	
49½	15.0	16.0	6.7	125	
50	12.2	13.2	5.5	122	
51	13.8	14.8	6.2	117	
51¾	11.5	12.5	5.3	113	
52½	11.7	12.7	5.3	109	
53¼	13.0	14.0	5.9	104	
54	13.3	14.3	6.0	100	
55	12.0	13.0	5.5	95	
55¾	10.6	11.6	4.9	91	
56½	11.4	12.4	5.2	88	
57½	12.3	13.3	5.6	82	
58	10.3	11.3	4.8	79	
59	10.7	11.7	4.9	74	
60	10.0	11.0	4.6	69	
61	10.8	11.8	5.0	64	
61½	10.6	11.6	4.8	62	
62½	10.9	11.9	5.0	57	
63¼	10.2	11.2	4.7	54	
64¼	11.2	12.2	5.1	49	
65	10.0	11.0	4.6	45	
66	12.2	13.2	5.6	41	
66½	8.8	9.8	4.1	39	
67¾	9.4	10.4	4.4	33	

Chlorine Balances		
Time Run Min.	% Accounted	
16	97.0	
41	87.2	
56	97.0	

Table 12.11 Continued

Time Run Min.	TiCl ₄ Rate gm./min.		TiO ₂ Remov. Rate gm./min.	Weight TiO ₂ in Bed gm.			
	Measured	Total					
68½	8.5	9.5	4.0	31			
69½	7.3	8.3	3.5	27			
70½	7.0	8.0	3.4	23			
Tail Gas Data				Barometer 763 mm.Hg.			
Time Run Min.	Temp. °C	Rate gm./min.	Analysis % by Volume				
			Cl ₂	TiCl ₄	CO ₂	CO	N ₂
16	21.0	16.3	11.8	1.29	14.2	12.1	60.5
41	22.0	15.1	17.0	1.37	14.7	12.9	54.0
56	23.0	17.2	26.0	1.44	11.8	8.6	52.3

- * TiCl₄ feed to the reactor was commenced after 35 minutes run.
The succeeding values of TiCl₄ rate are measured values minus
the TiCl₄ feed rate (13.8 gm./min.)

Table 12.12

Run 9

Time Run Min.	TiCl ₄ Rate gm./min.		TiO ₂ Remov. Rate gm/min.	Weight TiO ₂ in Bed gm.	
	Measured	Total			
3	14.3	15.6	6.6	479	
3 $\frac{3}{4}$	28.2	29.5		465	
4 $\frac{3}{4}$	19.8	21.1	8.9	451	
5 $\frac{3}{4}$	19.5	20.8	8.8	442	
7	20.0	21.3	9.0	431	<u>Charge:</u> 700 gm.
7 $\frac{3}{4}$	17.9	19.2	8.1	425	<u>Temp.:</u> 900°C
9	16.8	18.1	7.6	415	<u>Partial Pressure:</u>
10 $\frac{1}{4}$	15.6	16.9	7.1	406	Cl ₂ 0.5 ats.
11 $\frac{1}{2}$	16.0	17.3	7.3	396	TiCl ₄ 0.076 ats.
12 $\frac{3}{4}$	15.1	16.4	6.9	387	N ₂ 0.424 ats.
15 $\frac{1}{2}$	16.5	17.8	7.5	367	<u>Flows to Reactor:</u>
16 $\frac{3}{4}$	15.7	17.0	7.1	358	Cl ₂ 6.0 1./min.
18	16.1	17.4	7.3	349	TiCl ₄ 0.8721 1./min.
19 $\frac{1}{2}$	16.3	17.6	7.4	339	6.9 gm./min.
20 $\frac{1}{2}$	15.9	17.2	7.2	332	N ₂ 5.13 1./min.
21 $\frac{3}{4}$	15.4	16.7	7.0	323	<u>Residues:</u>
23	16.4	17.7	7.5	314	Reactor 112 gm.
24 $\frac{1}{2}$	15.4	16.7	7.0	303	48.2% TiO ₂
25.5	15.7	17.0	7.2	294	Cyclone 7.5 gm.
27	16.1	17.4	7.3	285	8.0% TiO ₂
28	14.8	16.1	6.8	278	<u>Chlorine Balances:</u>
29 $\frac{3}{4}$	16.2	17.5	7.4	266	Time
31	14.2	15.5	6.5	258	Run
32 $\frac{1}{4}$	15.2	16.5	6.9	249	Min.
33 $\frac{1}{2}$	15.5	16.8	7.1	240	%
34 $\frac{3}{4}$	16.1	17.4	7.3	232	Accounted
36	13.9	15.2	6.4	224	13 93.5
37 $\frac{1}{2}$	15.1	16.4	6.9	214	41 95.5
39	13.1	14.4	6.1	204	63 87.9
40 $\frac{1}{2}$	14.3	15.6	6.6	199	
41 $\frac{3}{4}$	13.1	14.4	6.1	186	
43 $\frac{1}{2}$	12.4	13.7	5.5	174	
45	13.5	14.8	6.2	165	

Table 12.12 Continued

Time Run Min.	TiCl ₄ Rate gm./min.		TiO ₂ Remov. Rate gm./min.	Weight TiO ₂ in Bed gm.
	Measured	Total		
47	9.2	10.5	4.4	152
49	9.2	10.5	4.4	140
50.5*	9.8*	10.9	4.6	130*
51½	9.8	10.9	4.6	124
53	9.8	10.9	4.6	115
54	9.5	10.6	4.5	109
55½	17.0	18.1	7.6	101
56½ ∅	14.6	15.7	6.6	98
57½	12.3	13.4	5.7	89
58¾	12.8	13.9	5.9	82
59½	12.2	13.3	5.0	78
60½	11.7	12.8	5.4	73
61½	11.0	12.1	5.1	68
63	10.0	11.1	4.7	60
64	10.2	11.3	4.8	55
65¼	10.4	11.5	4.8	49
66¼	8.9	10.0	4.2	45
68	8.0	9.0	3.8	37
69	8.1	9.2	3.9	33
70½	8.4	8.5	4.0	28
71¾	6.4	7.5	3.2	24
74	4.6	5.7	2.4	17
75¼	3.1	4.2	1.8	15

Tail Gas Data			Barometer 760 mm.Hg.				
Time Run Min.	Temp. °C	Rate gm/min.	Analysis % by Volume				
			Cl ₂	TiCl ₄	CO ₂	CO	N ₂
13	23.5	16.4	11.0	1.51	13.7	12.8	61.4
41	23.0	18.3	15.7	1.45	12.4	12.9	57.6
63	22.5	17.6	22.0	1.38	11.5	11.3	53.8

* TiCl₄ feed started succeeding values are measured rate minus TiCl₄ feed rate (6.9 gm./min.) ∅ Blockage in inlet to liquid trap. Bypass opened to bypass bubbler.

Table 12.13

Run 10

Time Run Min.	TiCl ₄ Rate gm./min.		TiO ₂ Remov. Rate gm./min.	Weight TiO ₂ in Bed gm.	
	Measured	Total			
4½	18.0	18.9	8.0	486	
5½	18.8	18.9	8.4	457	
6¾	18.4	19.3	8.1	449	
7¾	17.1	18.0	7.6	438	
9	17.8	18.7	7.9	431	
10	17.4	18.3	7.7	421	
11¼	17.6	18.5	7.8	413	<u>Charge:</u> 700 gm.
12¼	16.2	17.1	7.2	403	<u>Temp.:</u> 900°C
14	16.6	17.5	7.4	396	<u>Partial Pressure</u>
15	16.5	17.4	7.3	383	Cl ₂ 0.5 ats.
16	16.9	17.8	7.5	380	TiCl ₄ 0.229 ats.
17	16.9	17.8	7.5	373	N ₂ 0.271 ats.
18½	15.8	16.7	7.0	365	<u>Flows to Reactor</u>
19¾	16.5	17.4	7.3	355	Cl ₂ 6.0 1./min.
21	16.1	17.0	7.2	346	TiCl ₄ 2.6 1./min.
22	15.7	16.6	7.0	336	21.7 gm./min.
23½	15.6	16.5	6.9	330	N ₂ 3.4 1./min.
24½	16.7	17.6	7.4	312	
27	15.2	16.1	6.8	301	
28½	16.0	16.9	7.1	294	
29½	15.5	16.4	6.9	284	
31	15.4	16.3	6.9	277	
32	14.5	15.4	6.5	266	
33¾	16.6	17.5	7.4	259	
34¾	14.5	15.4	6.5	247	
35½	15.8	16.7	7.0	241	
37½	14.5	15.4	6.5	229	
39	15.0	15.9	6.7	222	
40½	13.8	14.7	6.2	213	
42	13.6	14.5	6.1	203	
43	14.2	15.1	6.4	193	
45	13.7	14.6	6.1	187	
46	13.1	14.0	5.9	175	

Table 12.13 Continued

Time Run Min.	TiCl ₄ Rate gm./min.		TiO ₂ Remov. Rate gm./min.	Weight TiO ₂ in Bed gm.				
	Measured	Total						
48	13.4	14.3	6.0	169	<div>Chlorine Balances</div> <div><div>Time Run Min.</div><div>% Accounted</div><div>5298.0</div><div>63105.0</div></div>			
48 $\frac{3}{4}$ *	17.9*	18.8	7.9	156*				
50	16.7	17.6	7.4	152				
51	17.9	18.8	7.9	142				
52	17.1	18.0	7.6	134				
53	17.6	18.5	7.8	126				
54 $\frac{1}{2}$	16.9	17.8	7.5	119				
55 $\frac{1}{2}$	17.1	18.0	7.6	107				
56 $\frac{1}{2}$	16.8	17.7	7.5	100				
57 $\frac{1}{2}$	16.8	17.7	7.5	92				
59	13.1	14.0	5.9	85				
60	10.6	11.5	3.8	74				
61	25.0	25.9	10.9	66				
62	16.2	17.1	7.2	52				
63 $\frac{1}{2}$	14.5	15.4	6.5	42				
64 $\frac{3}{4}$	12.1	13.0	5.5	35				
66	10.1	11.0	4.6	28				
67 $\frac{1}{2}$	8.3	9.2	3.9	21				
68 $\frac{3}{4}$	8.5	9.4	4.0	16				
69 $\frac{1}{2}$	off			13				
Tail Gas Data							Barometer 773 mm.Hg.	
Time Run Min.	Temp. °C	Rate gm./min.	Analysis % by Volume					
			Cl ₂	TiCl ₄	CO ₂	CO	N ₂	
52	22.0	13.9	14.8	1.36	17.8	15.9	50.0	
63	22.0	16.0	27.6	1.36	11.7	10.8	48.5	

* TiCl₄ Feed started succeeding values are measured rate minus Feed Rate (21.7 gm./min.)

Table 12.14

Run 11

Time Run Min.	TiCl ₄ Rate gm./min.		TiO ₂ Remov. Rate gm./min.	Weight TiO ₂ in Bed gm.	
	Measured	Total			
7½	14.3	15.4	6.5	393	
9	18.0	19.1	8.0	383	
10	16.5	17.6	7.4	375	
11¼	16.2	17.3	7.3	366	
12¼	16.9	18.0	7.6	358	
13½	17.9	19.0	8.0	349	Charge: 700 gm.
14½	17.0	18.1	7.6	341	Temp.: 900°C
16	16.8	17.9	7.5	330	Partial Pressures
17	18.4	19.5	8.2	322	Cl ₂ 0.5 ats.
18	17.7	18.8	7.9	315	TiCl ₄ 0.0 ats.
19	16.8	17.9	7.5	308	N ₂ 0.5 ats.
20¼	16.3	17.4	7.3	299	Flows to Reactor
21½	16.1	17.2	7.2	290	Cl ₂ 6 l./min.
23	16.1	17.2	7.2	279	TiCl ₄ 0.0 l./min.
24	16.1	17.2	7.2	272	N ₂ 6.0 l./min.
25	16.5	17.6	7.4	264	
26	16.2	17.3	7.3	257	Residues
28½	15.6	16.7	7.0	240	Reactor 102 gm.
30	15.7	16.8	7.1	230	49.7% TiO ₂
31	15.1	16.2	6.8	223	Cyclone 9 gm.
32½	14.7	15.8	6.6	213	10.4% TiO ₂
33¾	16.0	17.1	7.2	204	Chlorine Balances
35½	14.1	15.2	6.4	194	Time
36¾	13.9	15.0	6.3	184	Run
38	14.6	15.7	6.6	176	Min.
39¼	13.5	14.6	6.1	169	%
41	14.7	15.8	6.6	158	Accounted
42¼	14.1	15.2	6.4	150	15 101.0
44	12.2	13.3	5.6	139	45 94.5
45½	12.5	13.6	5.7	130	65 96.8
47½	14.3	15.4	6.5	119	
49	11.3	12.4	5.2	111	
51	10.6	11.7	4.9	100	

Table 12.14 Continued

Time Run Min.	TiCl ₄ Rate gm./min.		TiO ₂ Remov. Rate gm./min.	Weight TiO ₂ in Bed gm.			
	Measured	Total					
53	10.4	11.5	4.8	91			
55	10.0	11.1	4.7	81			
56 $\frac{3}{4}$	10.6	11.7	4.9	73			
59	10.1	11.2	4.7	62			
60 $\frac{3}{4}$	10.4	11.5	4.8	55			
62 $\frac{1}{4}$	14.5	15.6	6.6	48			
64	9.0	10.1	4.2	41			
67	7.0	8.1	3.4	30			
69 $\frac{1}{2}$	6.1	7.2	3.2	23			
75	3.4	4.5	1.9	83			
Tail Gas Data Barometer 755 mm.Hg.							
Time Run Min.	Temp. °C	Rate gm/min.	Analysis % by Volume				
			Cl ₂	TiCl ₄	CO ₂	CO	N ₂
15	19.5	16.5	13.4	1.20	13.7	12.2	59.5
45	20.0	19.5	20.7	1.24	10.7	11.3	56.3
65	20.0	21.0	28.4	1.24	7.2	8.9	54.1

Table 12.15

Table 12

Time Run Min.	TiCl ₄ Rate gm./min.		TiO ₂ Remov. Rate gm./min.	Weight TiO ₂ in Bed gm.	
	Measured	Total			
-5	12.5				
-4	12.7				
-3	16.5				
-2	16.0				
0	17.8	18.6	7.8	454	<u>Charge:</u> 700 gm.
$\frac{1}{2}$	20.6	21.4	9.0	449	<u>Temp.:</u> 900°C
1	25.7	26.5	11.3	445	<u>Partial Pressure</u>
3	20.3	21.1	8.8	427	Cl ₂ 0.5 ats.
4	21.6	22.4	9.4	419	TiCl ₄ 0.227 ats.
5	16.5	17.3	7.3	409	N ₂ 0.273 ats.
6	25.1	25.9	10.9	401	<u>Flows to Reactor</u>
7	20.0	20.8	8.8	392	Cl ₂ 6.0 l./min.
8	19.7	20.5	8.6	383	TiCl ₄ 2.62 l./min.
$9\frac{1}{4}$	18.6	19.4	8.2	373	21.7 gm./min.
10	17.7	18.5	7.8	364	N ₂ 3.4 l./min.
$11\frac{1}{4}$	17.1	17.9	7.4	358	<u>Residues</u>
$12\frac{1}{2}$	26.9	27.7	11.8	345	Reactor 87 gm.
13	19.2	20.0	8.4	341	55.8% TiO ₂
$14\frac{1}{2}$	18.1	18.9	8.0	328	Cyclone 17 gm.
16	18.4	19.2	8.1	316	7.6% TiO ₂
17	17.9	18.7	7.9	308	<u>Weight of TiCl₄</u>
18	16.9	17.7	7.5	300	<u>Feed to Reactor:</u>
19	14.3	15.1	6.4	292	1475 gm.
$20\frac{1}{4}$	16.5	17.3	7.3	281	<u>Calculated TiCl₄</u>
$21\frac{1}{4}$	18.7	19.5	8.2	273	<u>Feed Rate</u>
$22\frac{1}{4}$	17.9	18.7	7.9	265	21.4 gm./min.
$23\frac{1}{4}$	18.3	19.1	8.0	257	
$24\frac{3}{4}$	19.5	20.3	8.5	245	
$25\frac{3}{4}$	18.0	18.8	7.9	237	
27	18.2	19.0	8.0	227	
28	15.0	15.8	6.7	219	
29	19.7	20.5	8.6	212	
30	15.7	16.5	7.0	204	

Table 12.15 Continued

Time Run Min.	TiCl ₄ Rate gm./min.		TiO ₂ Remov. Rate gm./min.	Weight TiO ₂ in Bed gm.			
	Measured	Total					
31 $\frac{1}{4}$	18.6	19.4	8.2	194	<u>Chlorine Balances</u> Time Run Min. % Accounted 13 95.8 35 94.5 55 93.0		
32 $\frac{1}{2}$	16.5	17.3	7.3	185			
33 $\frac{1}{2}$	15.3	16.1	6.8	177			
35	15.4	16.2	6.8	166			
36	15.6	16.4	6.9	159			
37	16.2	17.0	7.2	151			
38 $\frac{1}{4}$	15.1	15.9	6.7	142			
39 $\frac{1}{4}$	19.0	19.8	8.3	135			
40 $\frac{1}{4}$	17.9	18.7	7.9	128			
41 $\frac{1}{2}$	15.4	16.0	6.7	120			
43	17.5	18.3	7.7	109			
44	15.2	15.8	6.4	103			
45 $\frac{1}{4}$	15.5	16.3	6.9	95			
47 $\frac{3}{4}$	13.3	14.1	5.9	79			
49	12.0	12.8	5.4	71			
50	14.5	15.3	6.4	66			
51 $\frac{1}{4}$	10.7	11.5	4.8	59			
52 $\frac{3}{4}$	15.0	15.8	6.6	50			
54	13.6	14.4	6.1	44			
55 $\frac{1}{4}$	7.3	8.1	3.4	38			
56 $\frac{1}{2}$	10.5	11.3	4.8	33			
58	8.5	9.3	3.9	26			
59 $\frac{1}{2}$	8.1	8.8	3.7	20			
61	6.5	7.3	3.1	15			
62 $\frac{1}{2}$	6.7	7.5	3.2	11			
64	4.1	4.9	2.1	7			
Tail Gas Data							
				Barometer 764 mm.Hg.			
Time Run Min.	Temp. °C	Rate gm./min.	Analysis % by Volume				
			Cl ₂	TiCl ₄	CO ₂	CO	N ₂
13	18.0	12.9	10.3	1.08	22.2	18.2	49.2
35	18.5	15.0	13.3	1.10	20.6	18.0	47.2
55	19.0	17.1	27.1	1.13	10.2	11.1	50.6

Chlorine Balances

Time Run Min.	% Accounted
13	95.8
35	94.5
55	93.0

N.B. TiCl₄ rates recorded are actual measured rates minus TiCl₄ feed rate (21.7 gm./min.)

Table 12.16

Run 13

Time Run Min.	TiCl ₄ Rate gm./min.		TiO ₂ Remov. Rate gm./min.	Weight TiO ₂ in Bed gm.	
	Measured	Total			
12½	18.7	19.6	8.2	406	
13½	18.6	19.5	8.2	398	
15	15.9	16.8	7.9	386	
16¼	17.6	17.5	7.4	376	
17¾	18.9	19.8	8.3	364	Charge: 700 gm.
19	16.5	17.4	7.3	354	Temp.: 900°C
20¼	19.2	20.1	8.5	346	Partial Pressure
21½	17.9	18.8	7.9	338	Cl ₂ 0.5 ats.
22¾	17.0	17.9	7.5	326	TiCl ₄ 0.146 ats.
24¼	17.9	18.8	7.2	314	N ₂ 0.354 ats.
25½	17.1	18.0	7.6	304	Flows to Reactor
27	19.8	20.7	8.7	293	Cl ₂ 6.0 l./min.
28	18.2	19.1	8.0	285	TiCl ₄ 1.75 l./min.
29¾	18.1	19.0	8.0	271	13.82 gm./min.
30¾	18.2	19.1	8.0	263	N ₂ 4.25 l./min.
32	18.7	19.6	8.2	253	Residues
33¼	19.2	20.1	8.5	243	Reactor 94.5 gm.
34½	16.2	17.1	7.2	234	61.2% TiO ₂
36	19.8	20.7	8.7	222	Cyclone 7 gm.
37	16.2	17.1	7.2	214	37.1% TiO ₂
38½	16.2	17.1	7.2	203	Weight of TiCl ₄
40	16.3	17.2	7.2	191	Feed to Reactor
41¼	18.2	19.1	8.0	182	1030 gm.
42¾	15.2	16.1	6.8	170	Calculated TiCl ₄
44	16.1	17.0	7.2	161	Feed Rate
45	15.2	16.1	6.8	154	13.6 gm./min.
45¾	19.0	19.9	8.4	148	
46½	15.8	16.7	7.0	143	
47	15.1	16.0	6.7	139	
48	13.5	14.4	6.1	132	
48½	16.1	17.0	7.2	128	
49½	16.0	16.9	7.1	121	

Table 12.16 Continued

Time Run Min.	TiCl ₄ Rate gm./min.		TiO ₂ Remov. Rate gm./min.	Weight TiO ₂ in Bed gm.			
	Measured	Total					
50	15.1	16.0	6.7	118	<div>Chlorine Balances</div> <div><div>Time Run Min.</div><div>% Accounted</div><div>1896.0</div><div>3898.4</div><div>55104.5</div></div>		
51	14.1	15.0	6.3	111			
51½	14.5	15.4	6.5	107			
53	14.2	15.1	6.4	97			
54	13.5	14.4	6.1	91			
54½	14.4	15.3	6.4	88			
55¼	11.8	12.7	5.4	83			
56	11.6	12.5	5.3	78			
57¾	13.0	13.9	5.9	68			
58½	15.0	15.9	6.7	63			
50¼	12.7	13.6	5.7	59			
60	13.3	14.2	6.0	55			
60¾	11.4	12.3	5.2	51			
61¾	11.9	12.8	5.4	46			
62½	12.2	13.1	5.5	43			
63½	8.7	9.6	4.0	38			
64	12.4	13.3	5.5	36			
65	9.1	10.0	4.2	33			
66	7.2	8.1	3.4	27			
67	7.0	7.9	3.3	23			
68	6.3	7.2	3.0	20			
70	7.0	7.9	3.3	13			
Tail Gas Data					Barometer 762 mm.Hg.		
Time Min. Run	Temp. °C	Rate gm./min.	Analysis % by Volume				
			Cl ₂	TiCl ₄	CO ₂	CO	N ₂
18	19.5	13.7	11.7	1.18	18.2	15.6	53.8
38	19.0	15.8	14.9	1.12	16.1	15.3	52.7
55	19.0	17.4	27.0	1.12	11.6	11.8	48.5

N.B. TiCl₄ rates recorded are actual measured rates minus TiCl₄ feed rate. (13.8gm./min.)

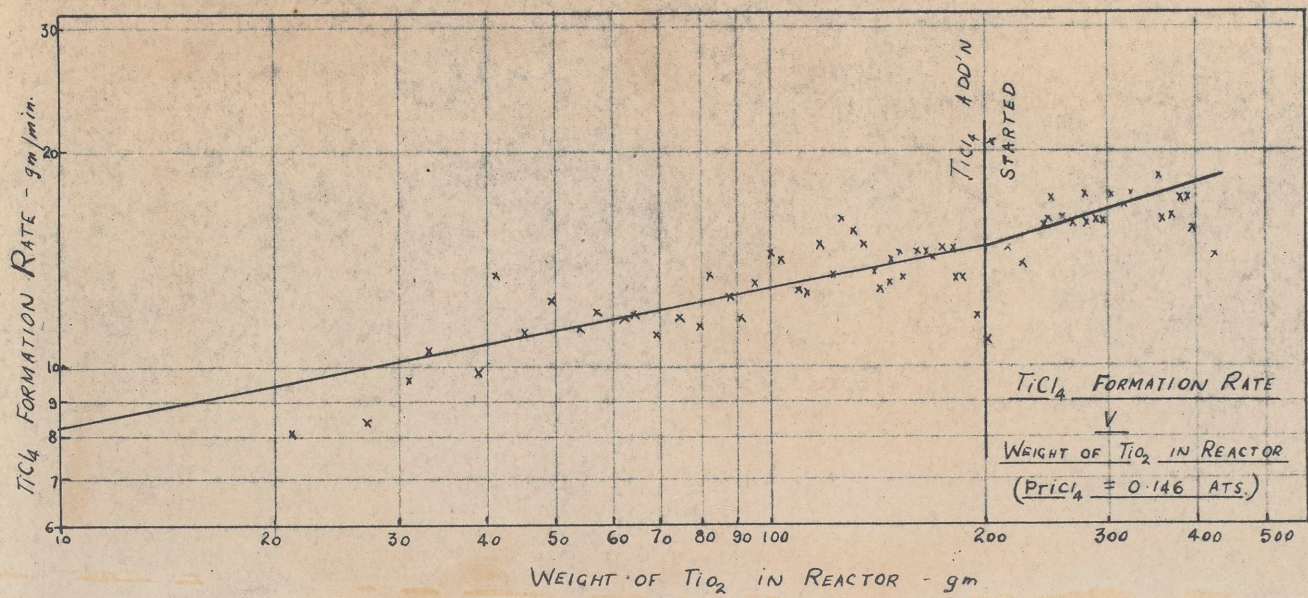
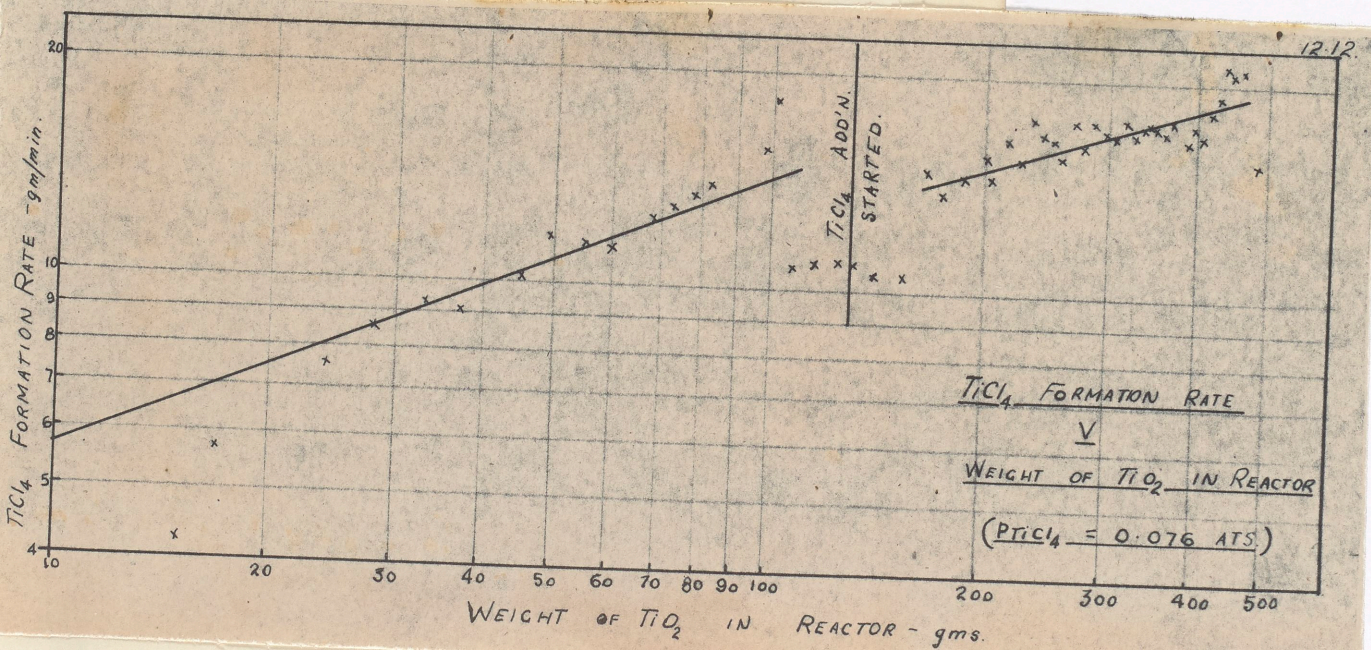


Figure 12.11



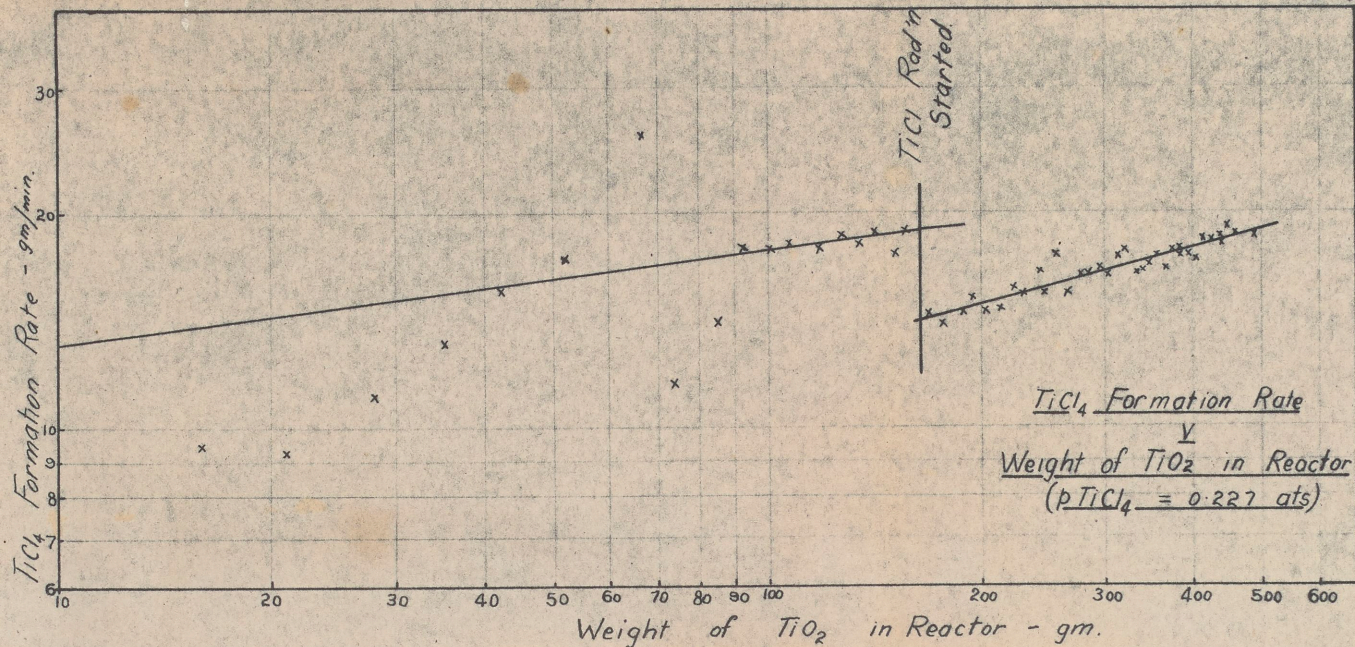
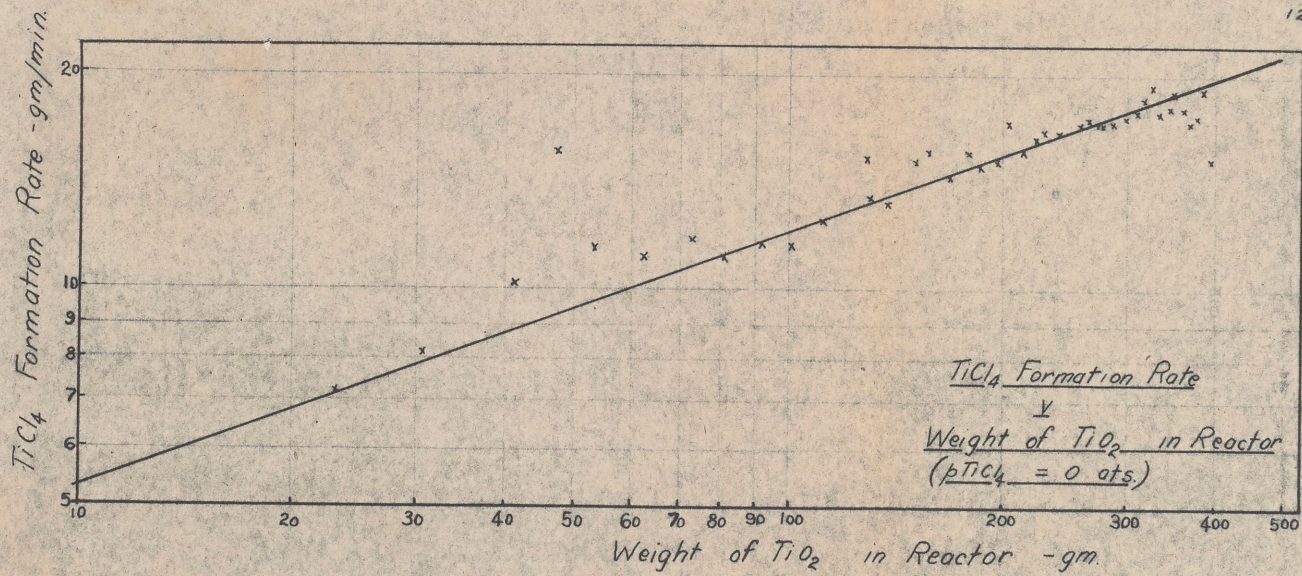


Figure 12.13



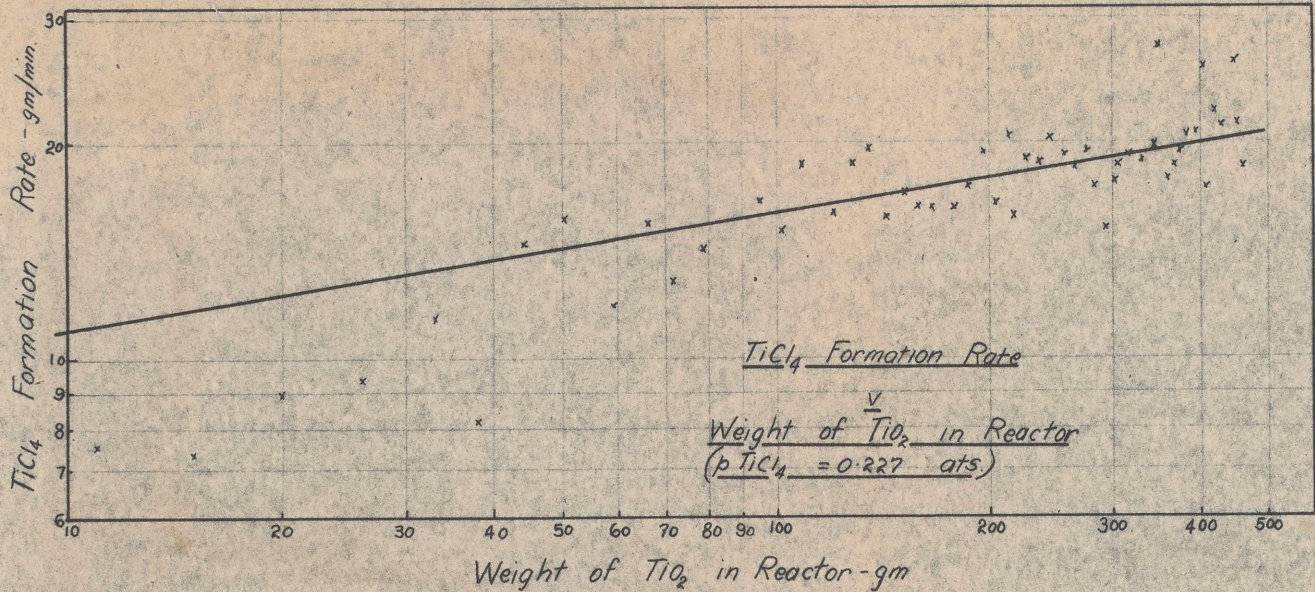
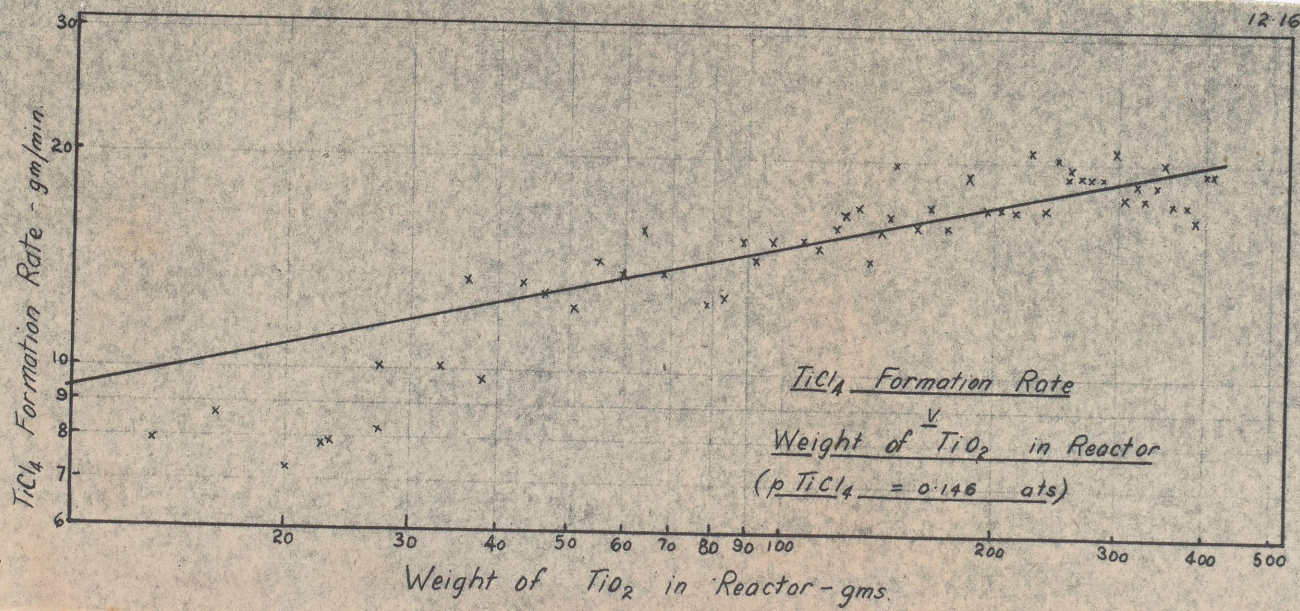


Figure 12.15



The rates of formation of titanium tetrachloride for runs 3R and 8 to 13 extrapolated to a reactor bed content of 10 gm. of titanium dioxide, are given in the following table, together with inlet partial pressures of titanium tetrachloride used.

Table 12.17

TiCl_4 Formation Rate at 10 gms. TiO_2
for inlet TiCl_4 Partial Pressures

Run No.	P_{TiCl_4} ats.	TiCl_4 Formation Rate gm./min.
3R	0.00	4.8
8	0.146	8.2
9	0.076	5.7
10	0.227	13.0
11	0.00	5.3
12	0.227	11.0
13	0.146	9.4

These results are plotted in Figure 12.17 and although the accuracy is not as good as in other runs a significant increase at the rate of formation of titanium tetrachloride with increase of partial pressure of titanium tetrachloride in the reactor is shown.

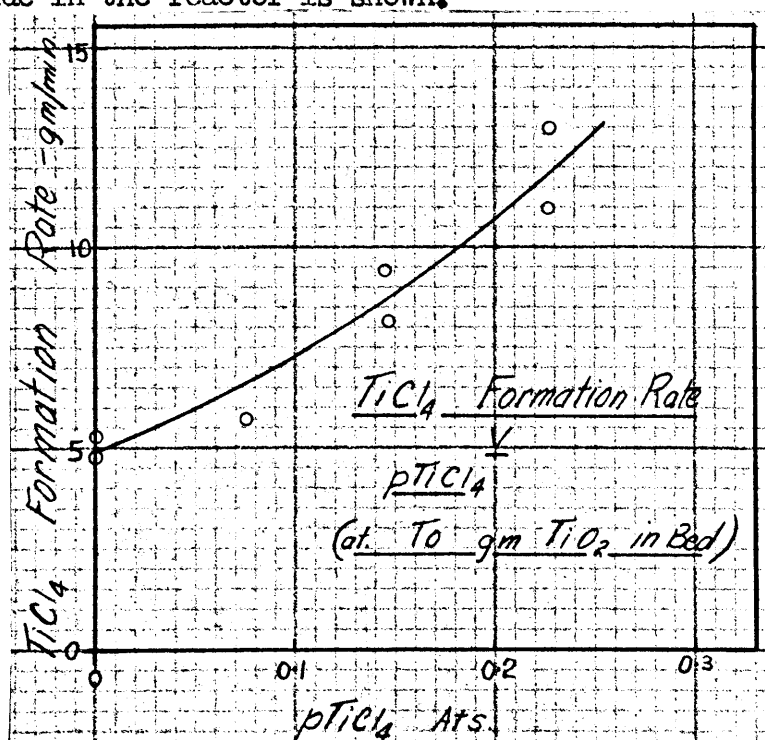


Figure 12.17

This means that the chlorination of rutile in the presence of carbon is autocatalysed by titanium tetrachloride. This product must then enter into the reaction forming intermediate compounds or complexes.

A characteristic of such autocatalysed reactions is shown in the results of runs 3R, 6, 7, 8 and 11 (Figures 12.4, 12.8, 12.9, 12.11 and 12.13) in which the rate of formation of titanium tetrachloride at the start of the run shows a gradual increase before the full rate is obtained. In such a process the rate at the start is limited by the concentration of the product and cannot reach a maximum until the sufficient titanium tetrachloride has been formed to maintain the full reaction rate. In the results of runs 12 and 13, (Figures 12.15 and 12.16) in which titanium tetrachloride was fed to the reactor before the start of the chlorination, such a gradual increase in the reaction rate does not occur, the limitation due to the concentration of the product being absent.

This gradual increase in the rate of reaction at the start of the run could be caused by the gas mixing characteristics of the fluid bed. For such a bed there are two extreme cases of flow through the bed, that of piston flow as for a fixed bed, and the characteristic of gas bypassing through the bed and back mixing from the top of the bed which would cause complete mixing of the gas in the bed. For piston flow the gas passes through the bed as a front displacing the gas before it. Under these conditions alteration of the composition of the gas at the inlet of the bed will not change the exit gas composition until the gas front has passed through the bed, when the exit composition will change sharply to the inlet composition. In the gas of complete mixing the gas composition through the bed uniform, and for any change in the inlet composition the mixing in the bed will hold the gas composition of

the bed constant and the exit gas will change gradually until the new inlet composition is reached. Any large amount of bypassing and back mixing occurring in the fluid beds used would then cause the gradual increase in reaction rate noted at the start of the runs, but this would seem to be precluded by the immediate increase in the condensation rate of titanium tetrachloride noted in runs 12 and 13 when the chlorination was commenced. It may therefore be concluded that little back mixing occurred in the beds used and that the gas flow through these beds approached piston flow.

In runs 12 and 13 in which titanium tetrachloride was fed to the reactor to establish a steady condensation rate before the start of the chlorination, it was observed that seven to ten minutes elapsed before titanium tetrachloride began to collect at a rate approaching the feed rate. Calculation shows that this is about three times the time required to saturate the system, and would suggest that titanium tetrachloride is absorbed on the charge.

Chlorination using Carbon Monoxide instead of Carbon as the Reducing Agent in the Reaction

As discussed at the start of the chapter it was decided that as previous experiments had shown that carbon monoxide instead of solid carbon appeared to be involved in the initial step of the reaction, the chlorination of rutile using carbon monoxide as the reducing agent should be investigated before studying the partial pressure effect of carbon monoxide in the presence of carbon.

The equipment used to supply carbon monoxide formed by the conversion of carbon dioxide with carbon has been described in Chapter VI, and is shown schematically and in detail in Figures 6.1 and 6.11 respectively. The method proved to be most satisfactory for the laboratory supply of large quantities of

carbon monoxide, and where high purities are required the small amounts of unconverted carbon dioxide may easily be removed by scrubbing with sodium hydroxide solution. In the initial tests carried out on the apparatus carbon dioxide was passed through an eighteen inch deep fluid bed of crushed 'Norit' activated carbon held at a temperature of 1250°C . At a feed rate of fourteen litres of carbon dioxide per minute a product containing only 0.4% carbon dioxide was obtained. This temperature however caused failure of the silica tube, and as no alundum tubes could be obtained, the maximum temperature used in succeeding runs was 1050°C , which was considered to be the highest permissible operating temperature for silica. At this temperature carbon monoxide containing from 0.4 to 10% carbon dioxide was produced, the carbon dioxide content depending on the feed rate. As previous experiments had shown that carbon dioxide exerts no effect on the reaction rate, it was considered unnecessary to remove this residual carbon dioxide.

Two runs were carried out using carbon monoxide in the chlorination instead of carbon, and the reaction rates obtained were insufficient to saturate the tail gas and allow condensation of the product. In run fourteen, carried out at 870°C , chlorine at 6 l./min. and carbon monoxide at 9 l./min. were passed through a bed containing 500gms., of rutile. During the first thirty minutes chlorination no condensation of titanium tetrachloride occurred, although the occurrence of some reaction was shown by the formation of the characteristic white fumes formed by titanium tetrachloride when the tail gas was allowed to escape into the atmosphere. After the above period the gas rates were reduced to three and four litres per minute respectively, but there was still no condensation of titanium tetrachloride. In these runs the carbon monoxide feed varied between 94.4 and 97.8% carbon monoxide.

The conditions of run fifteen are given in Table 12.18, the charge to the reactor being 468.5 gms. of rutile.

Table 12.18

Conditions used in Run 15 for Chlorination using CO

Time Run Min.	Rates to React. l./min		Reactor Temp. °C		CO Feed CO%
	CO	Cl ₂	No. 1	No. 2	
10	4	4	875	935	
20	4	4	920	990	93.2
32	4	4	930	970	94.8
35	6	4			
45	6	4	930	965	89.6
52	4	6			
57	4	6	935	965	92.1
69	off	off			

After ten minutes running it was noted that a red deposit of ferric chloride had formed on the entrance to the knockout drum and as the run proceeded this deposit spread further through the apparatus. White fumes formed by titanium tetrachloride were formed when the tail gas was allowed to escape into the atmosphere, but at no time during the run was there any sign of condensation of titanium tetrachloride. Variation of the ratio of carbon monoxide to chloride from a fifty percent stiochiometric excess to a fifty percent stiochiometric deficiency did not materially effect the rate of the reaction. The reactor residue after the run was 437.5 gms., whence the weight of rutile removed during the run was 31 gms. giving a removal rate of 0.45 gm./min. From this a titanium tetrachloride formation rate of 1.1 gms./min. is obtained.

These experiments show that the chlorination using carbon monoxide as the reducing agent is very slow compared with the chlorination in the presence of solid carbon; and it is apparent that solid carbon is important in the

reaction mechanism which yields the high rates of reaction obtained in the latter system.

These experiments also show that the reaction mechanism proposed in Chapter 3 is not possible for the fluid bed chlorination.

The Effect of Variation of the Partial Pressure of Carbon
Monoxide on the Reaction

The effect of carbon monoxide on the reaction rate of the chlorination in the presence of solid carbon was investigated by varying the partial pressure of this gas in the reactor. Carbon monoxide was introduced in the reactor feed, and its partial pressure in the reactor varied as in the experiments on carbon dioxide and titanium tetrachloride.

Three runs were carried out at carbon monoxide partial pressures of 0.125, 0.25 and 0.5 atmospheres, while the partial pressure of chlorine was held at 0.5 ats. In each run a 700 gm. charge was used, mixed as previously described using materials which had been prepared for the runs on the variation of the partial pressure of titanium tetrachloride, and the reactor temperature was held at 900°C. The results of these experiments are given in Tables 12.19, 12.20 and 12.21, and plotted in Figures 12.18, 12.19 and 12.20.

Table 12.19

Run 16

Time Run Min.	TiCl ₄ Rate gm./min.		TiO ₂ Removal Rate gm./min.	Weight TiO ₂ in Bed gm.	
	Measured	Total			
7.0	18.4	19.5	8.2	398	
8.0	18.2	19.3	8.1	390	
9.5	17.6	18.7	7.9	380	
10.25	18.0	19.1	8.1	376	
11.5	17.9	19.0	8.0	366	
12.5	16.7	17.8	7.5	358	
13.75	17.6	18.7	7.8	348	<u>Charge:</u> 700 gms.
14.75	16.4	17.5	7.4	340	<u>Temp.:</u> 900°C
16.25	14.5	15.6	6.6	330	<u>Partial Pressures</u>
17.5	13.4	14.5	6.1	322	Cl ₂ : 0.5 ats.
18.25	14.4	15.5	6.5	311	CO : 0.5 ats.
20.5	13.8	14.9	6.3	303	N ₂ : 0.0 ats.
22.0	14.2	15.3	6.5	294	<u>Flows to Reactor</u>
23.25	14.6	15.7	6.6	287	Cl ₂ : 6.0 l./min.
24.75	15.5	16.6	7.0	275	CO : 6.0 l./min.
26.0	15.6	16.7	7.0	266	N ₂ : 0.0 l./min.
27.5	14.8	15.9	6.7	256	<u>Residues:</u>
28.75	14.3	15.4	6.5	248	Reactor: 186 gms.
30.25	15.4	16.5	7.0	238	71.5% TiO ₂
31.25	16.3	17.4	7.3	231	Cyclone: 6 gms.
32.5	15.7	16.8	7.1	222	<u>Av. CO Feed</u> 90.7%
33.75	15.0	16.1	6.8	213	CO
35.25	14.7	15.8	5.5	202	
36.5	15.7	16.8	7.0	195	
37.75	14.7	15.8	6.7	185	
39.25	13.7	14.8	6.2	171	
40.75	14.5	15.6	6.5	165	
42.0	13.7	14.8	6.2	157	
43.75	12.8	13.9	5.9	149	
45.25	12.2	13.3	5.6	137	
47.0	12.4	13.5	5.7	128	
48.5	10.7	11.8	5.0	119	

Table 12.19 Continued

Time Run Min.	TiCl ₄ Rate gm./min.		TiO ₂ Remov. Rate gm./min.	Weight TiO ₂ in Bed gm.	
	Measured	Total			
50.75	10.3	11.4	4.8	108	
52.5	9.0	10.1	4.3	95	
55.0	8.4	9.5	4.0	90	
57.25	7.8	8.9	3.8	79	
60.0	7.1	8.2	3.5	72	
62.0	off				

Tail Gas Data				Barometer 762 mm.Hg.			
Time Run Min.	Temp. °C	Rate gm./min.	Analysis % by Volume				
			Cl ₂	TiCl ₄	CO ₂	CO	N ₂
20	20.5	16.5	16.5	1.25	16.5	65.7	-
45	20.5	19.9	28.5	1.25	14.1	56.2	-
55	21.5	21.3	38.1	1.32	12.1	48.5	-

Table 12.20

Run 17

Time Run Min.	TiCl ₄ Rate gm./min.		TiO ₂ Rate Remov. gm./min.	Weight TiO ₂ in Bed gm.	
	Measured	Total			
6.0	19.8	21.3	9.0	401	
7.25	18.5	20.0	8.4	392	
8.5	15.2	16.7	7.1	383	
9.75	15.5	16.6	7.0	374	
11.0	15.3	16.8	7.1	365	
12.2	15.3	16.8	7.1	356	
13.5	17.6	19.1	8.1	347	<u>Charge:</u> 700 gm.
14.75	14.8	16.3	6.9	338	<u>Temp.</u> 900°C
16.0	16.1	17.6	7.4	330	<u>Partial Pressure</u>
17.2	14.1	15.6	6.6	321	Cl ₂ : 0.5 ats.
18.75	17.2	18.7	7.9	311	CO : 0.25ats.
19.75	14.3	15.8	6.7	304	N ₂ : 0.25ats.
21.5	14.2	15.7	6.6	294	<u>Flows to Reactor</u>
22.5	15.6	17.1	7.2	286	Cl ₂ : 6.0 l./min.
24.0	14.2	15.7	6.6	276	CO : 3.0 l./min.
25.25	13.1	14.6	6.2	268	N ₂ : 3.0 l./min.
27.0	12.8	14.3	6.0	257	<u>Av. CO Feed</u>
30.2	12.2	13.7	5.8	237	99.0% CO
31.75	12.5	14.0	5.9	228	<u>Residues</u>
33.5	12.5	14.0	5.9	218	Reactor: 130 gms.
34.0	11.7	13.2	5.6	215	52.4% TiO ₂
35.75	11.0	12.5	5.3	204	Cyclone: 10.5 gms.
38.5	12.0	13.5	5.7	194	
40.5	10.6	12.1	5.1	181	
42.0	10.5	12.0	5.1	173	
44.0	10.5	12.0	5.1	162	
45.0	10.3	11.8	5.0	157	
47.0	10.6	12.1	5.1	147	
49.5	10.4	11.9	5.0	135	
50.75	9.1	10.6	4.5	128	
53.75	9.7	11.2	5.3	119	
56.25	9.2	10.7	4.5	102	
58.0	9.3	10.8	4.6	95	

Table 12.20 Continued

Time Run Min.	TiCl ₄ Rate gm./min.		TiO ₂ Remov. Rate gm./min.	Weight TiO ₂ in Bed gm.			
	Measured	Total					
60.5	8.0	9.5	4.0	84			
63.0	7.5	9.0	3.8	76			
66.0	6.0	7.5	3.2	62			
68.0	11.3	12.8	5.4	47			
72.75	8.5	10.0	4.2	38			
74.5	5.4	6.9	2.9	33			
79.0	3.9	5.4	2.3	22			
81.0	off						
Tail Gas Data					Barometer 765 mm.Hg.		
Time Run Min.	Temp. °C	Rate gm./min.	Analysis % by Volume				
			Cl ₂	TiCl ₄	CO ₂	CO	N ₂
11	25.0	17.8	13.4	1.62	14.9	39.8	30.4
34	25.5	19.7	21.5	1.67	11.7	37.7	28.9
61	25.0	21.2	29.3	1.62	8.7	32.2	28.8

Table 12.21

Run 18

Time Run Min.	TiCl ₄ Rate gm./min.		TiO ₂ Removal Rate gm./min.	Weight TiO ₂ in Bed gm.	
	Measured	Total			
3.5	17.3	18.7	7.9	436	
4.75	16.1	17.5	7.4	426	
6.25	17.0	18.4	7.8	414	
7.25	15.7	17.1	7.2	408	<u>Charge:</u> 700 gm.
8.5	17.9	19.3	8.1	398	<u>Temp.</u> 900°C
9.75	15.0	16.4	6.9	388	<u>Partial Pressures:</u>
11.0	16.3	17.7	7.4	379	Cl ₂ 0.5 ats.
12.0	15.5	16.9	7.1	371	CO 0.125 ats.
13.5	15.9	17.3	7.3	360	N ₂ 0.375 ats.
14.25	15.9	17.3	7.3	355	<u>Flows to Reactor:</u>
15.75	15.1	16.5	7.0	344	Cl ₂ : 6.0 l./min.
17.0	13.7	15.1	6.6	335	CO : 1.5 l./min.
18.75	15.6	17.0	7.2	322	N ₂ : 4.5 l./min.
19.5	15.0	16.4	6.9	317	<u>Av. CO Feed</u>
21.25	15.5	16.9	7.2	305	99.4% CO
22.5	14.0	15.4	6.5	298	<u>Residues:</u>
23.0	14.1	15.5	6.5	293	Reactor: 197.5 gms.
25.25	14.5	15.9	6.7	279	64.1% TiO ₂
26.75	16.0	17.4	7.3	267	Annulus: 62 gms.
28.0	13.4	14.8	6.2	259	76.4% TiO ₂
29.5	14.3	15.7	6.6	249	Cyclone: 5 gms.
30.75	12.7	14.2	6.0	241	
32.5	13.3	14.8	6.2	230	
33.75	13.1	14.6	6.2	223	
35.5	13.6	15.3	6.5	212	
37.0	11.2	12.8	5.4	203	
39.0	12.8	14.2	6.0	191	
40.5	11.7	13.1	5.5	183	
42.0	12.0	13.6	5.7	174	
44.75	10.8	12.4	5.2	160	
45.75	10.8	12.4	5.2	154	
47.25	10.8	12.4	5.2	146	
49.25	11.9	13.5	5.7	137	
51.0	10.2	11.8	5.0	127	
52.0	off				

Table 12.21 Continued

Tail Gas Data			Barometer 770 mm.Hg.				
Time Run Min.	Temp. °C	Rate gm./min.	Analysis % by Volume				
			Cl ₂	TiCl ₄	CO ₂	CO	N ₂
11.0	19.5	16.1	12.1	1.70	14.4	26.3	45.6
26.0	19.5	17.7	17.5	1.70	11.9	25.4	43.6
46.0	19.5	20.0	25.5	1.70	9.2	21.7	41.9

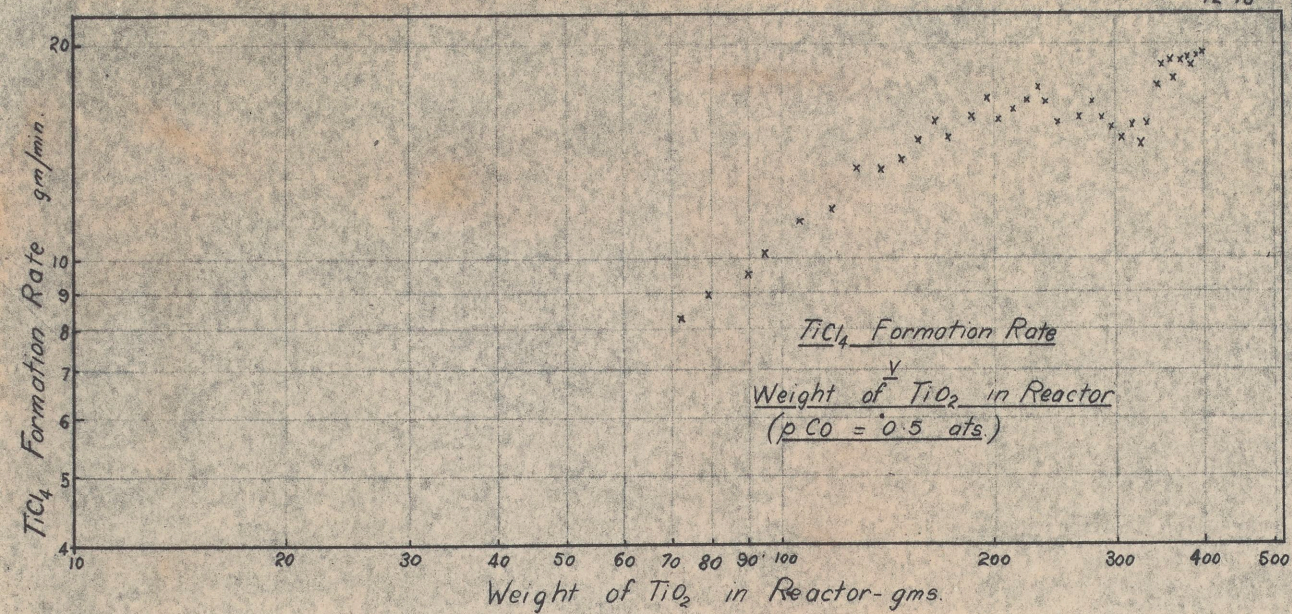
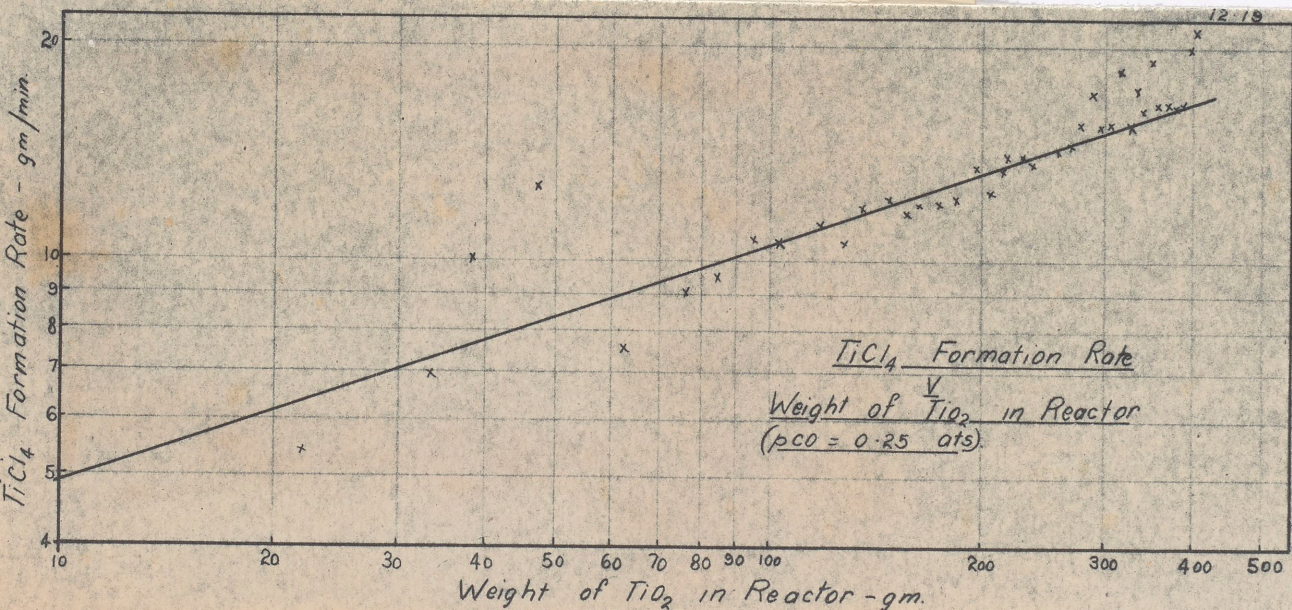
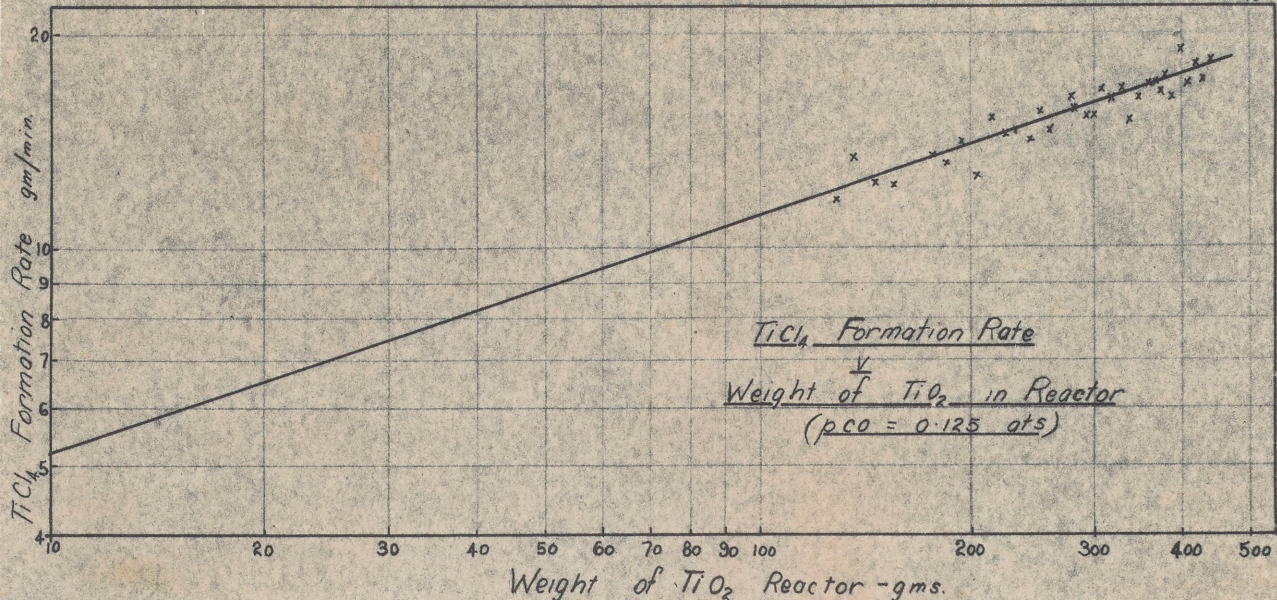


Figure 12.18





From these results the rates of formation of titanium tetrachloride in a bed containing ten grams of titanium dioxide are plotted in Figure 12.21 against the inlet partial pressure of carbon monoxide. This plot shows no significant variation in the rate of formation of titanium tetrachloride with change in the partial pressure of carbon monoxide in the reactor. The total range of experiment allowing for the carbon monoxide formed by reaction was 0.03 to 0.28 ats. This would be expected from the very slow reaction rates obtained in runs 14 and 15 for chlorination using carbon monoxide instead of carbon as the reducing agent.

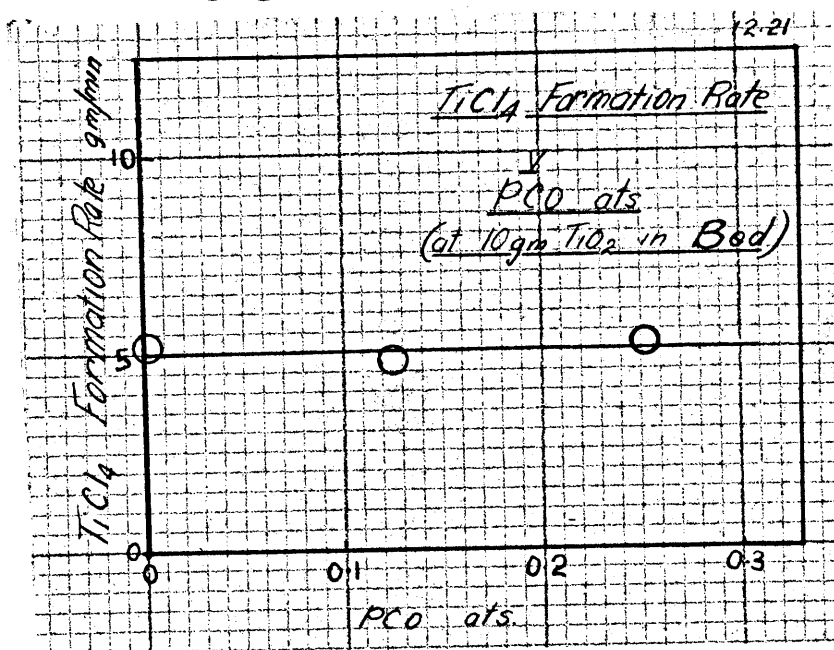
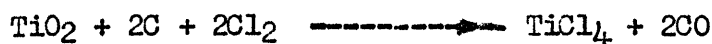


Figure 12.21

Chlorination Using a Reduced Carbon to Rutile Ratio

The importance of solid carbon in the reaction system having been shown by the results of the experiments on chlorination using carbon monoxide as the reducing agent and on the variation of the partial pressure of carbon monoxide in the reactor, run 19 was carried out to determine the effect of variation of the ratio of carbon to rutile in the charge to the reactor. In previous runs a carbon to rutile ratio sufficient for the reaction



had been used, with the results that as carbon dioxide was formed during the reaction the ratio of carbon to rutile increased. Run 19 was carried out on a charge containing insufficient carbon to allow complete chlorination of the charge by the reaction



As carbon monoxide is formed in the reaction occurring the carbon to rutile ratio in the charge is rapidly decreased.

A charge containing 538 gms. of rutile and 62 gms. of carbon was prepared by premixing, using the materials prepared for the experiments on the variation of the partial pressure of titanium tetrachloride. The chlorination was carried out under the same conditions as run 11 (Table 12.14), that is using a chlorine partial pressure of 0.5 ats. and the same temperature and weight of rutile in the reactor feed. The results of the run are given in Table 12.22.

Table 12.22

Run 19

Time Run Min.	TiCl ₄ Rate gm./min.		TiO ₂ Remov. Rate gm./min.	Weight TiO ₂ in Bed gm.	Carbon Remov. Rate gm./min.	Weight Carbon in Bed gm.
	Measured	Total				
5.0	9.3	10.4	4.3		0.82	
6.25	12.5	13.6	5.7	486	1.1	45.8
8.0	11.8	12.9	5.4	476	1.04	44.2
9.5	12.3	13.4	5.6	470	1.09	42.9
11.25	11.9	13.0	5.5	458	1.05	41.3
13.0	11.1	12.2	5.4	449	1.05	39.8
14.75	11.9	13.0	5.5	440	1.08	38.3
16.25	10.8	11.9	5.0	430	1.00	37.1
18.25	10.7	11.8	5.0	420	1.00	35.5
20.5	9.2	10.3	4.4	411	0.88	32.8
22.75	9.0	10.1	4.3	400	0.86	31.3
24.75	8.8	9.9	4.2	392	0.82	30.0
27.0	8.0	9.1	3.8	383	0.73	28.7
29.5	7.6	8.7	3.7	374	0.70	27.4
32.5	6.8	7.9	3.3	366	0.63	26.1
35.0	6.6	7.7	3.3	358	0.63	25.0
39.0	4.7	5.9	2.5	347	0.48	23.6
43.0	4.4	5.6	2.3	337	0.44	22.5
49.5	3.1	4.3	1.8	324	0.34	21.4
52.0	off			320		21.0

Tail Gas Data

Barometer 765 mm.Hg.

Time Run Min.	Temp. °C	Rate gm./min.	Analysis % by Volume				
			Cl ₂	TiCl ₄	CO ₂	CO	N ₂
15	20.0	19.9	28.4	1.21	7.3	7.9	54.5
27	20.5	21.2	37.3	1.24	7.1	5.9	54.5
40	21.5	23.8	40.2	1.31	3.9	3.0	51.6
8 15 20 27 40	CO CO ₂ 100% %CO ₂	<u>Charge</u> Rutile 538 gms. Carbon 62 gms. <u>Temp.</u> 900°C <u>Partial Pressure</u> Chlorine 0.5 ats. Nitrogen 0.5 ats. <u>Flows to Reactor</u> Chlorine 6.0 l./min. Nitrogen 6.0 l./min. <u>Residues</u> Reactor 276 gms. 92.0% Rutile Annulus 74 gms. 89.5% Rutile					
	55.5						
	51.3						
	49.0						
	54.4						
	56.3						

The carbon removal rate was calculated from the ratio of carbon dioxide to carbon monoxide in the tail gas and the rate of formation of titanium tetrachloride. The ratio was plotted against time and the ratio at the time concerned was used.

In Figure 12.22 the rate of formation of titanium tetrachloride is plotted against the weight of titanium dioxide in the bed. The bottom curve shows the results of run 19, while the top curve is taken from the plot of the results of run 11 (Table 12.14) in which the carbon content of the bed exerted no control. The dotted curve is compounded from the two curves to remove the variation in the results of nineteen due to the decrease of the weight of titanium dioxide in the bed. The wide difference between the results of runs 11 and 19, show the carbon content of the bed to have a strong effect on the rate.

Figure 12.23 shows the plot of the rate of formation of titanium tetrachloride against the weight of carbon on the bed, the dotted curve showing the results corrected for change in the titanium dioxide content of the bed. Figure 12.24 shows the plot of rate versus carbon content using the corrected data, and also the data from run 11 to give a point at a higher carbon content of the bed. A smooth curve is obtained showing clearly the dependance of the rate of reaction on the carbon content of the bed. For the reactor conditions used, the reaction rate falls off very rapidly with reduction of the carbon contents of the bed below about fifty grams. of carbon, that is about 70% of the stiochiometric amount of carbon for the reaction which would form carbon dioxide as the only product.

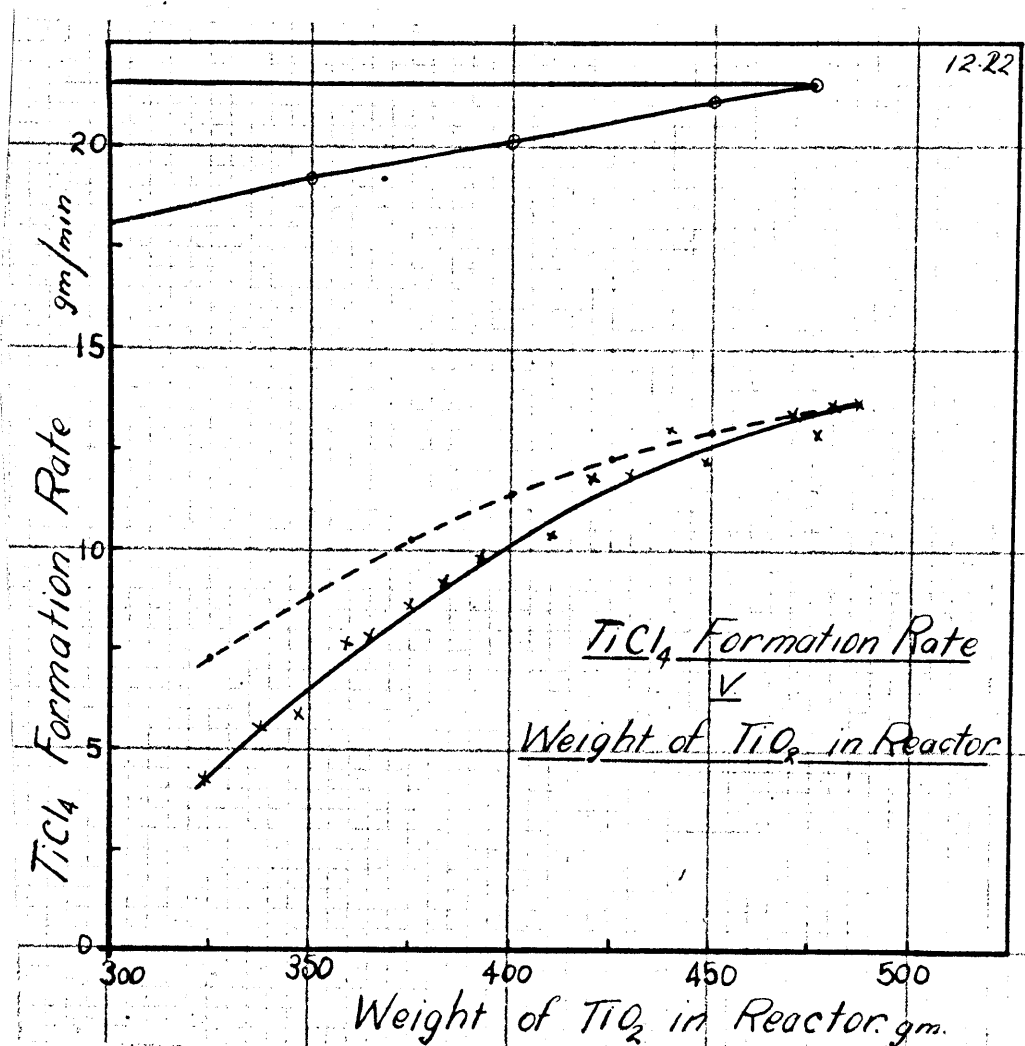


Figure 12.22

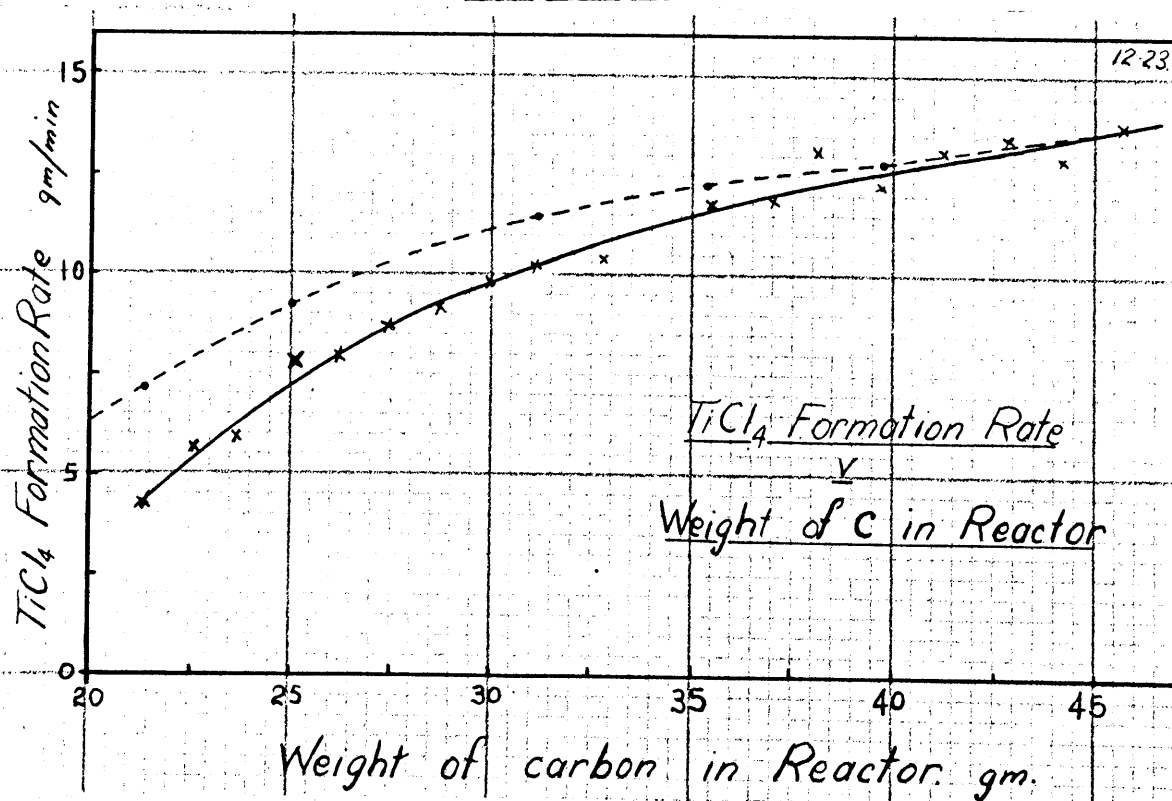


Figure 12.23

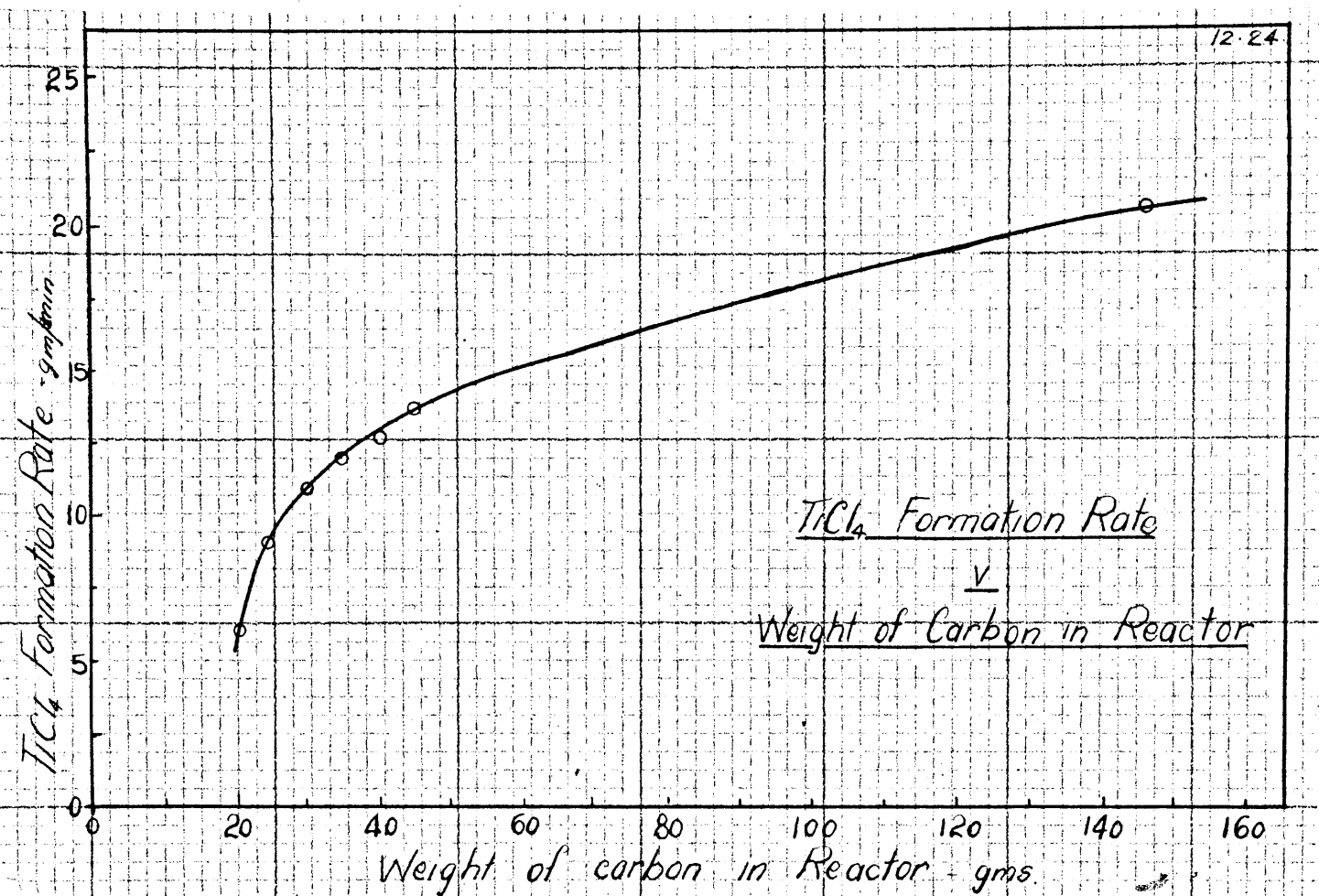


Figure 12.24

An interesting result of the run is that the percentage of carbon dioxide in the carbon monoxide - carbon dioxide mixture formed as a product of the reaction, changes very little with the large change in the carbon content of the bed; a reduction from 44 to 23 grams causing a change from 55.5 to 56.3%. This may also be compared with the results of the previous runs of series III experiments in which higher carbon contents were used. Table 12.23 gives the percentage of carbon dioxide in the carbon monoxide - carbon dioxide product from those runs in which carbon monoxide or carbon dioxide was not added to the reactor.

In these runs the carbon dioxide percentage at the start is very similar to that at the start of run 19, although the carbon content of the bed was approx. three times that at the start of the latter run. A second trend is also apparent in these results, that as the run proceeds, there is a fall in the percentage of carbon dioxide in the product. This could be accounted for by

the increase in the carbon to rutile ratio which occurred in these runs, and which would promote the formation of carbon monoxide.

Table 12.23

Percentage Carbon Dioxide in the CO - CO₂ Product
in Reaction

Run No.	CO ₂ %	Run No.	CO ₂ %	Run No.	CO ₂ %
1	55.0	4	45.5	11	53.3
	50.6		46.1		49.6
	45.0		43.6		44.8
2	51.0	8	54.1	12	54.5
	50.5		53.2		53.3
	47.5		57.8		47.8
3	49.7	9	51.6	13	53.6
	42.8		49.0		51.2
	46.3		50.4		49.5
3R	52.4	10	52.7		
	49.0		52.0		
	46.8				

The almost constant composition of the carbon monoxide - carbon dioxide product of the reaction with a seven fold increase in the carbon content of the reactor suggests that at 900°C both oxides of carbon are formed as direct products of the chlorination mechanism in the ratio of approximately 45 parts of carbon monoxide to 55 parts of carbon dioxide, and are not formed by subsequent reaction of oxygen or carbon dioxide with carbon.

Chlorination in the Absence of Reducing Agents

One run was carried out to check the work of Kangro and Jahn (8) on the reaction of chlorine with titanium dioxide in the absence of reducing agents to remove the oxygen formed, and to check the thermodynamic prediction that

This reaction will take place to a limited extent.

Five hundred grams of rutile were charged to the reactor which had been cleaned to remove any carbon, and a mixture of chlorine and nitrogen was passed at a total flow rate of twelve litres per minute using a chlorine partial pressure of 0.5 ats. and a temperature of 900°C. These conditions allow comparison with runs 14 and 15. Chlorine was passed for one hour.

During the run a greenish yellow deposit was formed on the glass surfaces of the knockout drum and cyclone and when the tail gas was allowed to escape to atmosphere very small amounts of fume characteristic of titanium tetrachloride were formed. Tests of the deposits formed showed the presence of both soluble titanium and iron at the exit of the reactor. This shows that some chlorination of the charge had occurred. Post chlorination weighing of the charge showed a loss of weight of two grams.

It may therefore be concluded that at 900°C the reaction



does occur but at a very slow rate.

Chapter XIII

Discussion of the Reaction Mechanism of the Fluid Bed Chlorination of Rutile in the Presence of Carbon

Energy of Activation

The energy of activation, the function E in the Arrhenius equation

$$k = Ce^{-E/RT}$$

where

k = Velocity Constant

R = Gas Constant 1.98 cal.,

T = Temperature °K

and C = Constant

is the most important factor in determining the rate of reaction, since the function $e^{-E/RT}$ varies so rapidly with T and E. The energy of activation is fundamental in determining the factors controlling the rate of reaction, as this factor is in effect the barrier to the reaction. If the value of this factor is known the type of control can be stated, as present knowledge in surface chemistry has allowed values to be assigned to the energies of activation occurring for the various processes. As discussed in Chapter III diffusion processes have very low energies of activation, physical adsorption takes place with an energy of activation of less than 5 KCal./gm./mol. while chemisorption has an energy of activation is excess of 20 KCal./gm.mol.

From the restatement of the Arrhenius equation as

$$\log k = C - E/RT$$

it is apparent that the value of the energy of activation for a reaction may be determined by plotting log k against $1/T$, when the slope of the line gives the value of E, R being known.

While a rigorous calculation of the energy of activation for the reaction system is not possible without a more complete knowledge of the reaction

mechanism; an approximation has been attempted using the data from runs 15 and 16 of series two experiments on the variation of reaction rate with temperature. In addition experiment has shown that the reaction is unretarded by the products, and is of the 0.6 order with respect to chlorine.

For a static system the velocity constant for such a reaction would be given by the equation

$$-dp/dt = k p^{0.6}$$

where k = velocity constant

p = partial pressure of chlorine

t = time

In a flow system, in which constant conditions of flow and total pressure are maintained in the reactor, the rate of reaction ($-dp/dt$ for the static system) is given by the rate of formation of the product, which here is the rate of formation of titanium tetrachloride expressed in grams per minute. Thus the velocity constant k may be expressed as

$$k = F \left(\frac{\text{Rate of Formation of TiCl}_4}{p_{\text{Cl}_2}^{0.6}} \right)$$

where F is a multiplication factor to bring the expression to the correct units. This factor may be neglected in determining the energy of activation from the plot of $\log k$ against $1/T$.

As the experiments in which the temperature variation of the reaction system was determined were carried out in deep beds in which a large variation in chlorine concentration existed between the top and bottom of the bed, the values for the partial pressure of chlorine used in calculation of the above expression were determined by taking the log mean partial pressures calculated on the inlet and exit conditions. As no inerts were fed to the reactor in these experiments the inlet partial pressure was taken at one atmosphere while

the exit partial pressure was calculated from the conversion obtained for a given time and the analysis of the tail gas.

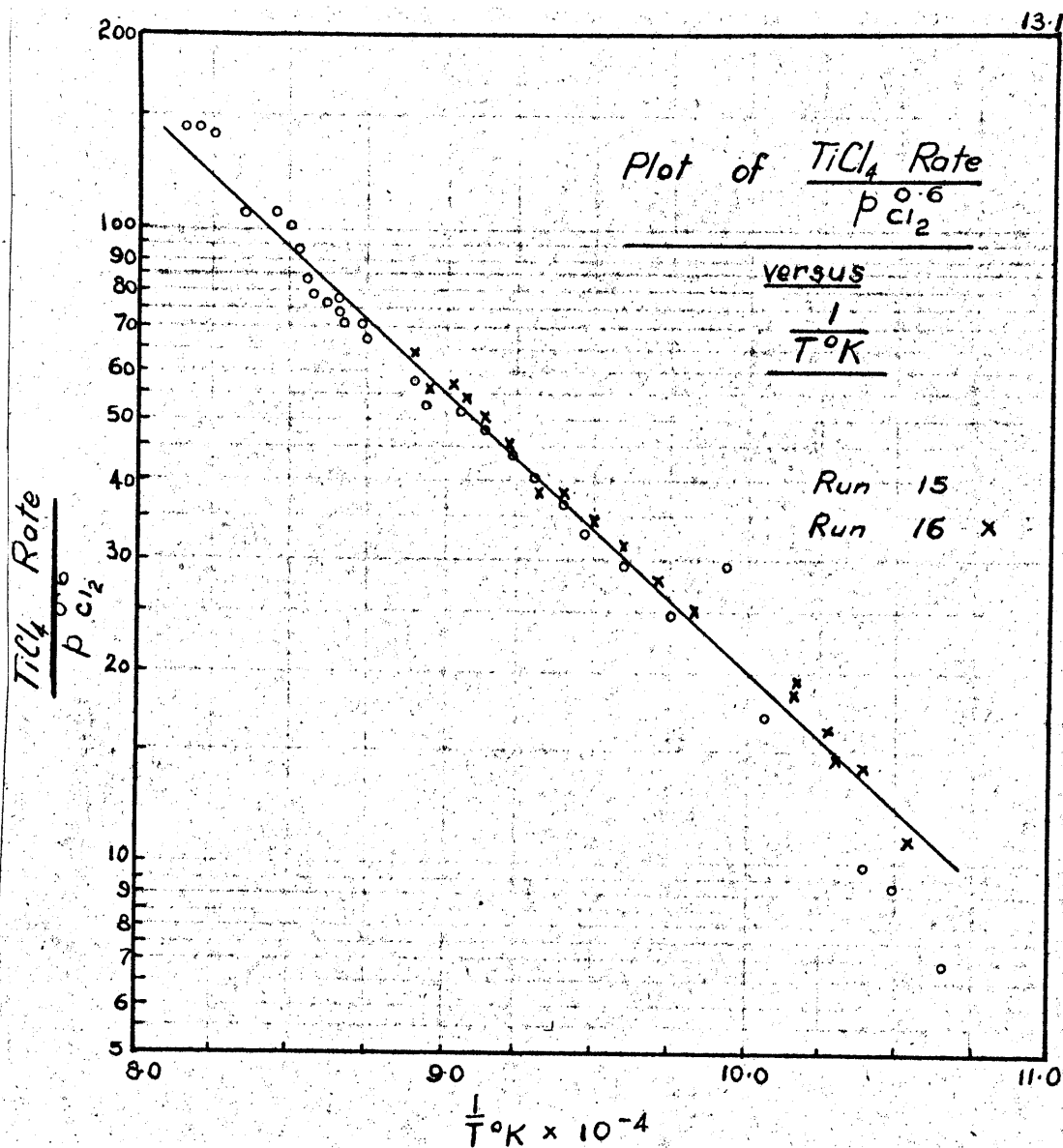


Figure 13.1

Figure 13.1 shows the plot of the function k against $1/T$ for the data of runs 15 & 16 Series II experiments, and shows good linear agreement of the data. Calculation of the energy of activation of the reaction from the slope of this line gives a value of 20 KCal./gm./mol.

While this value is subject to error due to the approximations made and the scant knowledge of the mechanism of the reaction, it is as would be expected of the same order as the energy of activation of chemisorption processes, and indicated that the rate of reaction is controlled by such a process. It is interesting to note that this value is of the same magnitude as the energy of

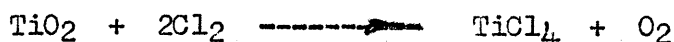
activation determined by Garner (47) for the chemisorption of CO on a variety of oxides.

Mechanism of Reaction

While the experiments discussed in previous chapters have yielded results which allow certain mechanisms previously considered probable to be eliminated, and have produced fresh evidence on the mechanisms itself, the data is still incomplete and no mechanism could be put forward with certainty without further work.

The experimental results obtained which are significant in determining the mechanism of the reaction are summarised below:

- a. The reaction commences at about 400°C, proceeding at appreciable rates above 650°C. The energy of activation is 20 KCal./gm./mol.
- b. The reaction is of fractional apparent order (0.6) with respect of chlorine.
- c. The reaction is unretarded by concentrations of carbon monoxide or carbon dioxide in the system.
- d. The reaction is autocatalysed by titanium tetrachloride, the rate of reaction increasing with increase in the partial pressure of titanium tetrachloride in the system.
- e. The adsorptions of chlorine and titanium tetrachloride appear to be the rate controlling steps.
- f. The reaction using carbon monoxide instead of carbon as the reducing agent in the chlorination is slow, the rates being in the ratio of approximately 1 to 20.
- g. At 900°C the reaction

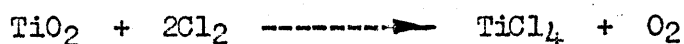


can be detected, but the rate is extremely slow.

- h. The reaction rate falls off very rapidly below a carbon to rutile ratio of approximately 0.2:1.

- i. Both carbon monoxide and carbon dioxide are formed as products of the reaction. At 900°C a tail gas containing approximately 55% of carbon dioxide is formed, the ratio of dioxide to monoxide changing little with reduction of the carbon content of the bed.
- j. Variation of the temperature changes the ratio of carbon monoxide to carbon dioxide in the tail gas, high temperatures favouring the formation of the monoxide.

The very low rate of the reaction of titanium dioxide and chlorine in the absence of reducing agents eliminates the possibility of the reaction mechanism shown by the equations



and



occurring, for, as discussed in Chapter III, it should be possible to achieve rates for the first step similar to those for the overall reaction by sweeping away the products of reaction in a fast stream of gas, thus disturbing the reaction equilibrium. This does not occur.

The mechanism suggested in Chapter III of adsorption of carbon monoxide and chlorine on the titanium dioxide surface, followed by the desorption of titanium tetrachloride and carbon dioxide, has also been shown to be of little importance in the fluid bed chlorination in the presence of carbon, for, had the chlorination occurred according to this scheme, the reaction rates obtained in experiments using carbon monoxide instead of carbon should have been of the same order in each case. Further evidence against this mechanism was obtained from the experiments showing that variation of the bed partial pressure of carbon monoxide had no effect on the reaction rate, and that the rate was in fact dependant on the amount of carbon in the bed.

The autocatalytic effect of titanium tetrachloride is most readily accounted for by a mechanism in which titanium tetrachloride is chemisorbed on the surface of titanium dioxide to form an intermediate compound. From the chemistry of titanium and related elements the most probable intermediate compound formed would seem to be the oxychloride TiOCl_2 , and although there is a derth of information on such a compound in the literature, both vanadium oxychloride (VOCl_2) and zirconium oxychloride (ZrOCl_2) have been isolated, the former as a liquid boiling at 127°C , the latter as a series of hydrated salts. This suggests that titanium oxychloride does exist, and from the properties of the related compounds it is not unreasonable to expect that it may be a gas at the chlorination temperature.

If the first step of the reaction is the formation of this oxychloride, the role of the carbon surface in the reaction may be accounted for by the transfere of the oxychloride to this surface, and its reaction there with adsorbed chlorine to yields the tetrachloride and oxygen which would then react with the carbon surface to give carbon monoxide and carbon dioxide.

Such a reaction mechanism requires the following steps:

- a. The chemisorption of titanium tetrachloride on the titanium dioxide surface to form titanium oxychloride.
- b. The desorption of titanium oxychloride
- c. The chemisorption of titanium oxychloride on the carbon surface and its reaction there with adsorbed chlorine to yield titanium tetrachloride, and the oxides of carbon.
- d. The desorption of titanium tetrachloride and the oxides of carbon from the carbon surface.

It has been shown experimentally that the adsorption of chlorine and titanium tetrachloride on the surfaces involved are the rate determining steps, and for

this mechanism it must be supposed that each of these rates are of comparable magnitude.

In the light of the experimental data one defect of this suggested mechanism is that it does not account for the constant CO:CO₂ ratio in the tail gas which does not vary with the amount of carbon in the bed, changing only with change in bed temperature.

A second possible mechanism could be the reaction of titanium tetrachloride and carbon monoxide on a carbon surface to form a co-ordination complex $\text{TiCl}_4 \cdot 2\text{CO}$ and the subsequent chemisorption of this complex on the titanium dioxide surface to form surface carbonate and dichloride followed by the adsorption of chlorine and the desorption of titanium tetrachloride and carbon dioxide. This mechanism is however less acceptable as it seems unlikely that the complex would be at all stable at the temperatures involved, if indeed it exists at all, and secondly in such a system carbon monoxide could only be formed by the secondary reaction of carbon dioxide with carbon; variation of the carbon content of the bed would alter the ratio of the oxides of carbon in the tail gas.

It is felt that these results have added to the understanding of the mechanism of the chlorination and that additional work should be carried out to further elucidate what has been shown to be a complex reaction system. The first steps in such work should be a study of the possible complexes formed by titanium tetrachloride with the other components of the reaction system, and of the part played by the carbon surface in the reaction mechanism.

Chapter XIV

Discussion of the Optimum Conditions for the Fluid Bed Chlorination of Rutile

The foregoing experimental investigation has shown that the overall reaction occurring in the fluid bed chlorination of rutile is represented by the equation



in which the ratio of carbon dioxide to carbon monoxide in the products of reaction varies with the reaction temperature and with the carbon to rutile ratio in the bed.

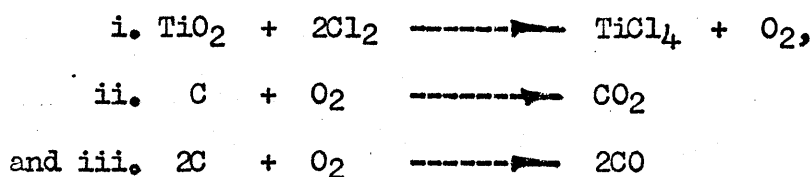
The optimum conditions for the reaction can best be discussed under the following headings:

- a. Temperature
- b. Rutile to Carbon Ratio
- c. Rutile and Carbon particle size
- d. Bed depth and Chlorine velocity
- e. Reactor Design
- f. Minimum size for an Autothermic Reactor

Temperature: As discussed in Chapter 11 the reaction commences at about 400°C and reaches a sufficient velocity to saturate the tail gas from the reactor with titanium tetrachloride at approximately 650°C. As the temperature is further increased the reaction rate-temperature relationship is linear to 1000°C which was the highest temperature reached, within which range the temperature coefficient was 0.166 gm/min./centigrade degree and the energy of activation was 20 KCal/gm.mol. Complete conversion of the chlorine feed to the reactor was obtained at temperatures between 900 and 1000°C at the bed depths used.

The optimum temperature for the chlorination is that temperature which yields the most exothermic reaction, and gives a sufficiently high rate of reaction. This temperature should be kept to a minimum to simplify the materials of constructions required. The heat of the overall reaction will vary with the temperature at which the reaction is carried out and with the proportion of carbon dioxide formed in the reaction. This, as has been shown varies with the reaction temperature and, to a lesser extent, with the carbon content of the bed. For the purpose of calculating the heat of reaction at various temperatures the composition of the tail gas shown in Figure 11.6 curve 'c' has been selected, as this data is in close agreement with the data of series three experiments at 900°C.

The overall reaction can be broken down into the following simple reactions for which the heats of reaction can be calculated,



These have been calculated from the data given in Appendix I and are shown in the following tables:

Table 14.1
Heat of Reaction Data

Reaction	ΔH Cal./mol.
$\text{TiO}_2 + 2\text{Cl}_2 \longrightarrow \text{TiCl}_4 + \text{O}_2$	$48444 + 5.64T - 4.15 \times 10^{-3}T^2 + 4.3 \times 10^5T^{-1}$
$\text{C} + \text{O}_2 \longrightarrow \text{CO}_2$	$-93449 - 0.6T - 0.09 \times 10^{-3}T^2 + 1.10 \times 10^5T^{-1}$
$2\text{C} + \text{O}_2 \longrightarrow 2\text{CO}$	$-51159 - 0.42T - 1.55 \times 10^{-3}T^2 - 4.22 \times 10^5T^{-1}$

Table 14.2Variation of the Heat of Reaction with Temperature

Temp. °C		700	800	900	1000
ΔH Cal/mol.	TiCl ₄	50380	50124	49770	49244
	CO ₂	-94000	-94070	-94170	-94270
	CO	-53470	-53790	-54150	-54550

Table 14.3 shows the number of mols. of carbon dioxide and carbon monoxide produced for each mol. of titanium tetrachloride formed for the reaction occurring at the temperatures given in Table 14.2 using the data of curve 'c' Figure 11.6, and the amount of heat absorbed or liberated in the formation of one mol. of titanium tetrachloride and ^{of} these amounts of carbon dioxide and carbon monoxide. The total heat of reaction, which is the sum of these heats, is given in the last column.

Table 14.3

Temp. °C	Mol. formed/mol. TiO ₂ reacting		ΔH Cal./mol. of TiO ₂ Reacting			
	CO ₂	CO	TiCl ₄	CO ₂	CO	Total
700	0.78	0.44	50380	-73400	-23500	-46520
800	0.74	0.52	50120	-69600	-27900	-47380
900	0.69	0.61	49700	-64900	-33100	-48300
1000	0.65	0.71	49240	-61100	-38800	-50660

This variation of heat of reaction with change of temperature is shown graphically in Figure 14.1

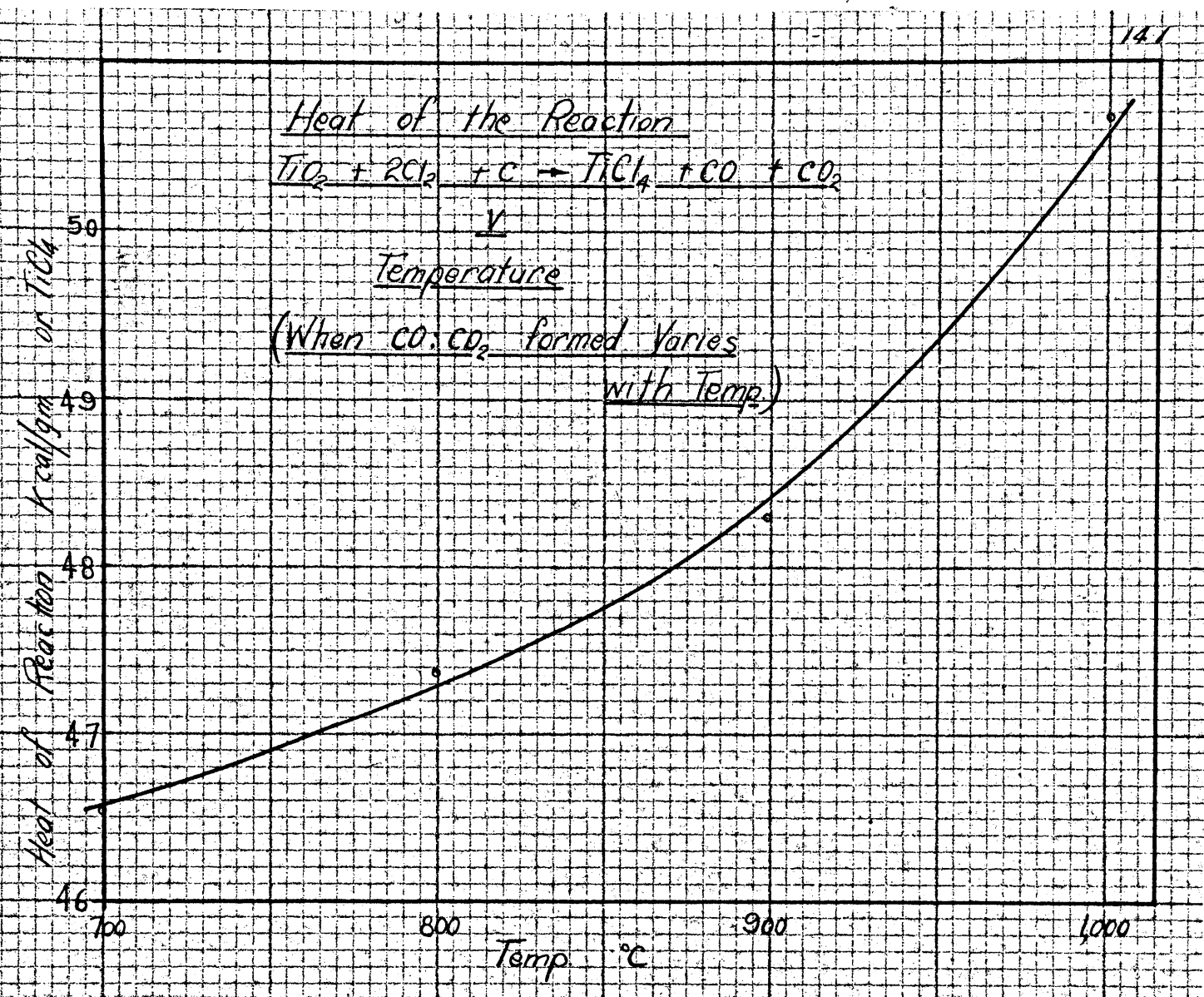


Figure 14.1

For continuous autothermic operation the sensible heat required to raise the reactants to operating temperature must be supplied from the heat of reaction as recovery of the heat from the gas leaving the reactor presents serious problems in construction and materials. Since the amount of carbon required for the reaction varies as the CO:CO₂ ratio changes with change in temperature, allowance must be made for this in calculation of the total sensible heat required. Table 14.4 shows the sensible heats required to bring the reactants from 25°C to the various reaction temperatures and the net heat of reaction under these conditions. Figure 14.2 shows the plot of net heat of reaction against temperature.

Table 14.4

Temp. °C	$\Delta H_{T_2 - T_1}$ Cal./mol. TiO_2 Reacting				Nett Heat of Reaction Cal./mol. TiCl_4
	TiO_2	Cl_2	C	Total	
700	11300	11600	3900	26800	-19720
800	13200	13400	4640	31200	-16180
900	15300	15200	5600	36100	-12200
1000	17400	17000	6600	41000	-9660

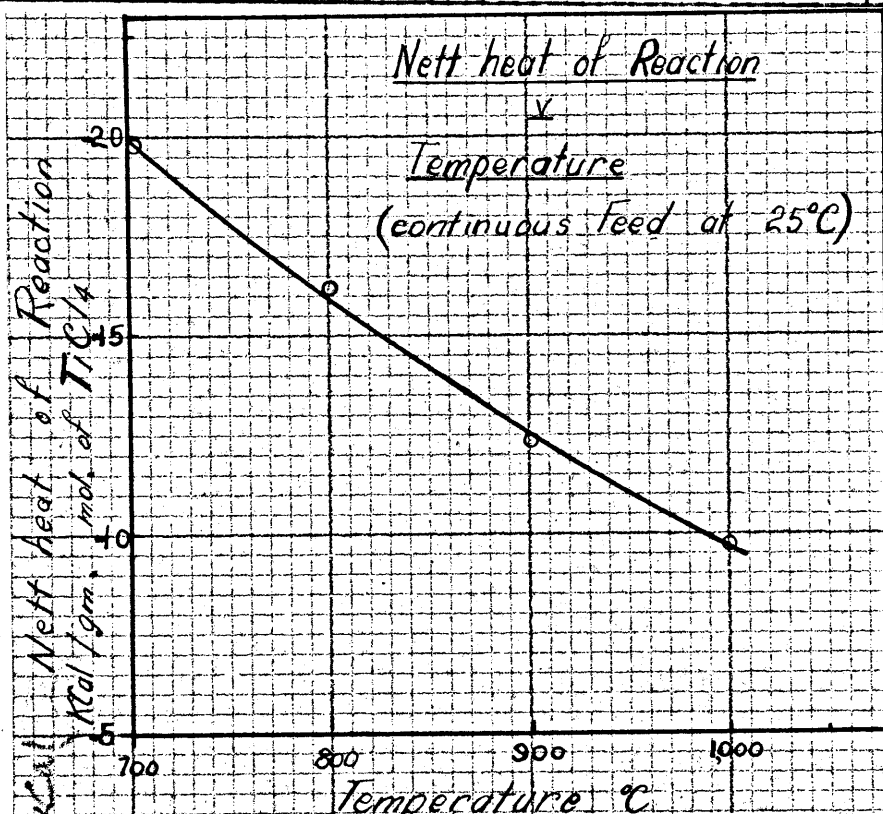


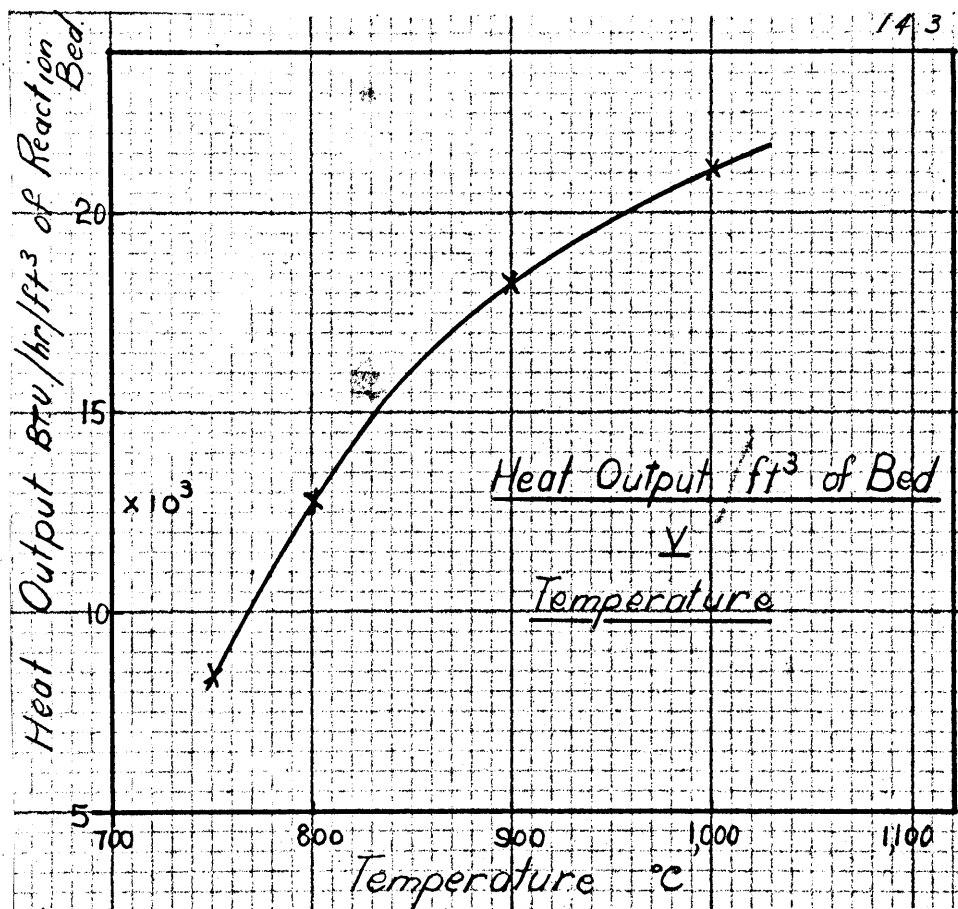
Figure 14.2

From the results of experiment 14 Series II complete chlorine conversion was obtained at 980°C for a bed containing 800 gms. of rutile using a chlorine feed of 36.5 gm./min. The total weight of the charge was then 1040 gms. with an unexpanded bed density of 1.66 gms./cc.; whence for a maximum bed expansion of 18% as determined from experiment, the length of diameter ratio (L/D) of the bed is 4.6:1, which gives an output of 3.5 lb./min. of titanium tetrachloride per cubic foot of bed volume. The formation rates shown in Table 14.5 at the tabulated temperatures were obtained from the data shown in Figure 11.5 for run 14. From these values and the above heats of reaction the heat outputs per cubic foot of bed have been calculated and are shown in

Table 14.5 and Figure 14.3

Table 14.5

Temperature °C	TiCl ₄ Formation Rate lb/min/ft ³	Heat Output BTU/hr/ft ³
750	0.83	8400
800	1.41	12700
900	2.56	18200
1000	3.74	21000

Figure 14.3

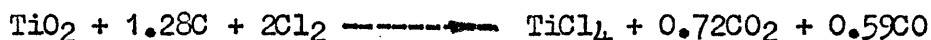
This data shows that the optimum temperature for the chlorination lies between 850 and 1000°C. In this range the rates of reaction achieved are high and the rate of increase in heat output is lower than in the range 750 and 850°C. Further factors influencing the optimum operating temperature are the effect of high temperatures on the construction materials of furnace and the melting point of the ash formed from the coke during the chlorination. As the choice of the lowest possible temperature will reduce the attack suffered by the furnace structure and will allow a wider choice of cokes, the optimum operating temperature would appear to be around 900°C.

Rutile to Carbon Ratio The results of run 19 of Series III experiments have shown that the optimum carbon content of the reaction bed is approximately 70% of the stiochiometric amount of carbon required for the reaction



This gives a rutile to carbon ratio of 4.75:1 by weight for the reaction bed.

It has also been shown that the carbon dioxide to carbon monoxide ratio in the tail gas varies little with change in the carbon content of the bed, remaining at approximately 56% carbon dioxide, giving the reaction



thus the rutile to carbon ratio in the feed should be 4.9 to 1. In operation the correct ratio should be checked periodically from analysis of the tail gas and of the carbon content of the bed.

Rutile and Carbon Particle Size The choice of particle size for rutile and carbon are governed by the following factors:

- a. Variation of fluidization characteristics with change in particle size.
- b. The increase in surface area available for reaction with decrease in particle size.
- c. The expense off fine grinding

Previous work has shown that the best fluidization characteristics are obtained using a range of particle sizes. In a continuous reactor this condition would be automatically obtained because of the gradual reduction of the size of the particles during chlorination, and although the rutile from beach sand is obtained as a closely sized material between 65 and 100 mesh, grinding would not be necessary, as such a feed would yield a size distribution in the bed giving high rates of reaction. Similar

considerations apply to, the carbon feed for which experiment has shown that a size range of 65 to 100 mesh would also be suitable. Separation of the fines from this ground material would be unnecessary as the loss of fines from a fluid bed is low due to a retaining effect exerted by the bed. Nevertheless some carryover of fines would occur and a cyclone should be used to separate these from the tail gas and return them to the reaction bed.

Chlorine Velocity: From the plot of bed depth to diameter ratio required for a given percentage chlorine conversion versus the chlorine feed rate (Fig. 9.9) it is seen that for the experimental reactor used the chlorine feed rate should not exceed 3.0 lbs./min./ft² of reactor cross section, as above this figure the L/D ratio required for the given conversion rises rapidly due to the increase in the bed slugging.

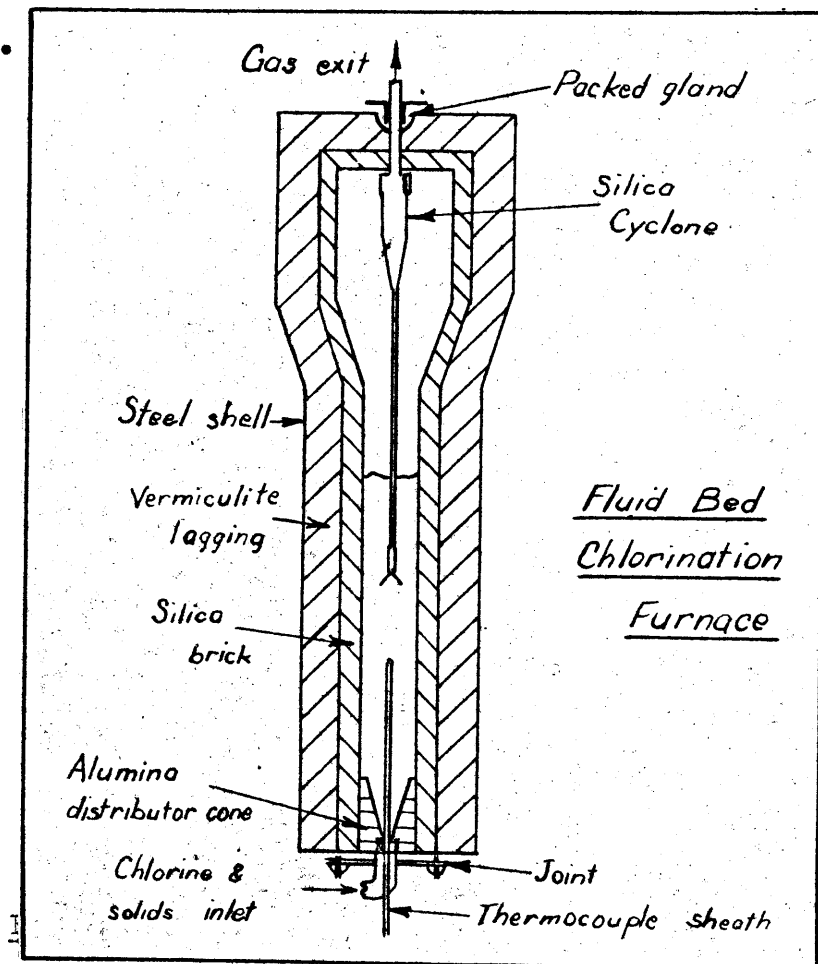
As the slugging tendency of the bed decreases with increase in the bed diameter, higher feed rates should be permissible in larger diameter beds. The extent to which these rates could be increased would have to be determined by experiment as no reliable data for scale-up is available.

Bed Depth: The depth of the reaction bed is necessarily determined by the characteristics of the fluid bed. The experimental runs have shown that slugging increases with increase in the bed depth, becoming very bad in rutile-carbon beds for a length to diameter ratio of 10:1. Although experiments (Nos. 14 and 15 of Series I) were carried out at an L/D ratio of 7.5:1 slugging was bad and could lead to difficulties in commercial operation. These experiments suggest that a maximum L/D ratio of 5:1 would be satisfactory for commercial reactors.

would a commercial reactor have a tube diam. of 2 1/4 in

Reactor Redesign: Figure 14.4 shows a reactor designed for an L/D ratio of 5:1. Since it is necessary to provide for the separation of solids carried up from the bed surface, free space must be provided above the bed. For the beds and gas velocities used these "streamers" of entrained solids seldom exceeded the diameter of the bed, and consequently a total L/D ratio of 7:1 for the reactor shaft should be satisfactory. This shaft should be surmounted by an enlarged section or "Knockout Drum" to allow for the disengaging of entrained solids at a lower gas velocity.

Figure 14.4



Early experiments showed that although the carryover of fines from the bed was relatively small (approx. 2% for the graded materials used) it was necessary to separate these to prevent blockages in the condensation system. This separation was carried out by a cyclone of the design shown in Perry's Chemical Engineering Handbook Third Edition using an inlet velocity of 50 ft/sec. For an industrial reactor this unit would be most suitably placed inside the knockout drum returning the separated material directly to the reaction bed. Such a unit could suitably be constructed, from fused silica.

from fused silica.

Measurements made on the experimental reactor tube and silica thermocouple sheath showed no appreciable attack after about forty hours operation at temperatures in the range of 900 - 1000°C, and it may be concluded that silica is a suitable material for the construction of the furnace shaft.

In the above reactor the shaft would be constructed from silica brick lagged with diatomaceous earth and the whole enclosed within a mild steel shell. The thickness of the lagging must be such as to reduce the heat losses to a reasonable level to allow autothermic operation and to hold the shell at a temperature at which chlorine attack will not occur. Ground rutile and coke would be continuously fed to the bed by entrainment in the chlorine feed, and the products of reaction would leave through the cyclone to pass to the condensation system. The feed to the reactor would be distributed by means of a silica distributing cone carrying a centrally placed thermocouple sheath, a solids discharge tube to allow periodical purging of the bed and a silica coil for heat removal and control of the bed temperature. The heat requirement of the reactor would be supplied by the heat of reaction after the reactor had initially been brought up to reaction temperature by burning coke in air in the bed. Once the coke bed had reached reaction temperature the reactant feed could be commenced and the startup air feed discontinued.

From the results of Series II experiments such a reactor having an expanded bed volume of 0.5 ft³ operating at 900°C would have an output of 1800 lbs. of titanium tetrachloride per day. Compared with the pilot plant results

reported by McTaggart this rate is approximately twenty times faster than the rates obtained for the chlorination of briquettes.

The Minimum Size for an Autothermic Reactor An autothermic reactor becomes possible when the net heat of reaction exceeds the heat losses from the reaction bed.

At a datum temperature equal to the temperature of reaction heat is lost from the bed by conduction through the walls of the reactor in contact with the bed and by radiation from the top of the bed to the remainder of the reactor surfaces. For a reactor of the shape described above the heat output increases as the third power of the diameter, while the heat loss increases approximately as the second power of the diameter. As heat losses will occur from a vanishingly small reaction space in which the heat output is negligible, it is apparent that there will be minimum size of reactor below which the reactor will not be thermally self supporting.

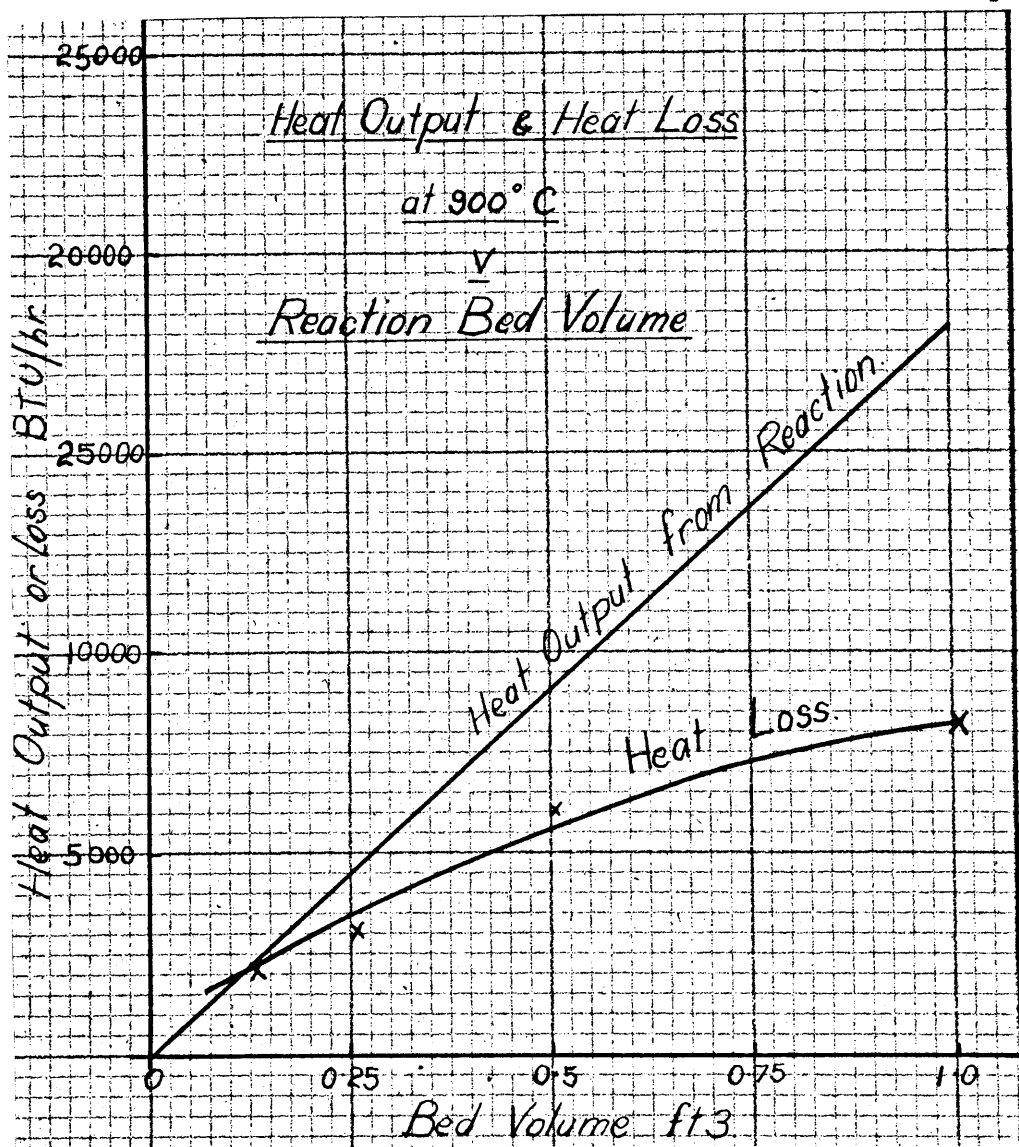


Figure 14.5

Figure 14.5 shows curves for the change of heat output and heat loss with change in the reaction bed volume for a reactor of the dimensions shown in Figure 14.4 using a lagging of four inches of diatomaceous earth. For bed volumes of 0.25 ft³ and below silica tube would be used instead of silica brick. The method of calculation the heat loss is shown in Appendix IV. This figure shows that for four inches of lagging and an operating temperature of 900°C autothermic operation could be obtained for reaction bed volumes in excess of 0.125 cubic feet.

These curves also show that above this minimum size reactor provision must be made to remove the heat of reaction in excess of that lost by conduction and radiation. Failure to remove this heat would result in runaway temperatures and damage to the reactor shaft.

As the total amount of heat to be removed is relatively small, 10,000 BTU/hr. for a reactor with a bed volume of one cubic foot, and the temperature gradient available is large, the greatest flexibility of operation would be achieved by circulating a suitable 'fluid' through a silica coil submerged in the fluid bed. As the temperature conditions preclude the use of all liquids other than liquid metals, the most suitable heat transfere medium would be a fine solid material in the lean phase fluidized state with air as the suspending medium. This would give suitably high heat transfere coefficients and a high heat removal per pound of heat transfere medium.

Conclusion

The investigation has shown that the fluid bed chlorination process is very attractive for the manufacture of titanium tetrachloride. Production rates may be obtained which are approximately twenty times faster than the old "briquette" chlorination, and at the optimum chlorination temperature (900°C) complete conversion of the chlorine feed is possible. Calculations based on experimental results show that continuous operation of an autothermic reactor should be possible for reactors with bed volumes in excess of 0.125 ft.³ such a reactor having titanium tetrachloride output of about 150 lb/hr./ft.³ of expanded bed volume.

These reactors would be simple and economical to operate.

APPENDICES

Appendix IThermodynamic DataTable ISpecific Heats of Substances

Substance	Temp. Range °K	Specific Heat Cal/°Mol.	Source
TiCl ₄	298.16	37.5	National Standards Bureau, Washington
TiCl ₄ (g)	"	22.8	"
FeTiO ₃ (c)	"	23.78	"
TiC (c)	"	"	"
TiO ₂	273/713	$C_p = 11.81 + 7.54 \times 10^{-3}T$ $- 0.419 \times 10^5 T^{-2}$	Kelley Compil.
C(graphite)	-1373	$2.673 + 2.617 \times 10^{-3}T$ $- 1.167 \times 10^5 T^{-2}$	"
CO(g)	-2500	$6.60 + 1.20 \times 10^{-3}T$	"
CO ₂ (g)	-1200	$10.34 + 2.74 \times 10^{-3}T$ $- 1.995 \times 10^5 T^{-2}$	"
Cl ₂ (g)	-200°	$8.28 + 0.56 \times 10^{-3}T$	"
O ₂ (g)	300-500	$8.27 + 0.258 \times 10^{-3}T$ $- 1.877 \times 10^5 T^{-2}$	"
Ti(c)	273-713	$8.91 + 1.14 \times 10^{-3}T$ $- 4.33 \times 10^5 T^{-2}$	"
TiCl ₄ (g)	298/1100	$25.74 + 0.1 \times 10^{-3}T$ $- 2.88 \times 10^5 T^{-2}$	Calculated (Appendix I)

TABLE II

Entropy, Heats and Free Energies of Formation

Substance	Temp. °K	K Cal. Mol ⁻¹		log ₁₀ KF	So Cal/ Degree mol	Source
		ΔH ^o	ΔF ^o			
TiO ₂ (c) (Rutile)	298.160	-218.0	-203.8	149.38	12.01	National Standards Bureau Compilation by
FeTiO ₃ (c)	"	-288.5	-268.9	197.1	25.3	
TiC	"	-54	-53	38.8	5.8	
TiCl ₄ (l)	"	-179.3	-161.2	118.6	60.4	
TiCl ₄ (g)	"				84.4	
Cl ₂ (g)	"				53.286	
C(B graph)	"				1.36 ± 0.003	
CO(g)		-26.42	-32.81	24.05	47.32	Rossini
CO ₂ (g)		-94.05	-94.25	69.09	51.08	1949

Latent Heat of Fusion TiCl₄ ΔH -23°C = 2.24 K cal.mol⁻¹

Entropy of Fusion of TiCl₄ ΔS -23°C = 9.0 Cal/°mol.

Latent Heat of Vapourisation of TiCl₄

ΔH = -8.62 Kal. mol⁻¹ National Standards Bureau, Rossini, 1949

ΔH = 13050 - 11.5 T cal. mol⁻¹ Kelley compilation.

Free Energy of Vapourisation of TiCl₄

ΔF₂₉₈ = -2.459 K.cal.mol⁻¹

ΔF = 13050 + 26.5 T log T - 101-10 T Kelley

Compilation

Entropy of Vapourisation of TiCl₄

ΔS_{409°K} = 20.4 Cal/°mol.

Calculation of the Specific Heat of Titanium Tetrachloride Vapour

The specific heat data for titanium tetrachloride could not be found in the literature, and has been calculated from Raman Spectra data for wave numbers.

$$\text{Then } C_p = \frac{3}{2} R + \frac{3}{2} R + R + C_v,$$

assuming the classical value of $\frac{3}{2} R$ for translational and rotational heat capacities, the molecule behaving as a symmetrical top.

The vibrational heat capacity for each level is given by the expression

$$C_v = \frac{3R x^2 e^x}{(e^x - 1)^2} \quad \text{for vibration}$$

along three different directions,

where

R = gas constant

$x = \frac{\theta}{T}$

$\theta = \frac{h\nu}{k} = 1.432 w$

k = Boltzman's constant

h = Planck's constant

ν = vibration frequency

w = wave No. cm^{-1}

The quantity x was calculated from wave numbers given by Weu "Vibration Spectra and Structure of Polyatomic Molecules", and the values of C_v obtained from tables given in Wenner's "Thermochemical Calculations" Page 345.

The values of C_p for titanium tetrachloride gas at various temperatures were then calculated, and a relationship of the form

$C_p = a + bT - cT^{-2}$ was obtained by setting up four simultaneous equations using the calculated values of C_p for a given temperature.

Calculation of Titanium Tetrachloride

Vapour Cp. Temperature Relationship

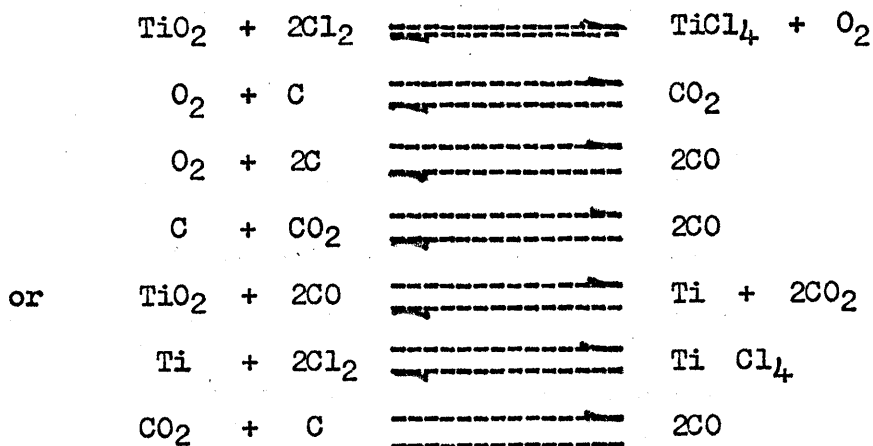
Level	W _{cm} ⁻¹	Degeneracy	θ	T=298.16°K		T=500°K		T=700°K		T=900°K		T=1100°K	
				x	Cv	x	Cv	x	Cv	x	Cv	x	Cv
1	386	1	552.7	1.85	1.505	1.11	1.795	0.79	1.887	0.61	1.930	0.50	1.946
2	119	2	170.4	0.57	3.867	0.34	3.935	0.24	3.954	0.19	3.961	0.16	3.964
3	419	3	703.1	2.36	3.823	1.41	5.064	1.00	5.488	0.78	5.667	0.64	5.768
4	139	3	199.0	0.67	5.742	0.40	5.882	0.28	5.922	0.22	5.936	0.18	5.943
Cv				14.957		16.674		17.251		17.494		17.621	
Cp				22.885		24.622		25.20		25.44		25.57	

Whence Cp = 25.74 + 0.1 x 10⁻³T - 2.88 x 10⁵T⁻²

Thermodynamic Survey of Chlorination

In the purpose of clarifying the reaction mechanism which takes place when chlorine is reacted with titanium dioxide in the presence of carbon, the following calculation of equilibrium constants for the possible reaction have been carried out.

The reactions which may occur are:



The equilibrium constants for the above reactions have been calculated from specific test data for the reaction, using the Van't Hoff isochore.

$$\frac{d \ln K_p}{dT} = \frac{\Delta H}{RT^2}$$

$$\text{in which } \Delta H = \int C_p dT$$

$$\text{then } \ln K_p = \int \frac{\Delta H}{RT^2} dT$$

Calculation of Equilibrium Constant for the Reaction:

$\sum C_p$ R.H.S.

$$C_p \text{ TiCl}_4 = 25.74 + 0.1 \times 10^{-3}T - 2.88 \times 10^5 T^{-2}$$

$$C_p \text{ O}_2 = \frac{8.27 + 0.26 \times 10^{-3}T - 1.88 \times 10^5 T^{-2}}{2}$$

$$\sum C_p = \frac{34.01 + 0.36 \times 10^{-3}T - 4.76 \times 10^5 T^{-2}}{2}$$

$\sum C_p$ L.H.S.

$$C_p \text{ TiO}_2 = 11.81 + 7.54 \times 10^{-3}T - 0.42 \times 10^5 T^{-2}$$

$$C_p 2\text{Cl}_2 = \frac{16.56 + 1.12 \times 10^{-3}T}{2}$$

$$\sum C_p = \frac{28.37 + 8.66 \times 10^{-3}T - 0.42 \times 10^5 T^{-2}}{2}$$

$$\Delta C_p = 5.64 - 8.30 \times 10^{-3}T - 4.34 \times 10^5 T^{-2}$$

$$\Delta H = H_0 + 5.64T - 4.15 \times 10^{-3}T^2 + 4.34 \times 10^5 T^{-1}$$

$$\Delta H(f)_{298^\circ} \text{ TiCl}_4(g) = \Delta H \text{ TiCl}_4(l) - \Delta H \text{ vap.}$$

$$= -179.3 + \frac{13050 - 11.5 \times 298}{1000}$$

$$= -179.3 + 9.6 - 169.7 \text{ K.cal.mol.}^{-1}$$

$$\Delta H_{298} = -169.7 + 218.0 = 48.3 \text{ K.cal.mol.}^{-1}$$

$$\therefore 48300 = \Delta H_0 + 5.64 \times 298 - 4.14 \times 10^{-3} \times 298^2 + \frac{4.34 \times 10^5}{298}$$

$$\Delta H_0 = 48300 - 1680.7 + 368.5 + 1456.4$$

$$= 48444$$

$$\therefore \Delta H = 48444 + 5.64T - 4.15 \times 10^{-3}T^2 + 4.34 \times 10^5 T^{-1}$$

$$\text{Now } \frac{d \ln K_p}{dT} = \frac{\Delta H}{RT^2}$$

$$= \frac{48444}{RT^2} + \frac{5.64}{RT} - \frac{4.15 \times 10^{-3}}{R} + \frac{4.34 \times 10^5}{RT^3}$$

$$\ln K_p = \frac{-48444}{RT} + \frac{5.64 \ln T}{R} - \frac{4.15 \times 10^{-3} T}{R} - \frac{2.17 \times 10^5}{RT^2} + I$$

$$\text{Also } \ln K_p = \frac{-\Delta F}{RT}$$

$$\begin{aligned} \Delta F_{298} \text{ TiCl}_4(g) &= \Delta F_{\text{TiCl}_4(l)} - \Delta F_{\text{vap.}} \\ &= -161.2 + \frac{(13050 + 26.5 T \log - 101.5 T)}{1000} \end{aligned}$$

$$\Delta F = -158.8 \text{ K.cal.mol.}^{-1}$$

$$\Delta F = -158.8 + 203.8 = 45.0 \text{ K.cal.mol.}^{-1}$$

$$\ln K_p = \frac{-45000}{1.98 \times 298} = -76.27$$

$$\therefore -76.27 = \frac{-48444}{1.98 \times 298} + \frac{2.30 \times 5.64 \times 2.476}{1.98} - \frac{4.15 \times 10^{-3} \times 298}{1.98}$$

$$\frac{-2.17 \times 10^5}{1.98 \times 8.88 \times 10^4} + I$$

$$\therefore I = -8.56$$

$$\therefore \ln K_p = \frac{-48444}{RT} + \frac{5.64 \ln T}{R} - \frac{4.15 \times 10^{-3} T}{R} - \frac{2.17 \times 10^5}{RT^2} - 8.56$$

Table III

Variation of K_p with Temperature

T°C	400	500	600	700	800	900	1000
ln K _p	-28.03	-23.08	-19.27	-16.36	-13.83	-11.81	-10.16
K _p	6.65 × 10 ⁻¹³	9.5 × 10 ⁻¹¹	4.3 × 10 ⁻⁹	7.9 × 10 ⁻⁸	9.8 × 10 ⁻⁷	7.5 × 10 ⁻⁶	3.9 × 10 ⁻⁵

$$K_p = \frac{P_{\text{TiCl}_4} \times P_{\text{O}_2}}{P_{\text{Cl}_2}^2}$$

for the reaction $\text{TiO}_2 + 2\text{Cl}_2 \rightleftharpoons \text{TiCl}_4 + \text{O}_2$

Let 100 α = the mol. % conversion of chlorine

Then mols. at equilibrium = $2(1 - \alpha) + 2\alpha = 2$

$$p_{\text{Cl}_2} = 1 - \alpha$$

$$\text{PTiCl}_4 = \text{PO}_2 = \frac{x}{2}$$

$$\therefore K_{p1000^\circ\text{C}} = \frac{\frac{x^2}{4}}{(1-x)^2} = 3.9 \times 10^{-5}$$

$$\therefore 0.5 = 0.00625 - 0.00625x$$

$$\therefore = 0.0125$$

$$\therefore \text{Conversion} = 1.25\%$$

(2) Calculation of Equilibrium Constant for Reaction

$$\begin{array}{rcl} \text{TiO}_2 + 2\text{CO} & \xrightarrow{\hspace{1cm}} & \text{Ti} + 2\text{CO}_2 \\ \text{Cp R.H.S. Ti} & = & 9.91 + 1.14 \times 10^{-3}T - 4 \times 10^5 T^{-2} \\ 2\text{CO}_2 & = & 20.68 + 6.48 \times 10^{-3}T - 3.92 \times 10^5 T^{-2} \\ \{ \text{CP} & 29.59 + 7.62 \times 10^{-3}T - 8.22 \times 10^5 T^{-2} & \\ & \text{=====} & \end{array}$$

$$\begin{array}{rcl} \text{Cp L.H.S. TiO}_2 & = & 11.81 + 7.54 \times 10^{-3}T - 0.42 \times 10^5 T^{-2} \\ 2\text{CO} & = & 13.20 + 2.40 \times 10^{-3}T \\ \{ \text{CP} & = & 25.01 - 9.94 \times 10^{-3}T - 0.42 \times 10^5 T^{-2} \\ & \text{=====} & \end{array}$$

$$\Delta \text{Cp} = 4.58 - 2.32 \times 10^{-3}T - 7.80 \times 10^5 T^{-2}$$

$$\Delta \text{H} = \Delta \text{H}_0 + 4.58T - 1.16 \times 10^{-3}T^2 + 7.80 \times 10^5 T^{-1}$$

$$\Delta \text{H}_{298} = -188.1 + 218 + 52.84$$

$$= 82.740 \text{ K.cal.mol.}^{-1}$$

$$\therefore 82740 = \Delta \text{H}_0 + 4.58 \times 298 - 1.16 \times 10^{-3} \times 8.88 \times 10^4 + \frac{7.8 \times 10^5}{298}$$

$$82740 = \Delta \text{H}_0 + 1368 - 104 + 2620$$

$$\Delta \text{H}_0 = 78656 \text{ cal.mol.}^{-1}$$

$$\therefore \Delta \text{H} = 78656 + 4.58T - 1.16 \times 10^{-3}T^2 + \frac{7.8 \times 10^5}{T}$$

$$\frac{d \ln K_p}{dt} = \frac{78686}{RT^2} + \frac{4.58}{RT} - \frac{1.16 \times 10^{-3}}{R} + \frac{7.8 \times 10^5}{RT^3}$$

$$\ln K_p = \frac{-78656}{RT} + \frac{4.58 \ln T}{R} - \frac{1.16 \times 10^{-3} T}{R} - \frac{3.9 \times 10^5}{RT^2} + I$$

$$\Delta F_{298} = -2 \times 94.25 + 2 \times 32.81 + 203.8$$

$$= 80.9 \text{ K.cal.mol.}^{-1}$$

$$\ln K_p = \frac{-80900}{1.98 \times 298} = -137.1$$

$$\therefore I = -13.8$$

$$\therefore \ln K_p = \frac{-78656}{RT} + \frac{4.58 \ln T}{R} - \frac{1.16 \times 10^{-3} T}{R} - \frac{3.9 \times 10^5}{RT^2} - 13.8$$

Table IV

Variation of Kp with Temperature

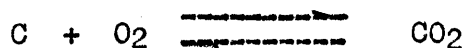
T°C	400	500	600	700	800	900	1000
ln Kp	-58.4	-50.4	-44.3	-39.4	-35.4	-32.0	-29.2
Kp	4×10^{-26}	1.3×10^{-22}	5×10^{-20}	8×10^{-18}	4×10^{-16}	1.2×10^{-14}	1.6×10^{-13}

Whence % Conversion at 1000°C = $4 \times 10^{-7}\%$

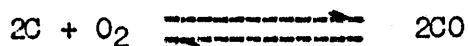
Equilibrium Constant for the Reaction of Carbon, Oxygen & the Oxides of Carbon

The log equilibrium constants tabulated in Table V have been calculated as in the above calculation from the specific heat, heats of reaction, and free energy tabulated above.

Then for the Reactions

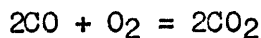


$$\ln K_p = \frac{9344.9}{RT} - \frac{0.6 \ln T}{R} - \frac{0.09 \times 10^{-3} T}{R} - \frac{0.55 \times 10^5}{RT^2} + 2.7,$$



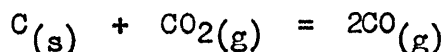
$$\ln K_p = \frac{51159}{RT} + \frac{0.42 \ln T}{R} - \frac{1.55 \times 10^{-3} T}{R} + \frac{2.11 \times 10^5}{RT^2} + 24.44$$

AND



$$\ln K_p = \frac{141990}{RT} - \frac{0.79 \ln T}{R} + \frac{1.41 \times 10^{-3} T}{R} - \frac{11.02 \times 10^5}{RT^2} - 30.5$$

The log equilibrium constant for the reaction



have been calculated from the equation

$$\ln K_p = \frac{-40910}{RT} + \frac{4.9 \ln T}{R} - \frac{0.00495T}{R} + \frac{0.051 \times 10^{-5} T^2}{R} + \frac{12.66}{R}$$

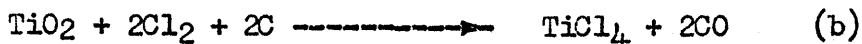
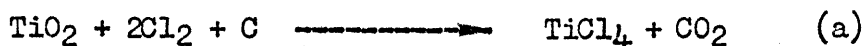
taken from the International Critical Tables.

Table V

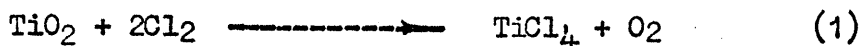
Variation of $\ln K_p$ with Temperature

No.	Reaction	$\ln K_p$				
		200°C	400°C	600°C	800°C	1000°C
1	$TiO_2 + 2Cl_2 \rightleftharpoons TiCl_4 + O_2$	-44.2	-28.03	-19.27	-13.83	-10.16
2	$C + O_2 \rightleftharpoons CO_2$	100.7	70.9	54.7	44.5	37.4
3	$2C + O_2 \rightleftharpoons 2CO$	78.8	60.7	51.1	45.3	39.9
4	$2CO + O_2 \rightleftharpoons 2CO_2$	119.1	74.1	49.7	34.1	23.8
5	$CO_2 + O_2 \rightleftharpoons 2CO$	-23.25	-9.78	-2.60	1.90	5.02

It is theoretically possible for the following overall reaction to take place



each of which may be written as two binary reactions, e.g.



$$\text{Now } K_p(1) = \frac{p_{\text{TiCl}_4} \times p_{\text{O}_2}}{p_{\text{Cl}_2}^2}$$

$$\text{then } K_p(2) = \frac{p_{\text{CO}_2}}{p_{\text{O}_2}}$$

$$\text{then } K_p(\text{a}) = \frac{p_{\text{TiCl}_4} \times p_{\text{CO}_2}}{p_{\text{Cl}_2}^2} = K_p(1) \times K_p(2)$$

$$\text{then } \ln K_p(\text{a}) = \ln K_p(1) + \ln K_p(2)$$

The values of the theoretical equilibrium constants for the overall reaction are given below

Table VI
Variation of Kp with Temperature

Reaction	Kp				
	200°C	400°C	600°C	800°C	1000°C
$\text{TiO}_2 + 2\text{Cl}_2 + \text{C} \longrightarrow \text{TiCl}_4 + \text{CO}_2$	1.3×10^{24}	5×10^{18}	9×10^{14}	2×10^{13}	7×10^{11}
$\text{TiO}_2 + 2\text{Cl}_2 + 2\text{C} \longrightarrow \text{TiCl}_4 + 2\text{CO}$	1.5×10^{14}	1.5×10^{15}	6.6×10^{13}	4.5×10^{13}	8×10^{12}
$\text{TiO}_2 + 2\text{Cl}_2 + 2\text{CO} \longrightarrow \text{TiCl}_4 + 2\text{CO}_2$	1.6×10^{28}	1.3×10^{20}	2.5×10^{13}	6.6×10^8	8.1×10^5

In every case these values of Kp correspond to 100% conversion. It is impossible, therefore, to state from this data which reaction is most likely to occur.

Appendix II

Sample calculation of the total titanium tetrachloride rate, the instantaneous weight of titanium dioxide in the bed, and the materials balances on the system for Series Ib experiments. The calculations are carried out on the results of Run 7.

Loss of TiCl_4 in the Tail Gas

The loss of titanium tetrachloride leaving the system in the tail gas was calculated on average values for the measured titanium tetrachloride rate, and the analysis of the tail gas.

Total Weight of TiCl_4 collected	1603 gm.
Time Run	41.5 min.
Average TiCl_4 Rate	38.9 gm/min.

Average Tail Gas Analysis for CO_2 and CO : 40% CO_2 60% CO

which leads to the reaction:



Whence the volume of CO and CO_2 formed is

$$\frac{38.7}{190} \times 24 \times \frac{2.5}{1.75} = 6.96 \text{ l/min. at R.T.P.}$$

$$\text{Unused chlorine in tail gas } 42 - \left(38.7 \times \frac{142}{190} \right) = 13 \text{ gm./min.}$$

Therefore the volume of Chlorine = 4.41./min.

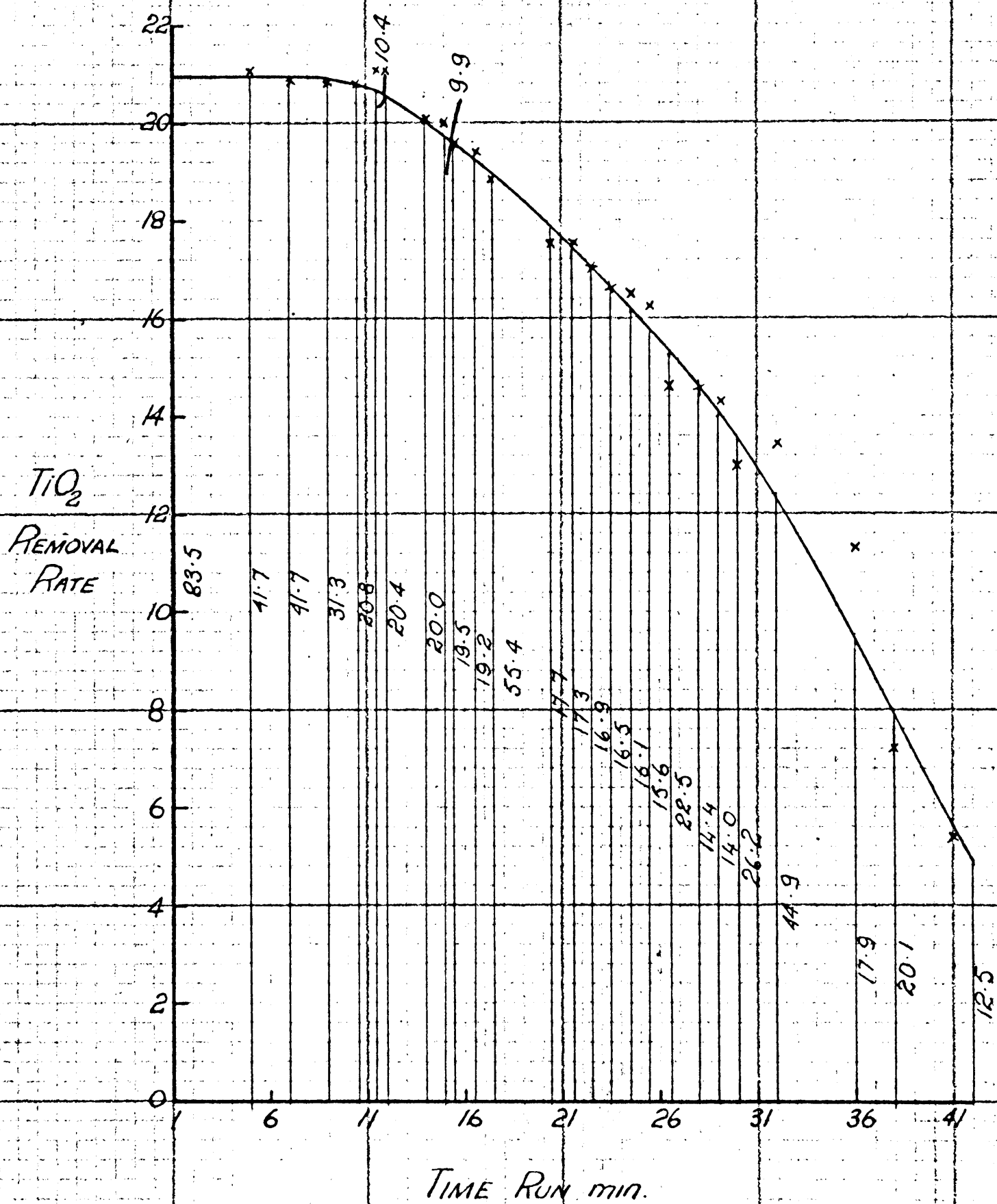
Therefore total Volume of Tail Gas = 11.36 l/min.

TiCl_4 in T.G. (assumed from previous Analysis) 2%

$$\text{Whence volume of } \text{TiCl}_4 = 11.36 \times \frac{2}{98} = 0.227 \text{ l./min.}$$

$$= 190 \times \frac{0.227}{24}$$

$$= 1.8 \text{ gm./min.}$$



Total TiCl_4 Production Rate

The total titanium tetrachloride rate is equal to the measured rate plus the amount of titanium tetrachloride leaving in the tail gas. The values for the total rate were then calculated by adding 1.8 gm./min. to the measured values as recorded in Table 8.8.

In later experiments the amount of $TiCl_4$ lost was calculated directly from the analysis and measured rate of flow of the tail gas as shown in Appendix III. This gave more accurate values than calculation from the measured titanium tetrachloride rate.

Instantaneous Wt. of TiO_2 in Bed

The rate of removal of titanium tetrachloride from the reactor is calculated from the total titanium tetrachloride rate using the molecular weights of the two substances.

Figure A2.1 shows the plot of TiO_2 removal rate versus time for the run, the figures in the individual areas giving the amount of titanium dioxide removed from the bed between each measurement of titanium tetrachloride rate. The total weight of TiO_2 in the bed at any time is then calculated by summation of these values and the weight of dioxide in the bed at the end of the run.

Residue in Reactor 112gm. TiO_2 content 39.6%

Therefore TiO_2 in reactor at end of run = 43 gm.

$$\begin{aligned}\text{Whence TiO}_2 \text{ in reactor after 36 min. run} &= 43 + 2.5 + 20.1 + 17.9 \\ &= 83.5 \text{ gm.}\end{aligned}$$

Materials BalancesTitanium Dioxide

Charge to bed = Total charge - material in annulus below gas distributor

$$= 1100 - 64 = 1036 \text{ gm.}$$

TiO₂ in bed at start of chlorination

$$= 1036 \times 76.8 \times 0.967$$

$$= 795 \text{ gm.}$$

Weight of TiCl₄ collected = 1603 gm.

Weight of TiCl₄ lost in tail gas = $41.5 \times 1.8 = 74.8 \text{ gm.}$

Total weight of TiCl₄ produced = 1677.8 gm.

Equivalent weight of TiO₂ = 710 gm.

Weight of TiO₂ in reactor residue = 43 gm.

Weight of TiO₂ in cyclone residue = 8 gm.

Total weight of TiO₂ accounted for = 761 gm.

i.e. Percentage of TiO₂ in charge = 96%

Carbon

Carbon in charge = $1036 \times 0.232 = 240 \text{ gm.}$

Carbon in reactor residue = $112 \times 0.604 \text{ gm.} = 67.5 \text{ gm.}$

Carbon in cyclone residue = $23 \times 0.638 \text{ gm.} = 14.7 \text{ gm.}$

Carbon removed by reaction:

From average reaction 1.75 mol. TiCl₄ formed removed 2.5 mol.

of carbon,

whence for 1678 gm. of TiCl₄ formed $\frac{1678}{190} \times \frac{2.5}{1.75} \times 12 = 151 \text{ gm.}$

of carbon are removed.

Therefore carbon accounted for at end of chlorination =

$$151 + 67.5 + 14.7 = 233.2 \text{ gm.}$$

i.e. 97% of carbon in the charge.

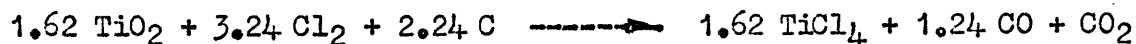
Chlorine

Calculated on Gas Sample I. (Table 8.8)

Cl_2 9.5%, CO_2 40.4%, CO 50.2%

Measured TiCl_4 rate = 47.5 gm./min.

Reaction occurring (from gas analysis)



whence volume of CO and CO_2 formed

$$= 47.5 \times \frac{24 \times 2.24}{190 \times 1.62} = 8.3 \text{ l./min. at R.T.P.}$$

$$\text{volume of chlorine} = 8.3 \times \frac{9.5}{90.5} = 0.87 \text{ l./min.}$$

whence volume of tail gas = 9.17 l./min.

and TiCl_4 in the tail gas = 1.42 gm./min.

Recalculation on the Total TiCl_4 rate

volume of chlorine = 0.91 l./min.

$$= 2.7 \text{ gm./min.}$$

∴ total chlorine leaving the reactor

$$= 48.9 \times \frac{142}{190} + 2.7 = 39.7 \text{ gm./min.}$$

$$\text{Chlorine accounted for} = \frac{39.7}{42.0} \times 100 = 94.5\%$$

In later experiments the weight of chlorine leaving the system was calculated from the analysis and rate of flow of the tail gas ^{as} shown in Appendix III.

Appendix IIICalculation of Tail Gas Rates and Chlorine Materials Balances

The chemical analysis and flow rate of the gas leaving the liquid separation system were determined at three points during each run. The weights of titanium tetrachloride and chlorine in the exit gas were calculated from these analysis and flow rate measurements.

In this calculation the analysis by volume was first converted to analysis by weight using the specific gravities of each component, and the flow rate determined in c.f.m. of air was converted to weight flow in grams of gas flowing per minute using the following equation

$$\text{Tail Gas Rate} = Q \times 3405 \times \rho^{\frac{1}{2}} \text{ gm./min.}$$

where Q = equivalent c.f.m. of air (read from chart)

ρ = calculated specific gravity of Tail Gas relative to air

specific gravities relative to air

$$\text{Cl}_2 = 2.486$$

$$\text{CO}_2 = 1.529$$

$$\text{CO} = 0.967$$

$$\text{N}_2 = 0.967$$

$$\text{TiCl}_4 = 6.66$$

The material balance on chlorine for each gas sample taken was then calculated from the rate of condensation of titanium tetrachloride, weight by weight analysis of the tail gas and the tail gas rate.

An example of this calculation is shown below in Sample I of Run III. II

Component	Cl ₂	TiCl ₄	CO ₂	CO	N ₂	
% by vol.	13.4	1.2	13.7	12.2	59.5	
x S.G.	33.4	8.0	21.0	11.8	57.6	= 123.8
% by wt.	27.0	6.46	17.0	9.5	46.5	

$$\text{Specific gravity} = 123.8/100 = 1.238$$

Flow Rate

Equivalent air rate determined from "Flow Rate" = 0.435 c.f.m.

$$\therefore \text{Tail Gas Rate} = 0.435 \times 34.05 \times 1.238^{\frac{1}{2}}$$

$$= 16.5 \text{ gm./min.}$$

$$\therefore \text{TiCl}_4 \text{ in Tail Gas} = 16.5 \times 0.0646 = 1.07 \text{ gm./min.}$$

$$\text{Chlorine in Tail Gas} = 16.5 \times 0.27 = 4.44 \text{ gm./min.}$$

Chlorine Balances

$$\text{Chlorine feed rate} = 17.75 \text{ gm./min.}$$

$$\text{TiCl}_4 \text{ condensation rate} = 17.0 \text{ gm./min.}$$

$$\begin{aligned} \text{TiCl}_4 \text{ tail gas rate} &= \underline{1.07} \text{ gm./min.} \\ &18.07 \text{ gm./min.} \\ &===== \end{aligned}$$

$$\text{Chlorine equivalent} = 13.5 \text{ gm./min.}$$

$$\text{Chlorine in tail gas} = \underline{4.44} \text{ gm./min.}$$

$$\begin{aligned} \text{Total chlorine activated} &= 17.9 \text{ gm./min.} \\ &===== \end{aligned}$$

$$\begin{aligned} \therefore \text{Chlorine Balance} &= \frac{17.9}{17.75} \times 100 \\ &= 101\% \end{aligned}$$

Appendix IV

Calculation of Heat Losses from the Reaction Bed

Using the reaction temperature (900°) as the datum temperature heat is lost from the reaction bed to the surroundings by conduction through the walls and bottom of the reactor in contact with the bed, and by radiation from the top of the bed to the top inside surfaces of the reactor.

Conduction Losses The temperature of the inside walls of the reactor is uniform within the bed at 900°C which for a bed L/D ratio of 5:1 and an expanded bed volume of 0.5 ft³ requiring a shaft diameter of 0.5 ft. gives a depth of 2.5 ft. Above the surface of the bed the wall temperature will decrease with increase in distance from the bed. For simplicity of calculation it will be assumed that heat is lost from the entire length of the shaft at a wall temperature of 900°C.

The heat loss through the wall is given by the equation

$$Q = \frac{\Delta T}{\frac{1}{h_1 A_1} + \frac{l_1}{k_1 A_2} + \frac{l_2}{k_2 A_3} + \frac{1}{(h_c + h_r) A_4}}$$

Where

- Q = Total heat transferred Btu/hr.
- ΔT = Temperature gradient. Reaction temp. 900°C - ambient temp. 27°C.
- h₁ = Heat transference coefficient between bed and shaft.
- k₁ = Thermal conductivity of silica brick 0.76 Btu/hr/ft²/°F/ft.
- k₂ = Thermal conductivity of Diatomaceous earth 0.074/Btu/hr/ft²/°F/ft.
- A₁ = Area of inner surface of the shaft ft²
- A₂ = Log mean area of Silica Brick 2.26 ft²/ft. run
- A₃ = " " " " " " 4.08 " "
- A₄ = Area of external surface of the lagging 5.2 ft²/ft.
- l₁ = Thickness of the silica brick 0.25 ft.
- l₂ = Thickness of lagging 0.33 ft.

$h_c + h_r$ = Combined convection and radiation coefficient

$$3 \text{ Btu/hr/ft}^2/\text{°F}$$

The resistance due to the mild steel shell and to the heat transference between the bed and the shaft may be neglected as each are small compared with the other resistances encountered.

From the above equation the total heat loss from the shaft wall is 4880 Btu/hr.

The heat loss from the bottom of the bed is reduced to a minimum as the heat flow in this direction is largely absorbed in heating the cold feed. Assuming the effective area for heat loss allowing for corner correction is a circle of radius from the centre line to the middle of the wall, this heat loss was calculated at 180 Btu/hr.

Radiation Loss Heat is lost from the top of the bed by radiation to the top and sides of the disengaging section of the reactor. The amount of heat lost in this way is dependant on the temperature of these surfaces, which are heated by the gas leaving the bed and by radiation from the bed itself, the actual temperature achieved depending on the balance of heat supplied from these sources and heat loss through the walls.

The maximum heat available from the gas by convection and radiation is the sensible heat between 900°C and the wall temperature. Assuming that the gas left the reactor at 100°C above the wall temperature the sensible heat supplied at various wall temperatures were calculated, to which values were added the heat supplied by radiation as calculated from the equation

$$Q = 0.173 \left[\left(\frac{T_1}{100} \right)^4 + \left(\frac{T_2}{100} \right)^4 \right] A F$$

Where

Q = Heat transferred Btu/hr.

T_1 = Bed temperature $^{\circ}\text{K}$

T_2 = Wall temperature $^{\circ}\text{K}$

A = Surface area of the bed ft^2

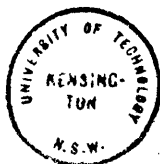
F = Shape factor determined at approximately 0.3

The heat loss through the walls and top of the reactor were then calculated as above for the shaft from a plot of heat supplied and heat loss versus the wall temperature the intersection of these curves gave an approximate wall temperature of 700°C . For this temperature the radiation loss from the surface of the bed was calculated to be 1200 Btu/hr.

Therefore the total heat loss from the bed

$$= 4880 + 120 + 1200 = 6200 \text{ Btu/hr.}$$

This heat loss is equivalent to the loss from the shaft only of a reactor with an L/D ratio of 10:1 and other points on the heat loss curve of Figure 14.5 have been determined using this approximation.



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