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RESEARCH FOR INDUSTRY

THE AUSTRALIAN MINERAL DEVELOPMENT LABORATORIES

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1/1/12

29th March, 1963

The Director,
Department of Mines,
Rundle Street,
ADELAIDE.

Dear Sir,

We are transmitting to you ten copies of AMDL Report 243 entitled "Chlorination of Ilmenite: a Thermodynamic Study", dated March, 1963.

This is the first of two final reports describing the experimental and theoretical work carried out on the project.

Yours faithfully,

L. Wallace Coffer

L. Wallace Coffer
Director.

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AMDL Report 243
March, 1963

CHLORINATION OF ILMENITE
A Thermodynamic Study

by

I. B. Ketteridge and R. E. Wilmshurst

to

SOUTH AUSTRALAIN GOVERNMENT
DEPARTMENT OF MINES

Investigated by: Industrial Chemistry Section
Officer in Charge: F. R. Hartley

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Adelaide South Australia

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ABSTRACT

A three-stage process has been proposed for producing ferric oxide and titanium dioxide as separate products from ilmenite.

Thermodynamic data available from the literature were insufficient for assessment of the process.

This report is an account of experiments performed to determine the necessary data and of an assessment of the process on the basis of these data.

1. INTRODUCTION

The process which is the subject of this study comprises oxidation of ilmenite with air and separation of the oxidised product into two components, ferric oxide and titanium dioxide.

Oxidised ilmenite is treated with chlorine gas to separate iron oxide as volatile ferric chloride, simultaneously releasing oxygen, and leaving a residue of titanium dioxide. The ferric chloride vapour is subsequently reacted with the oxygen to deposit ferric oxide and release chlorine for return to the chlorination process.

These reactions occur in accordance with expressions (1), (2) and (3). The overall process is summarised by expression (4).

Oxidation

$$\underset{\text{(ilmenite)}}{4\ FeO.TiO_2} + \underset{\text{(air)}}{O_2} \rightleftharpoons \underset{\text{(oxidised ilmenite)}}{2\ Fe_2O_3.TiO_2 + 2\ TiO_2} \tag{1}$$

Chlorination

$$\underset{\text{(oxidised ilmenite)}}{2\ Fe_2O_3.TiO_2 + 2\ TiO_2} + \underset{\text{(gas)}}{6\ Cl_2} \rightleftharpoons \underset{\text{(vapour)}}{4\ FeCl_3} + \underset{\text{(gas)}}{3\ O_2} + \underset{\text{(product)}}{4\ TiO_2} \tag{2}$$

Regeneration

$$\underset{\text{(vapour)}}{4\ FeCl_3} + \underset{\text{(gas)}}{3\ O_2} \rightleftharpoons \underset{\text{(gas)}}{6\ Cl_2} + \underset{\text{(product)}}{2\ Fe_2O_3} \tag{3}$$

Summary

$$\underset{\text{(ilmenite)}}{4\ FeO.TiO_2} + \underset{\text{(air)}}{O_2} \rightleftharpoons \underset{\text{(product)}}{2\ Fe_2O_3} + \underset{\text{(product)}}{4\ TiO_2} \tag{4}$$

In the process, ferric oxide is separated from titanium dioxide by selective chlorination. Iron and oxygen are subsequently separated from the resulting gas stream as ferric oxide, and chlorine is released for recycling by causing a shift in the gaseous ferric chloride - oxygen - chlorine equilibrium.

The purpose of the oxidation reaction is to introduce oxygen into the chlorination system in stoicheiometric proportion and so enable the regeneration reaction to proceed without the addition of further oxygen. The chlorination - regeneration cycle can then be continuously operated in a closed system by simple solid-gas separations. The shift in equilibrium is achieved by adjusting the temperature of the gaseous mixture.

The application of this process to the treatment of ilmenites from beach sand deposits is the subject of this work.

Fluidised bed reactors have been selected as the most suitable type for both the oxidation and chlorination reactions. For both reactions, reaction rate increases with increase in temperature. However at excessively high temperatures ilmenite, or oxidised ilmenite in the case of the chlorination reaction, sinters, and the reacting mass of solid particles cannot be kept in a fluidised condition.

Experience has shown that 1000°C is the optimum temperature for oxidation of ilmenite in a fluidised bed and that 1100°C is the optimum for chlorination.

On the basis of published data (Kangro 1957), 500°C would be a suitable temperature for the regeneration reaction.

A knowledge of the extent to which the three reactions proceed and the heats of reaction at these various temperatures is necessary before the feasibility of the process can be assessed.

Published data were insufficient for a thermodynamic study of the process to be made. Some thermochemical quantities were determined by measurement of equilibrium states.

2. SUMMARY

Experiments were performed to measure the extent of reaction between chlorine and ferric oxide and between chlorine and oxidised ilmenite at various temperatures. With data obtained from these experiments, supplemented with reliable published data, the extent was determined to which all three reactions involved in the process will proceed at various temperatures.

The formation of gaseous monomeric ferric chloride, its association to a dimeric form and its dissociation to ferrous chloride and chlorine are discussed. The extent of attack by chlorine on titanium dioxide under conditions prevailing in this process is also considered.

A heat balance for the process has been compiled and finally the practicability of the process is discussed in so far as the data allow.

3. LITERATURE SURVEY

Prior to planning the experimental work which forms the subject of this report, a search of available literature was made for information on the three chemical reactions involved in the process.

Sufficient thermodynamic data was found for calculation of the extent to which the regeneration reaction proceeds in the temperature range of greatest importance. However, little information was found on the high temperature oxidation of ilmenite with air, and no report of the chlorination of oxidised ilmenite was found.

Japanese workers, Yoskida and Takei (1957) and Hirakoso et al (1954) have reported finding only one compound, pseudobrookite ($Fe_2O_3 . TiO_2$) in the binary ferric oxide – titanium dioxide system. This is confirmed by the findings of Schmahl and Meyer (1959). Hirakoso et al report that during the roasting of ilmenite the following reaction occurs:

$$4\ FeO.TiO_2 + O_2 \rightleftharpoons 2\ Fe_2O_3.TiO_2 + 2\ TiO_2 \quad . . . . . . (1)$$

No quantitative measurements of the oxidation and chlorination reactions are available. An extensive literature search yielded insufficient thermodynamic data to calculate free energy changes for either reaction.

For the materials involved in the oxidation reaction, high temperature heat content and entropy data have been published by Kelley (1960). Standard entropies for the three solid compounds and for gaseous oxygen have been published by Kubaschewski and Evans (1958). Heats of formation at 298°K for ilmenite and for rutile are available from the same source, but no value for ferric titanate has been reported. Free energy values therefore could not be calculated.

For the chlorination reaction, data for chlorine and ferric chloride are required, in addition to the ferric titanate, oxygen and rutile involved in the oxidation reaction. Adequate data for chlorine are available from Kelley (1960) and Kubaschewski and Evans (1958), however the data available for ferric chloride are insufficient.

Anhydrous ferric chloride melts at 307°C and boils at 319°C (Kubaschewski and Evans, 1958). Ringwald (1949), surveying earlier investigations of the properties of ferric chloride, found that all previous workers reported that below 500°C the vapour density was in agreement with the formula Fe_2Cl_6. At higher temperatures it was reported that the dimeric form increasingly dissociates to the monomer according to reaction (5):

$$\underset{\text{(gas)}}{Fe_2Cl_6} \rightleftharpoons \underset{\text{(gas)}}{2\,FeCl_3} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \qquad (5)$$

Ringwald further states that most of the investigators observed the dissociation of gaseous ferric chloride to ferrous chloride and chlorine according to the reaction:

$$Fe_2Cl_6 \rightleftharpoons 2\,FeCl_2 + Cl_2 \quad . \; . \; . \; . \; . \; . \; . \qquad (6)$$

Stirneman (1925) reported that, with gaseous mixtures at 500°C, the partial pressure of chlorine was 0.1 atmosphere when the vapour pressure of ferric chloride was 10 atmospheres.

Partington (1937) gives vapour density measurements for ferric chloride at intervals over the temperature range 450° to 1300°C. According to these data, the vapour density corresponds to the formula Fe_2Cl_6 at 444°C and to $FeCl_3$ at 750°C. The degree of dissociation to ferrous chloride and chlorine increases with temperature but does not appear to be large at temperatures less than 1300°C.

This information indicates that, at the chlorinating temperature of 1100°C, ferric chloride exists mostly as the monomer and that the degree of dissociation to ferrous chloride and chlorine is not very great.

Kubaschewski and Evans (1958) give the data of Schäfer and Oehler (1953) for the reaction:

$$\underset{\text{(gas)}}{2\,FeCl_3} \rightleftharpoons \underset{\text{(gas)}}{Fe_2Cl_6} \quad . \; . \; . \; . \; . \; . \; . \; . \qquad (7)$$

Over the temperature range 778° to 978°K, the free energy change is given as:

$$\Delta G \text{ (calories)} = -32,550 + 31.65T \pm 1000.$$

By extrapolation, the free energy change at 1373°K (1100°C) for reaction (7) is 10.9 kilocalories. The equilibrium constant can then be calculated by means of the reaction:

$$\Delta G_T = -RT.\ln K_p$$

If x is the fraction of monomeric ferric chloride converted to the dimeric form, then

$$K_p = \left(\frac{x/2}{1 - x/2}\right)\left(\frac{1 - x/2}{1 - x}\right)^2$$

$$= \frac{x\,(2 - x)}{4\,(1 - x)^2}$$

The value of 10.9 kilocalories for the free energy change at 1100°C yields a value of 3.5 per cent for the fraction of monomeric chloride converted to the dimeric form.

On the assumption that monomeric and dimeric ferric chloride, ferrous chloride, and chlorine have densities in accordance with the formulae $FeCl_3$, Fe_2Cl_6, $FeCl_2$ and Cl_2 respectively, and that, at 1100°C, 3.5 per cent of monomeric ferric chloride associates to the dimer, then according to the vapour densities reported by Partington (1937), about 14 per cent of monomeric ferric chloride dissociates to ferrous chloride and chlorine.

It appears therefore that, at the chlorination temperature of 1100°C, a larger proportion of ferric chloride dissociates to ferrous chloride than is suggested by the data of Partington alone.

The accuracy of the data is questionable so, for the present, ferric chloride is regarded as existing only in the monomeric form in the temperature range 700° to 1100°C. This assumption is reconsidered later.

While no work on the chlorination of oxidised ilmenite has been reported, two reports of investigations of the ferric oxide - chlorine - ferric chloride - oxygen system are available. The most important of these is that of Galmiche (1948) on the chlorination of ferric oxide.

Galmiche measured the amount of chlorine converted to ferric chloride when chlorine was passed over a sample of ferric oxide at various temperatures. A series of tests with different chlorine flow-rates was carried out at each temperature and the proportion of chlorine converted to ferric chloride extrapolated to the equilibrium condition of zero chlorine flow. Equilibrium constants were calculated for the reaction:

$$\underset{\text{(solid)}}{2\,Fe_2O_3} + \underset{\text{(gas)}}{6\,Cl_2} \rightleftharpoons \underset{\text{(gas)}}{4\,FeCl_3} + \underset{\text{(gas)}}{3\,O_2} \quad . \quad . \quad . \quad . \quad . \qquad (8)$$

If x represents the mole fraction of chlorine converted to ferric chloride, then the equilibrium constant is given by the expression

$$K_p = \frac{2\,x^7}{81\,(1 - x)^6\,(1 + x/6)}$$

Tests were conducted over the temperature range of 1100°C to 700°C, below which the formation of dimeric ferric chloride becomes appreciable.

The variation of equilibrium constant with temperature is shown in Figure A-1.

Subsequent to Galmiche's work, Smullin (1952) approached the equilibrium for reaction (8) from the other direction. Steady flowing streams of ferric chloride, chlorine and oxygen were mixed at controlled temperatures and the rate of deposition of ferric oxide measured.

The flow-rate of ferric chloride was varied from test to test with flow-rates for oxygen and chlorine, the temperature being held constant. The rates of formation of ferric oxide were then plotted against the flow of ferric chloride and were extrapolated to obtain conditions for zero rate of formation. Equilibrium compositions were determined by this means for temperatures between 704° and 982°C.

Equilibrium constants were then calculated from the relation:

$$K_p = \frac{\left(\frac{M_{FeCl_3} \cdot P}{M}\right)^4 \left(\frac{M_{O_2} \cdot P}{M}\right)^3}{\left(\frac{M_{Cl_2} \cdot P}{M}\right)^6}$$

where M = moles of substance

P = absolute pressure in atmospheres.

Results are compared with those of Galmiche in Figure A-1.

To illustrate that the difference in the equilibrium constants is significant, the equilibrium vapour compositions according to Galmiche's method have been calculated from the equilibrium constants reported by Smullin. Plots of chlorine conversion against temperature calculated from the data of Smullin are compared in Figure A-2 with chlorine conversion measured by Galmiche.

Insufficient detail is reported by Smullin for assessment of his experimental method, but it would seem that accurate measurement of the rate of formation of ferric oxide according to his method would be difficult. Smullin's results are much more inconsistent within themselves than are those of Galmiche.

In view of the inconsistencies in the data reported by Galmiche and Smullin and of the lack of data on the chlorination of oxidised ilmenite, it was decided to measure equilibrium conditions for both these reactions.

4. MATERIALS USED

The chlorine used in this work was commercial grade liquid chlorine purchased in steel cylinders.

The ferric oxide was "Extra Superfine Powdered Rouge" manufactured by W. Canning and Co. Ltd. of Birmingham, England. It contained 99.8 per cent ferric oxide and lost 0.20 per cent weight on ignition to 800°C.

Samples of ferric oxide were ignited at 800°C, cooled and weighed prior to each chlorination test.

The ilmenite was a concentrate produced by magnetic separation from a parcel of impure ilmenite obtained from dune deposits on Stradbroke Island, Queensland. It was oxidised at 1000°C with air in a fluidised bed and, after oxidation, gave the following analysis:

	Per cent
TiO_2	49.0
Fe_2O_3	46.8
FeO	Nil

The oxidised ilmenite was granular in appearance and closely sized. Sixty per cent was within the range minus 100 plus 150-mesh (BSS) and 100 per cent within the range minus 52- plus 200-mesh.

5. EXPERIMENTAL PROCEDURE AND RESULTS

Measured quantities of chlorine were passed at slow flow-rates separately through charges of ferric oxide and oxidised ilmenite at various temperatures. The loss in weight of the charge during an experiment was taken as the weight of ferric oxide which had reacted with the chlorine. The composition of the gaseous mixture leaving the charge was then calculated.

The experimental techniques used for ferric oxide and oxidised ilmenite differed slightly.

5.1 Chlorination of Ferric Oxide

A 5-inch length of $^7/_8$-inch I. D. aluminous porcelain tube was packed with ferric oxide, which was held in place with plugs of silica wool at each end. The two ends were ground to make conical joints with pieces of similar tubing. The three pieces were cemented together and were placed vertically inside an electrical resistance furnace. The bottom tube projected sufficiently far from the furnace for a rubber stopper to be used to seal a chlorine inlet connection. The top tube came only to the top of the furnace. Chlorine and ferric chloride were drawn from this outlet and absorbed in sodium hydroxide solution.

Temperatures were measured at the bottom of the charge with a Chromel - Alumel thermocouple in a silica sheath.

Chlorine flow-rates were measured with an orifice which had previously been calibrated by absorbing chlorine in aqueous sodium hydroxide followed by chemical analysis of the solution.

The pressure required to pass chlorine through the charge at the required flow-rate was measured with a water manometer.

Experiments were conducted by heating the charge to the required temperature and admitting chlorine at a controlled flow-rate for a measured period of time. At the conclusion of each experiment the system was purged with nitrogen, cooled, and the cemented joints were separated. Cement was carefully cleaned from the section of tube holding the charge, and the charge and the tube were weighed together.

The weight lost by the charge during the test was used as a measure of the ferric oxide which had reacted with the chlorine.

5.2 Chlorination of Oxidised Ilmenite

With oxidised ilmenite, only two pieces of aluminous porcelain tube were used. A charge of approximately 100 g of oxidised ilmenite was supported in the upper end of a 12-inch length of 7/8-inch I. D. tube with plugs of silica wool. The tube was held vertically in a resistance furnace as before, with the lower end projecting sufficiently far for a rubber stopper to be used to seal the chlorine inlet. The upper end was ground to a conical joint with a similar piece of tube which extended to the top of the furnace.

The lower piece of tube containing the charge was weighed before and after each test. Cemented joints were no longer necessary. Prior to each chlorination test,the tube with the charge was heated to 1100°C with air passing through it for 30 minutes. It was then cooled and weighed.

The first series of tests was carried out at 1100°C with chlorine flows of 0.075, 0.15 and 0.30 g per minute. The rate of chlorine flow had no significant effect on the measured chlorine conversion and experiments at other temperatures were conducted with chlorine flows of 0.15 and 0.30 g per minute only.

In other respects the experiments with oxidised ilmenite were similar to those with ferric oxide.

Results for the chlorination of ferric oxide are presented in Table A-1. The percentage of chlorine converted to ferric chloride has been calculated in accordance with reaction (8) :

$$\underset{(319.4)}{2\ Fe_2O_3} + \underset{(425.5)}{6\ Cl_2} \rightleftharpoons \underset{(648.9)}{4\ FeCl_3} + \underset{(96.0)}{3\ O_2} \quad . \quad . \quad . \quad . \qquad (8)$$

The results for the chlorination of oxidised ilmenite are presented in Table A-2. The chlorine conversion has been calculated in accordance with reaction (2),

$$2\ Fe_2O_3.TiO_2 + 2\ TiO_2 + 6\ Cl_2 \rightleftharpoons 4\ FeCl_3 + 3\ O_2 + 4\ TiO_2 \quad (2)$$

by which it is assumed that no reaction between titanium dioxide and chlorine occurs. This assumption is reconsidered later.

6. DISCUSSION

The following values have been selected from Table A-1 as probable equilibrium values at various temperatures:

Temperature ^0C	Chlorine Conversion %	Equilibrium Constant (natural logarithm)
865	18.0	-14.54
920	23.5	-12.27
956	31.0	- 9.72
1000	36.0	- 8.23
1028	43.8	- 6.09
1060	50.3	- 4.40
1100	56.0	- 2.92

From Table A-2 tests 3, 6, 9, 14, 15, 16 and 19 were rejected as the result of failure in the experimental technique, mostly through leakage of chlorine from the apparatus or failure to maintain correct temperature.

Of the remaining results, average values were taken at each temperature and the following equilibrium constants were calculated:

Temperature ^0C	Chlorine Conversion %	Equilibrium Constant (natural logarithm)
1000	30.15	- 9.94
1050	35.8	- 8.29
1100	42.5	- 6.44
1150	52.7	- 3.75
1200	64.5	- 0.52

Plots of chlorine conversions at various temperatures for the chlorination of ferric oxide and oxidised ilmenite are shown in Figure A-3. The data of Galmiche and Smullin for chlorination of ferric oxide are shown for comparison.

The data for chlorinating ferric oxide are in closer agreement with those of Galmiche than with those of Smullin. Galmiche reported higher conversion of chlorine than did Smullin and even higher conversions have been found in this work.

With this technique of reacting chlorine with ferric oxide, measurements of chlorine conversions would tend to be lower than true equilibrium values. The data measured in these experiments have therefore been accepted in preference to those of either Galmiche or Smullin.

The data for chlorination of oxidised ilmenite appear consistent with those determined for ferric oxide. Chlorine conversions are slightly less, which would be accounted for by a relatively small bond energy between ferric oxide and titanium dioxide. These data have therefore been accepted.

The data have been treated in the usual manner by establishing a linear relationship between the logarithm of the equilibrium constant and the reciprocal of temperature.

For the chlorination of ferric oxide the following relation has been obtained by the method of least squares:

$$\ln K_p = 56.0 - 80{,}600\ T^{-1}$$

A plot of the experimental data showing an essentially linear relationship is given in Figure A-4.

The mean heat of reaction over the temperature range for which experiments were performed can be calculated from the relationship:

$$\Delta H_T = R T^2 \frac{d \ln K_p}{dT}$$

$$= 160,000 \text{ cal (range } 1173^0 \text{ to } 1373^0\text{K)}$$

The reaction entropy is:

$$\Delta S_T = RT \frac{d \ln K_p}{dT} + R . \ln K_p$$

$$= 111 \text{ calories per degree (range } 1173^0 \text{ to } 1373^0\text{K)}$$

The free energy change for the reaction is given by:

$$\Delta G_T = -RT \ln K_p$$

$$= 160,000 - 111 \, T \text{ calories } (1173^0 \text{ to } 1373^0\text{K})$$

Free energy changes calculated from this relation are:

Temperature ^{0}C	ΔG cal
900	29,600
1027	15,500
1000	18,500
1100	7,400

Chlorine conversions calculated from these free energy changes are:

Temperature ^{0}C	Chlorine Conversion %
900	22.3
1000	39.3
1100	56.8

These are shown as the line of accepted values in Figure A-5.

The data for chlorination of oxidised ilmenite have been treated similarly. A plot of ln K_p against the reciprocal of temperature is shown in Figure A-6. These data could best be fitted by a smooth curve. However, for reasons which will be discussed later, a straight line has been fitted by the method of least squares:

$$\ln K_p = 57.7 - 87,100 \, T^{-1}$$

Consequently

$$\Delta H = 173,000 \text{ calories (range } 1273^0 \text{ to } 1473^0\text{K)}$$

$$\Delta S = 115 \text{ calories per degree } (1273^0 \text{ to } 1473^0\text{K})$$

$$\Delta G = 173,000 - 115 \, T \; (1273^0 \text{ to } 1473^0\text{K})$$

Free energy changes are therefore:

Temperature °C	ΔG cal
1000	27,100
1027	24,000
1100	15,600
1200	4,200

Corresponding chlorine conversions are:

Temperature °C	Chlorine Conversion %
1000	27.9
1100	45.2
1200	61.7

These data are shown in the line of accepted values in Figure A-7.

With these data, it is now possible to calculate the extent to which reactions (1), (2) and (3), which comprise the process, proceed and also to determine the heats of reaction at each stage of the process.

6.1 Oxidation Reaction

Subtraction of the data determined by experiment for the chlorination of oxidised ilmenite (reaction (2)) from the corresponding data for chlorination of hematite (reaction (8)) yields data for reaction (9):

$$2\ Fe_2O_3.TiO_2 + 2\ TiO_2 + 6\ Cl_2 \rightleftharpoons 4\ FeCl_3 + 3\ O_2 + 4\ TiO_2 \quad \ldots \quad (2)$$

$$2\ Fe_2O_3 + 6\ Cl_2 \rightleftharpoons 4\ FeCl_3 + 3\ O_2 \quad \ldots\ldots \quad (8)$$

$$2\ Fe_2O_3 + 2\ TiO_2 \rightleftharpoons 2\ Fe_2O_3.TiO_2 \quad \ldots\ldots \quad (9)$$

The heat of reaction, ΔH_T, between 1000°C and 1100°C is therefore -12,900 calories and ΔS_T is -3.4 calories per degree.

Published data are available from which the entropy change for reaction (9) may be calculated. The standard entropy at 298°K for pseudobrookite is available from Kubaschewski and Evans (1958) and the high temperature entropy from Kelly (1960):

$$S_{1300°K\ (Fe_2O_3)} = 70.0 \text{ calories per degree.}$$

Kelley and Mah (1959) give the following value for the entropy of rutile at 1300°K:

$$S_{1300°K\ (TiO_2)} = 36.4 \text{ calories per degree.}$$

The entropy change for reaction (9) may be obtained by difference as:

$$\Delta S_{1300^{\circ}K} = 213.3 - 140.0 - 72.8$$
$$= 0.5 \text{ calories per degree}$$

This may be compared with the value previously obtained by subtraction of the experimentally determined entropy change for reaction (2) from that for reaction (8):

$$\Delta S_{1300^{\circ}K} = 111.2 - 114.6$$
$$= -3.4 \text{ calories per degree}$$

Since both values are obtained by differences between comparatively large numbers, the difference between the two values for the entropy change is not regarded as significant.

With data for high temperature heat content from Kelley (1960), it is possible to calculate ΔH_{298} for reaction (10):

$$Fe_2O_3 + TiO_2 \rightleftharpoons Fe_2O_3 . TiO_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

$$\Delta H_{298} = -3800 \text{ calories.}$$

With a value for the heat of formation at 298°K for rutile from Kelley and Mah (1959) and for hematite from Kubaschewski and Evans (1958), it becomes possible to calculate the standard heat of formation of pseudobrookite:

$$\Delta H_{f298^{\circ}K}\ (Fe_2O_3 . TiO_2) = -426,000 \text{ calories.}$$

With values for heats of formation for ilmenite and rutile at 298°K Kelley and Mah (1959), it is possible to calculate the heat of reaction (1):

$$4\ FeO . TiO_2 + O_2 \rightleftharpoons 2\ Fe_2O_3 . TiO_2 + 2\ TiO_2 \quad . \quad . \quad . \quad . \quad (1)$$

$$\Delta H_{298} = -120,000 \text{ calories.}$$

With values for high temperature heat contents from Kelley (1960), it becomes possible to calculate the heat of reaction at 1300°K for reaction (1):

$$\Delta H_{1300^{\circ}K} = -118,000 \text{ calories.}$$

With high temperature entropy values from Kelly (1960) and with the heat of reaction at 1300°K previously calculated for reaction (1), it is now possible to calculate the free energy change at 1300°K for this reaction:

$$4\ FeO . TiO_2 + O_2 \rightleftharpoons 2\ Fe_2O_3 . TiO_2 + 2\ TiO_2 \quad . \quad . \quad . \quad . \quad (1)$$

$$\Delta G_{1300} = \Delta H_{1300} - T\Delta S_{1300}$$
$$= -57,000 \text{ calories}$$

The equilibrium pressure for oxygen may be found from the relation:

$$\Delta G = -R\ T\ \ln K_p$$
$$= R . T\ \ln\ (\ P\ (O_2)\ ).$$

The equilibrium oxygen pressure at 1300°K is:

$$P(O_2) = 2 \times 10^{-10} \text{ atmospheres.}$$

The dissociation pressure at 298°K, calculated in a similar manner, is 3×10^{-78} atmospheres.

Alternatively the free energy change for reaction (1) may be calculated from the free energy data available from Kubaschewski and Evans (1958) for the reactions:

$$4\,Fe + 2\,O_2 \rightleftharpoons 4\,FeO \quad \ldots\ldots\ldots \quad (11)$$

$$\Delta G_{1300^0K} = -170,500 \text{ calories}$$

$$4\,FeO + \tfrac{2}{3}\,O_2 \rightleftharpoons \tfrac{4}{3}\,Fe_3O_4 \quad \ldots\ldots\ldots \quad (12)$$

$$\Delta G_{1300^0K} = -47,700 \text{ calories}$$

$$\tfrac{4}{3}\,Fe_3O_4 + \tfrac{1}{3}\,O_2 \rightleftharpoons 2\,Fe_2O_3 \quad \ldots\ldots\ldots \quad (13)$$

$$G_{1300^0K} = -10,600 \text{ calories}$$

$$4\,FeO.TiO_2 \rightleftharpoons 4\,Fe + 2\,O_2 + 4\,TiO_2 \quad \ldots\ldots \quad (14)$$

$$\Delta G_{1300^0K} = 191,200 \text{ calories}$$

These data may be combined with the free energy change at 1300°K previously calculated for reaction (9):

$$2\,Fe_2O_3 + 2\,TiO_2 \rightleftharpoons 2\,Fe_2O_3.TiO_2 \quad \ldots\ldots \quad (9)$$

$$\Delta G_{1300^0K} = -8500 \text{ calories}$$

The free energy change for reaction (1) is obtained by summation:

$$4\,FeO.TiO_2 + O_2 \rightleftharpoons 2\,Fe_2O_3.TiO_2 + 2\,TiO_2 \quad \ldots \quad (1)$$

$$\Delta G_{1300^0K} = -46,000 \text{ calories}$$

The oxygen pressure corresponding to this free energy is 2×10^{-8} atmospheres.

The free energy changes for reaction (1), at 1300°K calculated by the two methods differ by some 10,000 calories. This difference appears to result from the use of data from different sources for the two calculations.

The difference is of no practical significance as the corresponding oxygen dissociation pressures are both extremely small. These data indicate the possibility of completely oxidising ilmenite to pseudobrookite with comparatively low partial pressures of oxygen. For example, carbonaceous fuels could be burnt with an excess of air and the resulting heated gas mixture, containing a few per cent of oxygen, used to oxidise ilmenite. The rate of oxidation under any given conditions could only be determined by experiment.

6.2 Chlorination Reaction

In the calculation of experimental results for the chlorination of oxidised ilmenite, no reaction was assumed to take place between titanium dioxide and chlorine. Results have been calculated on the basis of reaction (2):

$$2\ Fe_2O_3.TiO_2 + 2\ TiO_2 + 6\ Cl_2 \rightleftharpoons 4\ FeCl_3 + 3\ O_2 + 4\ TiO_2 \quad . \quad . \quad (2)$$

The validity of this assumption will now be assessed by first considering the reaction:

$$TiO_2 + 2\ Cl_2 \rightleftharpoons TiCl_4 + O_2 \quad . \ . \ . \ . \ . \ . \ . \ . \ . \ . \quad (15)$$

High temperature heat content and entropy data for substances participating in this reaction are available from Kelley (1960). Heats of formation at 298^{0}K and standard entropy values are available from Kubaschewski and Evans (1958). These data yield free energy changes for reaction (15) at 298^{0}K and 1373^{0}K of 39,200 and 24,700 calories respectively.

From the relation: $\Delta G = -RT.\ \ln K_p$ and on the basis of these free energy changes, the percentages of chlorine converted to titanium tetrachloride under equilibrium conditions are 8×10^{-13} and 2.1 at 298^{0}K and 1373^{0}K respectively.

Subtraction of three times the free energy change for reaction (15) from that of reaction (2) yields the free energy change for the reaction:

$$2\ Fe_2O_3.TiO_2 + 2\ TiO_2 + 3\ TiCl_4 \rightleftharpoons 4\ FeCl_3 + 7\ TiO_2 \quad . \ . \ . \quad (16)$$

The free energy change for this reaction at 1373^{0}K is therefore -58,500 calories.

If y is the fraction of titanium tetrachloride consumed by reaction (16) then:

$$K_p = \left(\frac{4\ y/_3}{1 + y/_3}\right)^4 \times \left(\frac{1 + y/_3}{1 - y}\right)^3$$

$$= \frac{9.48\ y^4}{(3 + y)\ (1 - y)^3}$$

A value for y may then be found from the relation

$$\Delta G = -RT\ \ln K_p$$

At 1100^{0}C, 99.93 per cent of titanium tetrachloride is consumed according to reaction (16).

Therefore no significant amount of titanium tetrachloride is formed during the chlorination of pseudobrookite until all the ferric oxide is removed.

This fact may be determined more precisely by considering the reactions which take place in a multiple stage chlorination reactor with substantially pure rutile in the bottom stage and oxidised ilmenite in the upper stages.

Reaction between chlorine and rutile occurs in the bottom stage according to reaction (17):

$$3\,TiO_2 + 6\,Cl_2 \rightleftharpoons 3\,TiCl_4 + 3\,O_2 \quad . \; . \; . \; . \; . \; . \; . \; . \qquad (17)$$

If x represents the moles of chlorine consumed by this reaction per mole of chlorine passing through the bottom stage, then the gas entering the upper stages will be depleted by x moles of chlorine and will contain $x/_2$ moles of titanium tetrachloride and $x/_2$ moles of oxygen.

This gaseous mixture then reacts in the upper stages according to reactions (2) and (16):

$$2\,Fe_2O_3.TiO_2 + 2\,TiO_2 + 6\,Cl_2 \rightleftharpoons 4\,FeCl_3 + 3\,O_2 + 2\,TiO_2 \quad . \; . \qquad (2)$$

$$2\,Fe_2O_3.TiO_2 + 2\,TiO_2 + 3\,TiCl_4 \rightleftharpoons 4\,FeCl_3 + 7\,TiO_2 \quad . \; . \; . \; . \qquad (16)$$

If a further y moles of chlorine are consumed by reaction (2) and z moles of titanium tetrachloride by reaction (12), then the resulting gaseous mixture contains:

	moles
Cl_2	$1 - x - y$
$TiCl_4$	$x/_2 - z$
$FeCl_3$	$^2y/_3 + {}^4z/_3$
O_2	$x/_2 + y/_2$
Total	$1 + y/_6 + z/_3$

Previous considerations have established that at 1373^0K, 2.1 per cent of chlorine is consumed by reaction (17) so that:

$$x = 0.021.$$

Equilibrium constants at 1373^0K for reactions (2) and (16) are known so that values can be found for y and z at 1373^0K from the relations:

Reaction (2)

$$K_p = \frac{6912\,(y/_6 + z/_3)^4 \quad (x/_6 + y/_6)^3}{(1 + y/_6 + z/_3) \quad (1 - x - y)^6}$$

Reaction (16)

$$K_p = \frac{256\,(y/_6 + z/_3)^4}{(1 + y/_6 + z/_3) \quad (x/_2 - z)^3}$$

Hence

$$y = 0.431$$
$$z = 0.0103$$

The gaseous mixture leaving the bottom stage therefore contains:

	moles
Cl_2	0.979
$TiCl_4$	0.0105
O_2	0.0105

The gaseous mixture leaving the top stage contains:

	moles
Cl_2	0.548
$TiCl_4$	0.00014
O_2	0.226
$FeCl_3$	0.301

Under equilibrium conditions the chlorine converted to titanium tetrachloride in the bottom stage of a multiple stage fluidised bed reactor amounts to 2.1 per cent of the total chlorine. Of the titanium tetrachloride so formed, 98.6 per cent is reconverted to titanium dioxide in the upper stages so that 0.03 per cent of the chlorine fed to the reactor leaves as titanium tetrachloride. This compares with 45.2 per cent leaving in the form of ferric chloride.

Substantially all of the titanium tetrachloride formed in the bottom stage should react with ferric oxide in the upper stages. The removal of titanium from the reactor as titanium tetrachloride should not be significant but there would be some titanium circulating between the bottom few stages.

Since, at most, 2.1 per cent of the chlorine passing through the reactor would be involved in this transport reaction, the amount of titanium recirculating is not likely to be of any consequence. The experimental measurement of the amount of titanium deposited as oxide from the tetrachloride would be useful as the rate of reaction may be sufficiently slow to influence the extent to which deposition of the oxide proceeds. One would expect rapid reaction between titanium tetrachloride vapour and oxygen released by reaction of chlorine with oxidised ilmenite. Investigation of this aspect lies outside the scope of the present work.

The equilibrium composition of the gaseous mixture leaving the top stage of a multiple stage reactor, which has been determined, is the same as the equilibrium composition of the chlorination gases leaving a single stage reactor containing oxidised ilmenite.

Therefore the assumption that no significant reaction occurs between chlorine and the titania content of oxidised ilmenite, on which calculation of the experimental data for the chlorination of oxidised ilmenite has been based, is justified.

The calculation of chlorination test results was made on the assumption that the only iron chloride formed was monomeric ferric chloride. Extrapolation of data from Kubaschewski and Evans (1958) has yielded a figure of 3.5 per cent for the proportion of monomer which associates to the dimeric form at 1100°C. As this involves extrapolation well outside the range over which the data were determined the result cannot be regarded as accurate. The degree of association is probably less than that obtained by linear extrapolation of the data. In any case the extent is small so that assuming association does not take place at all does not introduce any great error.

On the basis of data reported by Partington (1937) about 14 per cent of monomeric ferric chloride was shown to dissociate at 1100°C to ferrous chloride and chlorine. This reaction has been disregarded up to the present and should now be reconsidered.

Data are available (Kubaschewski and Evans 1958) from which the free energy of formation of gaseous ferrous chloride from its elements can be calculated over the temperature range 1300^{0}K to 1812^{0}K.

$$\mathrm{Fe} + \mathrm{Cl_2} = \mathrm{FeCl_2} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \qquad (18)$$

These data together with the experimental data for the chlorination of ferric oxide in accordance with reaction (8) afford means of calculating the degree of dissociation in the temperature range of interest:

$$2\,\mathrm{Fe_2O_3} + 6\,\mathrm{Cl_2} \rightleftharpoons 4\,\mathrm{FeCl_3} + 3\,\mathrm{O_2} \quad . \; . \; . \; . \; . \; . \; . \qquad (8)$$

$$\Delta G_{1373^{0}\mathrm{K}} = 7400 \text{ calories}$$

The free energy of formation at 1373^{0}K for ferric oxide may be calculated from the heat of formation at 298^{0}K for ferric oxide and the standard entropies at 298^{0}K for ferric oxide, iron and oxygen from Kubaschewski and Evans (1958) and the high temperature heat contents and entropies for ferric oxide, iron and oxygen from Kelly (1960).

These data yield a value for the free energy of formation of ferric oxide of:

$$\Delta G_{1373^{0}\mathrm{K}\,(\mathrm{Fe_2O_3})} = -112,200 \text{ calories.}$$

The free energy of formation of gaseous monomeric ferric chloride can then be obtained approximately from the free energy change for reaction (8):

$$\Delta G_{1373^{0}\mathrm{K}\,(\mathrm{FeCl_3})} = 54,200 \text{ calories.}$$

Combining such data with the free energy of formation for ferrous chloride yields the free energy change for reaction (19):

$$\underset{\text{(gas)}}{\mathrm{FeCl_3}} \rightleftharpoons \underset{\text{(gas)}}{\mathrm{FeCl_2}} + \underset{\text{(gas)}}{\tfrac{1}{2}\,\mathrm{Cl_2}} \quad . \; . \; . \; . \; . \; . \; . \qquad (19)$$

$$\Delta G_{1373^{0}\mathrm{K}} = 5000 \text{ calories.}$$

The equilibrium constant can then be evaluated.

If x represents the amount of monomeric ferric chloride which dissociates to ferrous chloride and chlorine then:

$$K_p = \left(\frac{x}{1 - x}\right) \left(\frac{x/2}{1 + x/2}\right)^{1/2}$$

This expression yields a value of 30.6 per cent for the fraction of ferric chloride which dissociates to ferrous chloride and chlorine at 1100^{0}C.

This figure is approximate since it is based on the original assumption on which calculations of experimental data for the chlorination of ferric oxide are based, namely that, in the reaction between ferric oxide and chlorine, only monomeric ferric chloride and oxygen are formed. A more accurate result could be obtained only by a lengthy iterative type of calculation, which in this instance is not justified.

The result of the present calculation, although approximate, does indicate that at 1100^{0}C the degree of dissociation is considerable.

Therefore the amount of ferrous chloride which is formed in the chlorination of hematite should be calculated. Again this is performed by an approximate method to avoid excessively lengthy calculations.

The experimentally determined free energy change for reaction (8) at 1100°C is:

$$2\ Fe_2O_3 + 6\ Cl_2 \rightleftharpoons 4\ FeCl_3 + 3\ O_2 \quad \ldots\ldots \quad (8)$$

$$\Delta G_{1373^0K} = 7400 \text{ calories.}$$

From previously determined free energies of formation for ferric oxide and ferrous chloride, the free energy change for reaction (20) can be calculated:

$$2\ Fe_2O_3 + 4\ Cl_2 \rightleftharpoons 4\ FeCl_2 + 3\ O_2 \quad \ldots\ldots \quad (20)$$

$$\Delta G_{1373^0K} = 27,300 \text{ calories.}$$

Equilibrium constants at 1100°C for reaction (8) and (20) corresponding to these free energy changes are 6.7×10^{-2} and 4.5×10^{-5} respectively.

The relative amounts of ferric and ferrous chlorides formed in the chlorination of hematite at 1100°C has been obtained in the following manner.

If x is the mole fraction of chlorine converted to ferric chloride according to equation (8) and y is the mole fraction converted to ferrous chloride according to equation (20), then the chlorination gases contain:

	moles
Cl_2	$1 - x - y$
$FeCl_3$	$2x/3$
$FeCl_2$	y
O_2	$x/2 + 3y/4$
Total	$1 + x/6 + 3y/4$

The equilibrium constant for reaction (8) is therefore:

$$Kp_{1373^0K} = \frac{(2x/3)^4\ (x/2 + 3y/4)^3}{(1 + x/6 + 3y/4)\ (1 - x - y)^6}$$

$$= 6.7 \times 10^{-2}$$

For reaction (20) the equilibrium constant is:

$$Kp_{1373^0K} = \frac{(y)^4\ (x/2 + 3y/4)^3}{(1 - x - y)^4\ (1 + x/6 + 3y/4)^3}$$

$$= 4.5 \times 10^{-5}$$

The solution of these two simultaneous equations gives:

$x = 0.50$

$y = 0.09$

In the calculation of experimental results for reaction (8) only ferric chloride was assumed to be formed and the amount formed was calculated from the weight loss of ferric oxide.

$$2\ Fe_2O_3 \ + \ 6\ Cl_2 \ \rightleftharpoons \ 4\ FeCl_2 \ + \ 3\ O_2 \quad . \quad . \quad . \quad . \qquad (8)$$

At 1100^0C the chlorine utilized was 56.9 per cent so that 6 moles of chlorine removed $0.569 \times 319.4 = 181.6$ grams of ferric oxide, 319.4 being twice the molecular weight of ferric oxide.

In fact only part of the ferric oxide was converted to ferric chloride and part was converted to ferrous chloride.

For this calculation the relative proportions of chlorine assumed to be converted to ferric and ferrous chlorides are the same as the ratio of the values for x and y, 0.50:0.09.

If z is the number of moles of chlorine converted to ferric chloride when 6 moles of chlorine are passed through the charge of ferric oxide, then 0.18z is the number of moles converted to ferrous chloride. The quantity of ferric oxide removed as ferric chloride is therefore:

$$z \times \frac{319.4}{6} = 53.2z \text{ grams}$$

That removed as ferrous chloride is:

$$0.18z \times \frac{319.4}{4} = 14.4z \text{ grams}$$

The total ferric oxide removed is:

$$53.2z + 14.4z = 67.6z \text{ grams}$$

The amount removed was calculated to be 181.6 grams so that:

$$z = \frac{181.6}{67.6} = 2.69 \text{ moles}$$

$$0.18z = 0.48 \text{ moles}$$

The value of z has been calculated on the basis of passing 6 moles of chlorine through the system, so that:

$$z = \frac{2.96}{6} = 44.8 \text{ per cent}$$

$$0.18z = \frac{0.48}{6} = 8.0 \text{ per cent}$$

In the chlorination of hematite at 1100^0C, about 44.8 per cent of chlorine is converted to ferric chloride and 8.0 per cent to ferrous chloride, giving a total utilization of 52.8 per cent. This compares with 56.8 per cent calculated on the basis that only monomeric ferric chloride is formed.

A similar calculation has been carried out for 1300^0K, the result being that 37.6 per cent of chlorine is converted to ferric chloride and 3.9 per cent to ferrous chloride. The total utilization is 41.5 per cent compared to 43.8 per cent calculated previously for the formation of ferric chloride alone.

Data are not available for the formation of gaseous ferrous chloride at 900^0C this being the lower limit of the temperature range for which experimental data for the chlorination of hematite are available. In fact ferrous chloride vapour liquefies when cooled below 1012°C. However, the vapour pressure at 900°C is quite high, namely 250 mm of mercury (Kubaschewski and Evans 1958). The data for the free energy of formation of ferrous chloride vapour have therefore been extrapolated to 1173°K and the amount of ferrous chloride formed in the chlorination of hematite has been calculated in the same way as for higher temperatures.

At 1173°K, 21.1 per cent of chlorine is converted to ferric chloride and 0.8 per cent to ferrous chloride. Total chlorine utilization is 21.9 per cent compared to 22.3 per cent calculated on the basis of forming only ferric chloride.

These results are presented graphically in Figure A-8. If x represents the moles of chlorine converted to ferric chloride per mole of chlorine reacted with ferric oxide and y represents the moles of chlorine converted to ferrous chloride, then the composition of the chlorination gases is as given previously on page 17.

The partial pressure of ferrous chloride in a system under a total pressure of P is therefore:

$$\frac{y}{1 + {}^{x}/_{6} + {}^{3y}/_{4}} \times P$$

The partial pressure of ferrous chloride in the gases produced by reacting chlorine with hematite can therefore be calculated from the gas composition determined previously for temperatures of 900°C, 1027°C, and 1100°C. Assuming a total pressure of one atmosphere, the partial pressures are 6.1, 27 and 54 mm of mercury respectively.

An expression for determining the vapour pressure over liquid ferrous chloride is given by Kubaschewski and Evans (1958). The vapour pressure of ferrous chloride according to this expression together with the partial pressure of ferrous chloride in gases produced by chlorination of hematite are presented in Figure A-9.

At temperatures below the boiling point of ferrous chloride, the partial pressure of ferrous chloride in the chlorination gases is much less than the vapour pressure over liquid. The figure shows that the partial pressure decreases as the temperature is lowered, resulting from reaction of ferrous chloride vapour with free chlorine. Therefore, if the gases produced by chlorination of ferric oxide at a temperature of, for example, 1100°C were cooled under such conditions that the gases remained in equilibrium, no liquid ferrous chloride would be deposited. Since the gases contain a small amount of ferrous chloride and an excess of free chlorine, and since the temperature range being considered is sufficiently high for reaction rates to be extremely fast, the temperature of the gases is unlikely to be quenched with sufficient speed to inhibit the reaction between ferrous chloride and chlorine and so precipitate liquid ferrous chloride.

The reaction between chlorine and oxidised ilmenite is now considered. The amount of ferrous chloride formed during the chlorination of oxidised ilmenite has been calculated by the method previously used for the chlorination of hematite.

The free energy change for the reaction of chlorine with oxidised ilmenite at 1100°C according to reaction (2) has been calculated previously from experimental data:

$$2\ Fe_2O_3.TiO_2 + 2\ TiO_2 + 6\ Cl_2 \rightleftharpoons 4\ FeCl_3 + 3\ O_2 + 4\ TiO_2 \quad . \quad . \quad (2)$$

$$\Delta G_{1373^0K} = 15,645 \text{ calories}$$

The free energy of formation of monomeric ferric chloride at 1100°C has already been calculated from experimental data for the chlorination of hematite:

$$\Delta G_{1373^0K\ (FeCl_3)} = -54,200 \text{ calories}$$

The free energy of formation of ferrous chloride at 1100°C has previously been calculated with data from Kubaschewski and Evans (1959).

The free energy change for the reaction of chlorine according to reaction (21) can therefore be obtained:

$$2\ Fe_2O_3.TiO_2 + 2\ TiO_2 + 4\ Cl_2 \rightleftharpoons 4\ FeCl_2 + 3\ O_2 + 4\ TiO_2 \quad . \quad . \quad .(21)$$

$$\Delta G_{1373^0K} = 35,600 \text{ calories}$$

According to calculations, 45.2 per cent of the chlorine reacts with oxidised ilmenite at 1100°C, assuming only ferric chloride is formed. With this value for the chlorine utilization and with free energy values calculated for equations (2) and (21), the amount of ferrous chloride formed during chlorination of oxidised ilmenite can be calculated in the same manner as previously employed for the chlorination of hematite. This results in a value of 36.6 per cent of chlorine forming ferric chloride and 5.7 per cent forming ferrous chloride when reacted with oxidised ilmenite at 1100°C.

Total chlorine utilization is then 42.3 per cent, compared with 45.2 per cent calculated previously on the basis of forming ferric chloride alone.

The partial pressure of ferrous chloride in the chlorination gases, calculated in the same way as was done for the chlorination of hematite, is 39 mm of mercury.

The composition of the gases produced by chlorinating oxidised ilmenite will now be compared with that of the gases produced by chlorinating hematite.

Expressions for equilibrium constants based on experimental data have been obtained for the chlorination of oxidised ilmenite according to equation (2) and for hematite according to equation (8):

$$2\ Fe_2O_3.TiO_2 + 2\ TiO_2 + 6\ Cl_2 = 4\ FeCl_3 + 3\ O_2 + 4\ TiO_2 \quad . \quad . \quad . \quad (2)$$

$$\ln K_p = 57.7 \frac{-87,180}{T}$$

range 1273^0 to 1473^0K

$$2\,Fe_2O_3 + 6\,Cl_2 \longleftrightarrow 4\,FeCl_3 + 3\,O_2$$

$$\ln K_p = 56.0 \frac{-80,600}{T}$$

range 1173^0 to 1373^0K

The temperature T_h, to which the gases produced by chlorinating oxidised ilmenite at temperature T_i can be cooled without precipitating hematite, is obtained by equating the expressions for the equilibrium constant:

$$57.7 \frac{-87,180}{T_i} = 56.0 \frac{-80,600}{T_h}$$

$$T_h = \frac{80,600}{87,100 \quad -1.7T_i}$$

Therefore if oxidised ilmenite is chlorinated at 1373^0K, the chlorination gases can be cooled to 1305^0K without precipitating ferric oxide. This does not mean that the gases produced by chlorinating oxidised ilmenite at 1373^0K have the same composition as those produced by chlorinating hematite at 1305^0K. Dissociation of ferric chloride to ferrous chloride increases with temperature, so that the partial pressure of ferrous chloride in the gases produced by chlorinating ilmenite at 1373^0K, previously determined as 39 mm of mercury, is greater than that produced by chlorinating hematite at 1305^0K. As the gases are cooled, ferrous chloride reacts with free chlorine until, at 1305^0K, the composition is the same as that produced by chlorinating hematite at that temperature. Further cooling results in reaction between ferric chloride and oxygen and the deposition of ferric oxide, as well as further reduction in the partial pressure of ferrous chloride.

The partial pressure of ferrous chloride in the gases produced by chlorinating hematite under equilibrium conditions at 1300^0K has been determined as 27 mm of mercury, so that the partial pressure of 39 mm for ferrous chloride in the gases produced in chlorinating oxidised ilmenite at 1373^0K is reduced on cooling to a little greater than 27 mm at 1305^0K.

This is illustrated in Figure A-9.

As shown in Figure A-8 the partial pressure of ferrous chloride during the cooling of the chlorination gases is always well below the vapour pressure. Therefore although an appreciable amount of ferrous chloride is formed in the chlorination of oxidised ilmenite, liquid ferrous chloride is not precipitated during the cooling of the chlorination gases. Had this been so it could have seriously affected the gas transport system. The deposition of liquid ferrous chloride would mean a constant removal of iron and chlorine from the cyclic gaseous system and a continually increasing imbalance in the residual gas mixture. Frequent corrective additions of components would then be necessary to restore the gaseous mixture to stoicheiometric proportions. Furthermore, deposition of liquid ferrous chloride in a fluidised bed could cause sintering .

However, the formation of ferrous chloride during the chlorination reaction is of no significance in the operation of the cyclic process and may be disregarded.

The significance of the formation of ferrous chloride in the assessment of experimental data for the chlorination of oxidised ilmenite can now be considered.

The heat of reaction has been determined from the gradient of the logarithm of the equilibrium constant with respect to temperature. The gradient and therefore the heat of reaction have been assumed to be constant over the temperature interval 1000° to 1200°C.

Two errors are thereby introduced:

> Firstly, the equilibrium constant calculated for the formation of ferrous chloride will differ from that calculated for the formation of ferric chloride.
>
> Secondly, while no great error is introduced by assuming that the heat of reaction for a single reaction is constant over a limited temperature range, a greater error may be introduced by assuming that the sum of two heats of reaction is constant when the relative proportions of the two reactions differ over the temperature range.

These errors are presumably the reasons for the consistent curvature in the plot of the logarithm of the equilibrium constant with the reciprocal of temperature.

However, the method of calculation used here seems the only practicable way of determining the heat of reaction for the chlorination reaction and, in spite of the errors involved, is probably as accurate as the experimental data warrant.

6.3 Regeneration Reaction

The reactions which occur during cooling of the chlorination gases can now be considered.

The amount of ferrous chloride formed during the chlorination reaction has been shown to be of no significance and may be disregarded. However, as monomeric ferric chloride is cooled from the chlorination temperature of 1100°C, association to dimeric ferric chloride becomes important.

Data for the association of ferric chloride over the temperature range 778 to 978°K have been given by Kubaschewski and Evans (1958):

$$2\,FeCl_3 \rightleftharpoons Fe_2Cl_6 \quad \ldots\ldots\ldots\ldots \quad (7)$$

$$\Delta G_{T\,(\text{calories})} = -32{,}550 + 31.65T.$$

The free energy changes for reaction (7) at 778°K and 978°K are -7900 and -1600 calories respectively. The corresponding equilibrium constants are 169 and 2.3.

If x represents the fraction of monomer which associates then,

$$Kp = \frac{x\ (2 - x)}{4\ (1 - x)^2}$$

The fraction of monomer which associates is therefore 96.2 per cent at 778°K and 68.5 per cent at 978°K.

On the basis of work reported by Kangro (1957), 500°C would be a suitable temperature at which to conduct the regeneration reaction.

The lower limit of the temperature range for which data for the association of monomeric ferric chloride are available is 778°K = 505°C. Therefore 505°C will be taken as the temperature at which the regeneration reaction is conducted.

At 505°C, 96.2 per cent of ferric chloride associates to the dimeric form. For the purpose of calculation this figure will be assumed to be 100 per cent.

The free energy of formation of ferric oxide at 505°C can be calculated from the heat of formation at 298°K, from the entropies at 298°K for ferric oxide, iron and oxygen, Kubaschewski and Evans (1958), and from the high temperature heat contents and entropies, Kelley (1960). These data yield a value of:

$$\Delta G_{f\ 778^0K\ (Fe_2O_3)} = -147,000 \text{ calories}$$

The free energy of formation of gaseous dimeric ferric chloride at 778°K is available from the data of Kelley and Mah (1959).

$$\Delta G_{f\ 778^0K\ (Fe_2Cl_6)} = -116,000 \text{ calories}$$

The free energy change for the regeneration reaction according to reaction (22) can therefore be calculated.

$$2\ Fe_2O_3 + 6\ Cl_2 \rightleftharpoons 2\ Fe_2Cl_6 + 3\ O_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad (22)$$

$$\Delta G_{778^0K} = 61,600 \text{ calories}$$

The corresponding equilibrium constant is:

$$Kp = 4.8 \times 10^{-18}$$

If x represents the fraction of chlorine which reacts with ferric oxide according to equation (22), then the equilibrium constant is given by:

$$Kp = \frac{x^5\ (1 - {}^{x}/_{6})}{72\ (1 - x)^6} = 4.8 \times 10^{-18}$$

Solution of this equation yields a value of 0.09 per cent for the fraction of chlorine which remains as dimeric ferric chloride at 505°C. Therefore the regeneration reaction should proceed almost to completion.

This step is the last required to show that, at least on the basis of thermodynamic data, the cyclic chlorination process is quite feasible.

6.4 Heats of Reaction

From previous considerations, the oxidation of ilmenite should proceed at 1000°C with almost complete utilization of oxygen; the chlorination of oxidised ilmenite at 1100°C should result in conversion of 45.2 per cent of chlorine to ferric chloride and, on cooling the chlorination gases to 505°C, substantially all of the chlorine should be recovered for further chlorination.

In effect, 45.2 per cent of the chlorine circulating in the system is usefully employed in the removal of iron from oxidised ilmenite.

Although gaseous ferrous chloride is formed during the chlorination reaction, it is present only in small amounts when the temperature of the chlorination gases is lowered below the boiling point of ferrous chloride. At no stage in the cooling operation will liquid ferrous chloride be precipitated and interfere with the gaseous transport system.

Monomeric ferric chloride formed during the chlorination reaction has been shown to associate to the dimeric form during the cooling operation. This effect is of no significance in the operation of the gaseous transport system.

The heats of reaction involved in each stage of the process can now be calculated.

The heat required for the overall process carried out at 298°K according to reaction (4) can be derived from the heats of formation at 298°K of ilmenite and rutile, Kelley and Mah (1959), and of ferric oxide, Kubaschewski and Evans (1958):

$$4\ \mathrm{FeO.TiO_2} + \mathrm{O_2} \rightleftharpoons 2\ \mathrm{Fe_2O_3} + 4\ \mathrm{TiO_2}\ . \quad . \quad . \quad . \qquad (4)$$

$$\Delta H_{298^0K} = -113{,}000 \text{ calories.}$$

The overall process is therefore exothermic, releasing 28,000 calories per gram molecular weight of ilmenite treated.

The heat required to preheat the reactants for the oxidation of ilmenite at 1000°C according to reaction (1) may be calculated from the data given by Kelley (1960):

$$4\ \mathrm{FeO.TiO_2} + \mathrm{O_2} \rightleftharpoons 2\ \mathrm{Fe_2O_3.TiO_2} + 2\ \mathrm{TiO_2}\ . \quad . \quad . \qquad (1)$$

$$H_{1273^0K} - H_{298^0K\text{ (reactants)}} = 125{,}000 \text{ calories}$$

The heat of reaction for the oxidation of ilmenite at 1000°C has already been determined.

$$\Delta H_{1273^0K\text{ (oxidation)}} = -118{,}000 \text{ calories}$$

The heat required to superheat the oxidised ilmenite from 1000°C to 1100°C can be calculated from the data given by Kelley (1960).

$$H_{1373^0K} - H_{1273^0K\text{ (oxidised ilmenite)}} = 14{,}200 \text{ calories.}$$

Forty five per cent of chlorine was converted to ferric chloride in the experiment on the chlorination reaction. The heat required to raise the temperature of the recirculated chlorine, including the unused excess, from the regeneration temperature of 505°C to the chlorination temperature of 1100°C has been calculated from data compiled by Kelley (1960).

$$H_{1373^0K} - H_{778^0K} \text{ (recycled chlorine)} = 77,900 \text{ calories.}$$

The heat of reaction between chlorine and oxidised ilmenite at 1100°C in accordance with reaction (2) has been determined previously from experimental data:

$$2\ Fe_2O_3.TiO_2 + 2\ TiO_2 + 6\ Cl_2 \rightleftharpoons 4\ FeCl_3 + 3\ O_2 + 4\ TiO_2 \quad . \quad . \quad (2)$$

$$\Delta H_{1373^0K} \text{ (chlorination)} = 173,000 \text{ calories.}$$

The heat which can be recovered from the titania produced by the chlorination of oxidised ilmenite can be calculated from data compiled by Kelley (1960):

$$H_{1373^0K} - H_{298^0K} \text{ (titania)} = -73,700 \text{ calories.}$$

No value is available for the high temperature heat content of monomeric ferric chloride vapour so that the sensible heat, which can be recovered by cooling the chlorination gases to the regeneration temperature of 505°C, cannot be calculated at present.

The heat evolved in the association of monomeric ferric chloride as it is cooled can be obtained from the data of Kubaschewski and Evans (1958), provided that the assumption is made that the heat of reaction remains constant over the temperature range 778°K to 978°K.

$$4\ FeCl_3 \rightleftharpoons 2\ Fe_2Cl_6 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (23)$$

$$\Delta H_{778^0K} \text{ (association)} = -65,100 \text{ calories.}$$

The heat of reaction at 505°C for the regeneration reaction can be calculated from heats of formation at 298°K for ferric oxide and for dimeric ferric chloride, as given by Kubaschewski and Evans (1958) and Kelley and Mah (1959) respectively, and from high temperature heat contents given by Kelley (1960).

$$2\ Fe_2Cl_6 + 3\ O_2 \rightleftharpoons 2\ Fe_2O_3 + 6\ Cl_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (24)$$

$$\Delta H_{778^0K} \text{ (regeneration)} = -82,300 \text{ calories}$$

The heats of reaction at 505°C for reactions (23) and (24) can be summed to give the heat of reaction for the regeneration reaction according to reaction (3):

$$4\ FeCl_3 + 3\ O_2 \rightleftharpoons 2\ Fe_2O_3 + 6\ Cl_2 \quad . \quad . \quad . \quad . \quad . \quad (3)$$

$$\Delta H_{778^0K} \text{ (regeneration)} = -147,400 \text{ calories.}$$

The sensible heat of the ferric oxide produced can be derived from the data given by Kelley (1960).

$$H_{778^0K} - H_{298^0K} \text{ (ferric oxide)} = -30,600 \text{ calories.}$$

The heat, which can be recovered by cooling the chlorination gases from the chlorination temperature of 1100°C to the regeneration temperature of 505°C, can now be obtained by the difference between the heat of reaction for the overall process at 298°K and the sum of the heats evolved at each stage of the process:

$$H_{1373^0K} - H_{778^0K} \text{ (chlorination gases)} = 133,800 \text{ calories.}$$

The heats evolved at the various stages of the process according to the following sequence of reactions are summarised below:

Oxidation (1000°C)

$$4\,FeO.TiO_2 + O_2 \rightleftharpoons 2\,Fe_2O_3.TiO_2 + 2\,TiO_2 \quad . \quad . \quad . \quad . \quad (1)$$

Chlorination (1100°C)

$$2\,Fe_2O_3.TiO_2 + 2\,TiO_2 + 6\,Cl_2 \rightleftharpoons 4\,FeCl_3 + 3\,O_2 + 4\,TiO_2 \quad . \quad . \quad (2)$$

Regeneration (505°C)

$$4\,FeCl_3 + 3\,O_2 \rightleftharpoons 2\,Fe_2O_3 + 6\,Cl_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Overall Process (25°C)

$$4\,FeO.TiO_2 + O_2 = 2\,Fe_2O_3 + 4\,TiO_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

The sensible heats and heats of reaction are:

Preheating oxidation reactants		
$H_{1273^0K} - H_{298^0K}$	125,000	calories
Oxidation reaction		
ΔH_{1273^0K}	-118,000	calories
Superheating oxidised ilmenite		
$H_{1373^0K} - H_{1273^0K}$	14,200	calories
Superheating recycled chlorine		
$H_{1373^0K} - H_{778^0K}$	73,900	calories
Chlorination reaction		
ΔH_{1373^0K}	173,000	calories

Heat from titania product		
$H_{1373^\circ K} - H_{298^\circ K}$	- 73,000	calories
Heat from chlorination gases		
$H_{1373^\circ K} - H_{778^\circ K}$	-134,000	calories
Regeneration reaction		
$\Delta H_{778^\circ K}$	-147,400	calories
Heat from ferric oxide product		
$H_{778^\circ K} - H_{298^\circ K}$	- 30,600	calories
Overall process		
$\Delta H_{298^\circ K}$	-116,900	calories

The summary shows that little heat is consumed by the oxidation reaction, the heat required to pre-heat the reactants being only a little greater than the heat released by the reaction.

The heat required for the chlorination reaction is considerable, being of the order of 260 kilocalories for 4 moles of ilmenite. Not only is the reaction endothermic but, since only about 45 per cent of the chlorine present is utilized in this reaction, excess chlorine has to be heated to the reaction temperature along with the reactants. Furthermore the heat has to be supplied at the high temperature of 1100°C.

The regeneration reaction is quite highly exothermic, which, together with the sensible heat of the chlorination gases, means that a large quantity of heat is recoverable at this stage in the process. However, the heat is recovered at the relatively low temperature of 500°C.

The overall process involves high heat consumption at 1100°C and the release of an even greater amount of heat at 500°C.

In the operation of the process on an industrial scale, a large installation of ancillary equipment for the recovery of waste heat would be necessary.

The regeneration temperature has been chosen rather arbitrarily and it is possible that the most economic temperature for conducting the regeneration reaction may be higher, even at the expense of recirculating some unreacted ferric chloride to the chlorination reactor. The influence of temperature upon the rate of reaction and on the physical nature of the iron oxide precipitate may be significant.

A great deal of study will be required for evaluation of all the factors influencing selection of the optimum temperature for the regeneration reaction.

7. CONCLUSIONS

Experiments have been performed to measure the extent of reaction between chlorine and oxidised ilmenite over the temperature range of greatest interest for the chlorination process. Similar work has been carried out on the reaction between chlorine and ferric oxide.

With the data obtained in these experiments supplemented by published data, the thermodynamics of the reactions involved in the process can be studied.

Ilmenite can be oxidised at 1000°C with air with complete utilization of oxygen in the air. The oxidation reaction is exothermic to the extent where the heat released is almost sufficient to supply the sensible heat of the reactants.

At a chlorination temperature of 1100°C, 45 per cent of the chlorine in contact with oxidised ilmenite is converted to ferric chloride. The reaction is endothermic and the heat of reaction has been determined.

Chlorine reacts with titanium dioxide to a small but measurable extent in the temperature range 1000° to 1200°C. However, titanium tetrachloride readily reacts with the iron content of oxidised ilmenite to deposit titanium dioxide and form gaseous ferric chloride. In a multiple stage countercurrent fluidised bed reactor being used for the chlorination of oxidised ilmenite, this results in some titanium being removed from the bottom stage as gaseous tetrachloride. This chloride reacts with oxygen or oxidised ilmenite in the upper stages and deposits the titanium content as titanium dioxide. The overall process in the reactor is one of selective chlorination of iron with no detectable amount of titanium leaving the reactor as titanium tetrachloride in the chlorination gas stream. Some titanium would however circulate around the bottom few stages of the reactor. This effect could cause blockage of gas distributors between stages.

Some ferrous chloride is formed during the chlorination of oxidised ilmenite. However, the amount formed is small and, as the temperature of the gaseous reaction products is lowered to the temperature at which the regeneration reaction is carried out, the ferrous chloride reacts with free chlorine to form ferric chloride. At no temperature is the partial pressure of ferrous chloride sufficiently high to precipitate liquid ferrous chloride.

The formation of ferrous chloride can therefore be disregarded in the chlorination reaction and only the formation of ferric chloride considered.

The gases produced by chlorination of oxidised ilmenite at 1100°C can be cooled to about 1030°C without deposition of iron oxide. This fact is probably of importance in the operation of the process, as the temperature of the chlorination gases can fall by 70°C without ferric oxide forming to block gas ports or other parts of the gaseous transport system.

The heat involved in the chlorination reaction has been calculated from measurements of equilibrium compositions.

Sufficient thermodynamic data have been published recently for evaluation of the reverse reaction in the temperature range 500° to 700°C. With this data gaseous ferric chloride has been shown to exist at 500°C almost entirely in the dimeric form. At 700°C dissociation to monomeric ferric chloride is appreciable.

At 500°C dimeric ferric chloride reacts with oxygen to the extent that virtually all of the chlorine is recovered for re-use in the chlorination reaction. Therefore, if the chlorination reaction is carried out at 1100°C under such conditions that the chlorination gases leaving the reactor are in equilibrium with oxidised ilmenite, 45 per cent of the chlorine circulating in the cyclic system is used in the transport of iron as gaseous chlorides. The remaining 55 per cent circulates continuously without participating in the chlorination and regeneration reactions.

The heats of reaction for both the association of monomeric ferric chloride to dimeric ferric chloride and the reaction of dimeric ferric chloride with oxygen at 500°C, both exothermic reactions, have been calculated. These data, together with sensible heats for the various reactants and products, have enabled the tabulation of the heat absorbed or released at each stage of the oxidation and cyclic chlorination and regeneration process.

The tabulation shows that the overall process, that is, the oxidation of ilmenite and separation of the oxidised product to ferric oxide and titanium dioxide, is exothermic. However, while the oxidation reaction is almost thermally neutral when sensible heats of reaction are considered, the chlorination reaction is endothermic and the regeneration is exothermic.

The chlorination reaction is carried out at the high temperature of 1100°C, while the regeneration reaction is carried out at a much lower temperature, about 500°C. Heat must therefore be supplied to the process at high temperature and recovered at low temperature.

The importance of the design of auxiliary heating and heat recovery equipment in the operation of the process on an industrial scale has been discussed.

A temperature of 500°C has been selected for the purpose of calculation as the regeneration reaction temperature. The optimum temperature may be higher than 500°C and some aspects to be considered in the selection of the optimum temperature for this reaction have been discussed.

On the basis of this work, the supply and removal of heat at various points in the process are seen to present major engineering problems in the operation of the process on an industrial scale.

Further development of the process would require an investigation of the rates at which the various reactions will proceed under operating conditions.

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APPENDIX A

TABLE A-1: CHLORINATION OF FERRIC OXIDE

Test No.	Temperature °C	Chlorine Flow gpm	Pressure Loss in. wg	Chlorine Conversion %
1	801	0.076	1.2	9.4
2	800	0.102	6.0	10.9
3	801	0.146	3.0	8.2
4	864	0.101	10.0	11.5
5	865	0.098	1.0	18.7
6	866	0.151	7.0	18.6
7	868	0.104	1.5	15.8
8	868	0.107	2.5	16.7
9	867	0.108	3.0	10.8
10	867	0.107	3.0	12.7
11	915	0.119	2.5	12.7
12	915	0.132	7.5	24.9
13	915	0.174	13.0	24.2
14	919	0.169	2.5	22.4
15	921	0.169	12.5	18.1
16	920	0.107	4.0	22.7
17	920	0.108	2.0	17.3
18	955	0.119	0	30.2
19	956	0.120	0	30.9
20	957	0.172	0	31.6
21	996	0.119	0	36.0
22	996	0.170	7.5	30.6
23	996	0.175	0	36.1
24	996	0.174	0	38.1
25	1000	0.169	2.5	35.4
26	1028	0.108	0.5	43.3
27	1028	0.171	0	44.3
28	1058	0.108	2.0	53.4
29	1059	0.171	2.0	51.7
30	1060	0.172	0	54.4
31	1063	0.160	1.0	46.6
32	1063	0.160	1.0	46.5
33	1100	0.108	0.2	56.0
34	1100	0.172	0	56.7
35	1104	0.159	1.0	49.8
36	1103	0.159	1.0	55.6

TABLE A-2: CHLORINATION OF OXIDISED ILMENITE

Test No.	Temperature °C	Chlorine Flow gpm	Pressure Loss in. wg	Chlorine Conversion %
1	1000	0.15	2.6	31.0
2	1000	0.30	8.6	31.0
3	1050	0.15	4.3	33.0
4	1050	0.15	4.9	36.8
5	1050	0.30	6.9	36.5
6	1100*	0.075	1.6	42.3
7	1100	0.075	2.9	43.5
8	1100	0.15	4.9	43.6
9	1100*	0.30	11.2	45.1
10	1100	0.30	4.9	43.6
11	1100	0.30	12.0	44.6
12	1150	0.15	5.7	54.1
13	1150	0.15	5.1	53.9
14	1150*	0.30	11.5	51.9
15	1150*	0.30	5.1	50.6
16	1150*	0.30	4.8	49.1
17	1150	0.30	10.4	52.7
18	1200	0.15	4.6	66.2
19	1200*	0.30	9.8	55.7
20	1200	0.30	9.1	65.3

* Test results rejected.

FIGURE A1

COMPARISON OF DATA OF GALMICHE (1948) AND SMULLIN (1952) FOR SYSTEM:

$2\ Fe_2O_3 + 6\ Cl_2 = 4\ FeCl_3 + 3O_2$

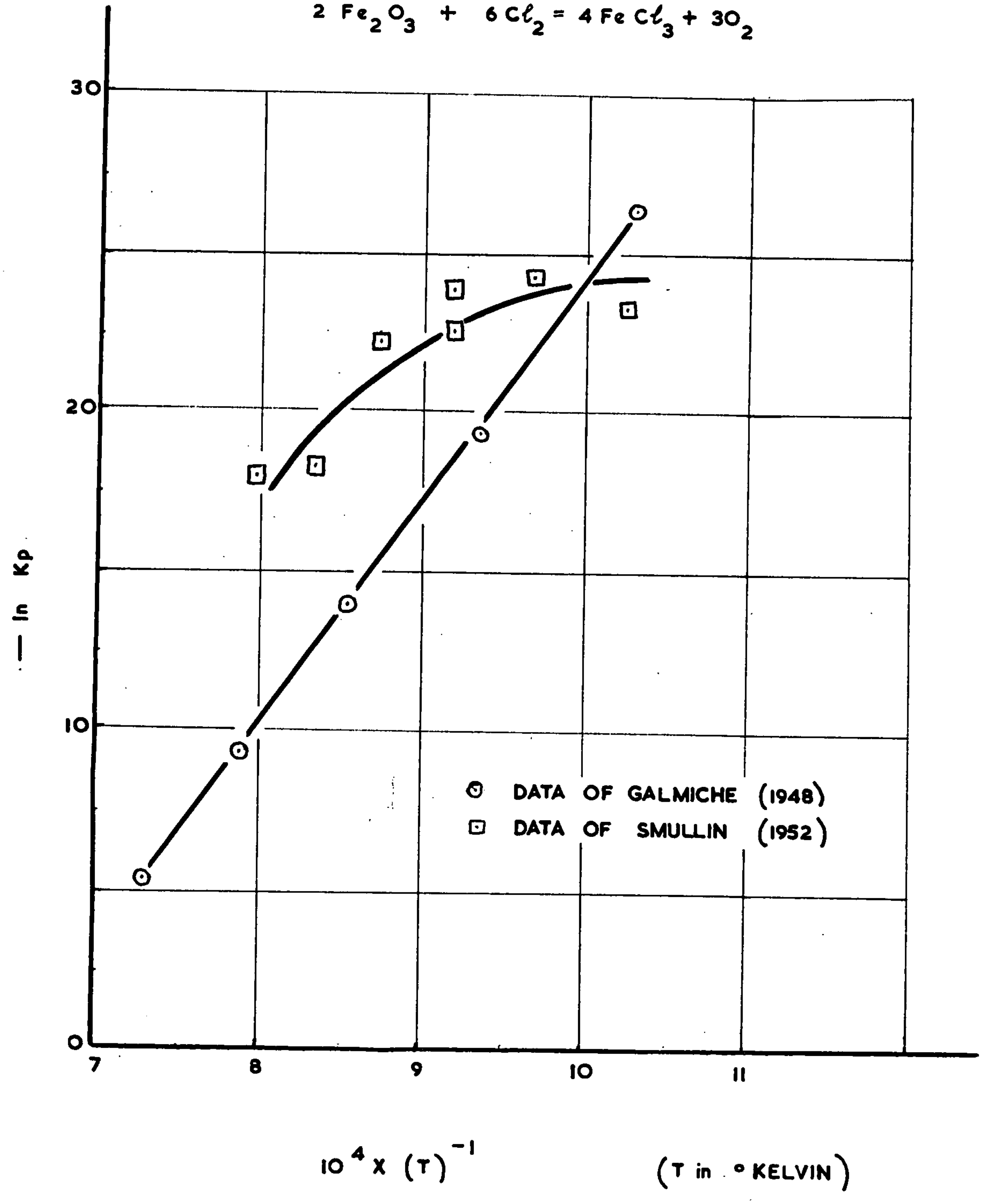

FIGURE A2

COMPARISON OF DATA FOR GALMICHE (1948) AND SMULLIN (1952) FOR REACTION:

$2\,Fe_2O_3 + 6Cl_2 = 4\,FeCl_3 + 3O_2$

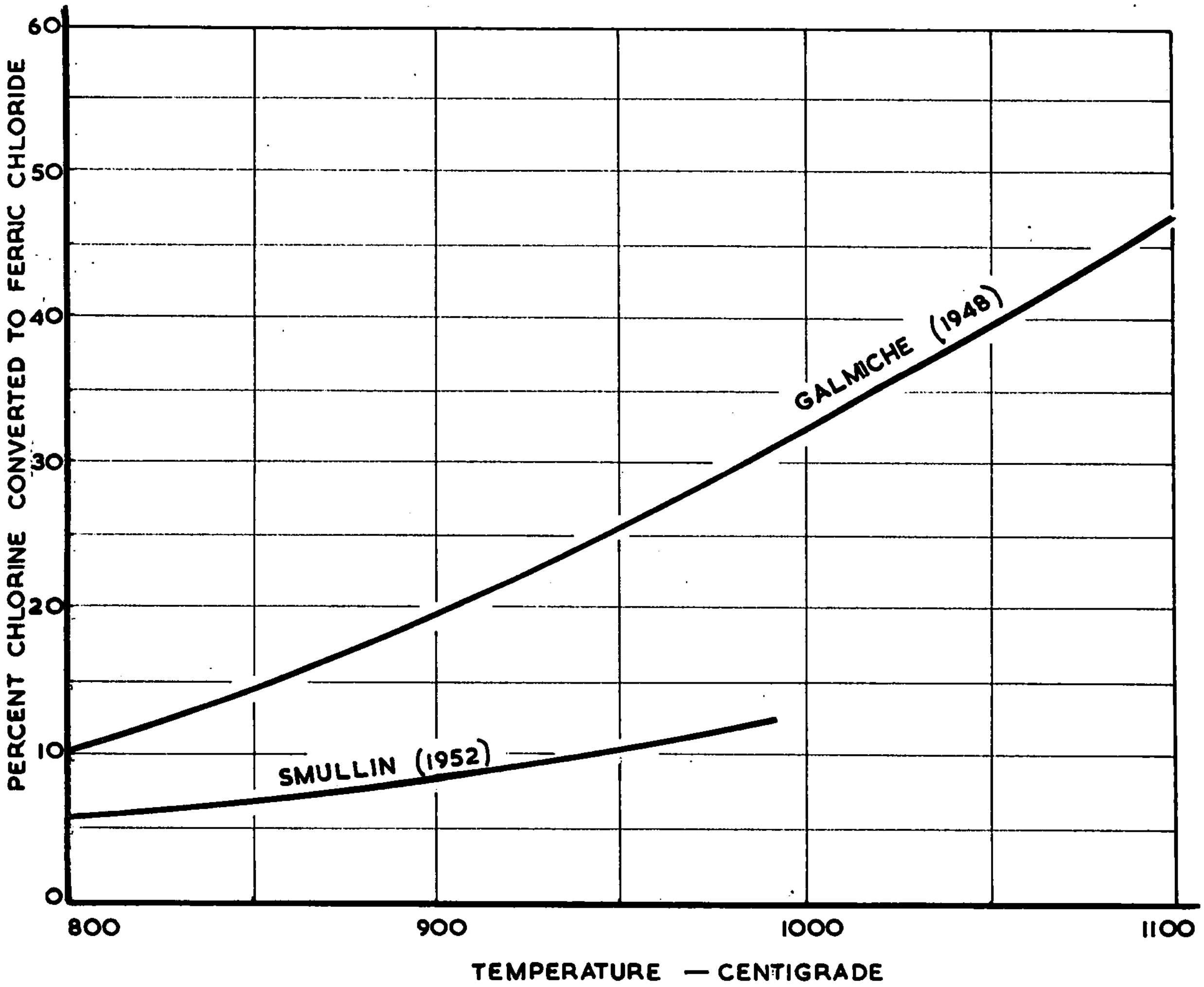

FIGURE A3

EXPERIMENTAL DATA FOR CHLORINATION OF HEMATITE (1) AND OF OXIDISED ILMENITE (2)

(1) $2Fe_2O_3 + 6C\ell_2 = 4FeC\ell_3 + 3O_2$

(2) $2Fe_2O_3\,TiO_2 + 6C\ell_2 = 4FeC\ell_3 + 3O_2 + 2TiO_2$

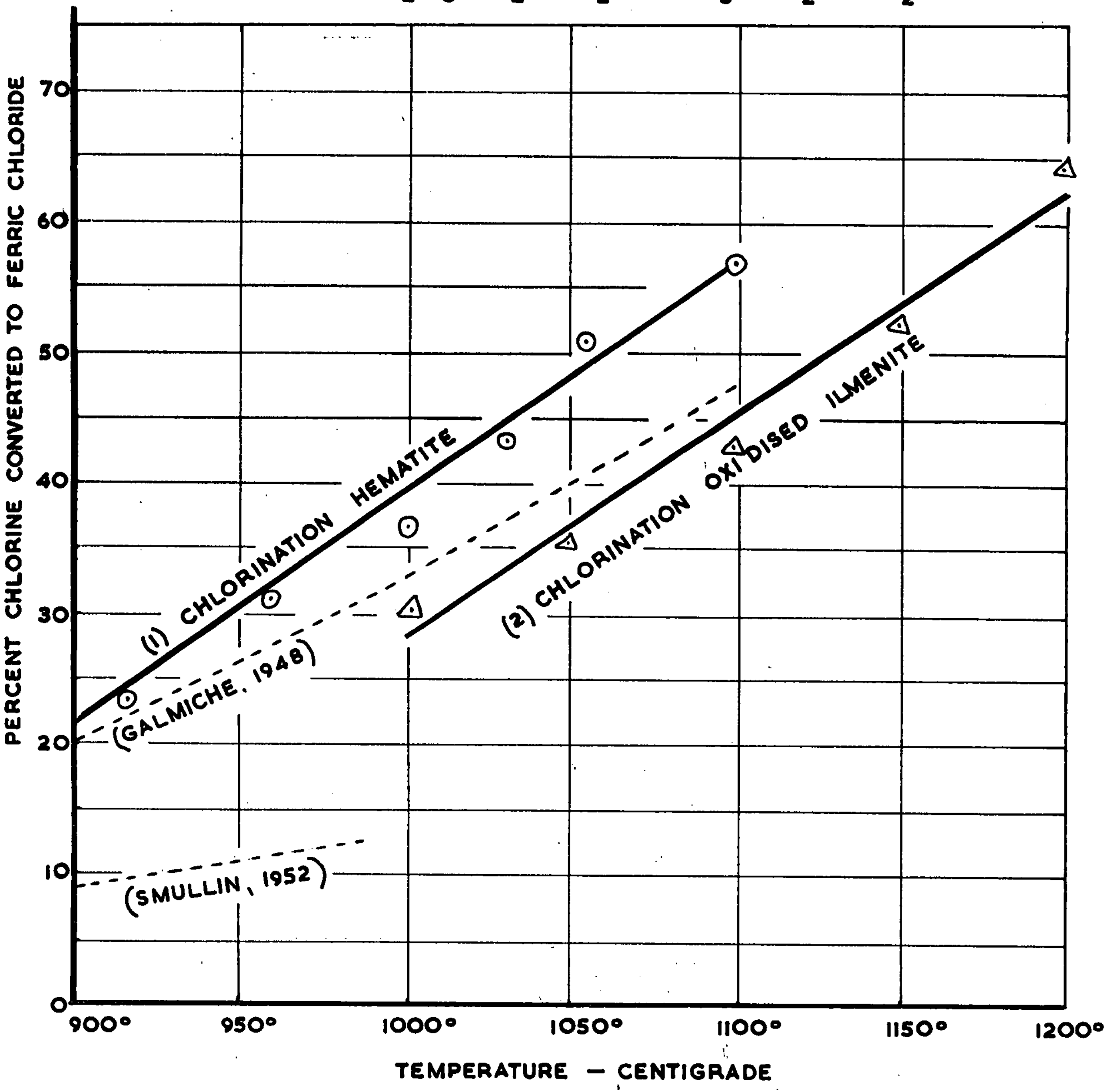

FIGURE A4

CHLORINATION OF FERRIC OXIDE.

$2Fe_2O_3 + 6C\ell_2 = 4FeC\ell_3 + 3O_2$

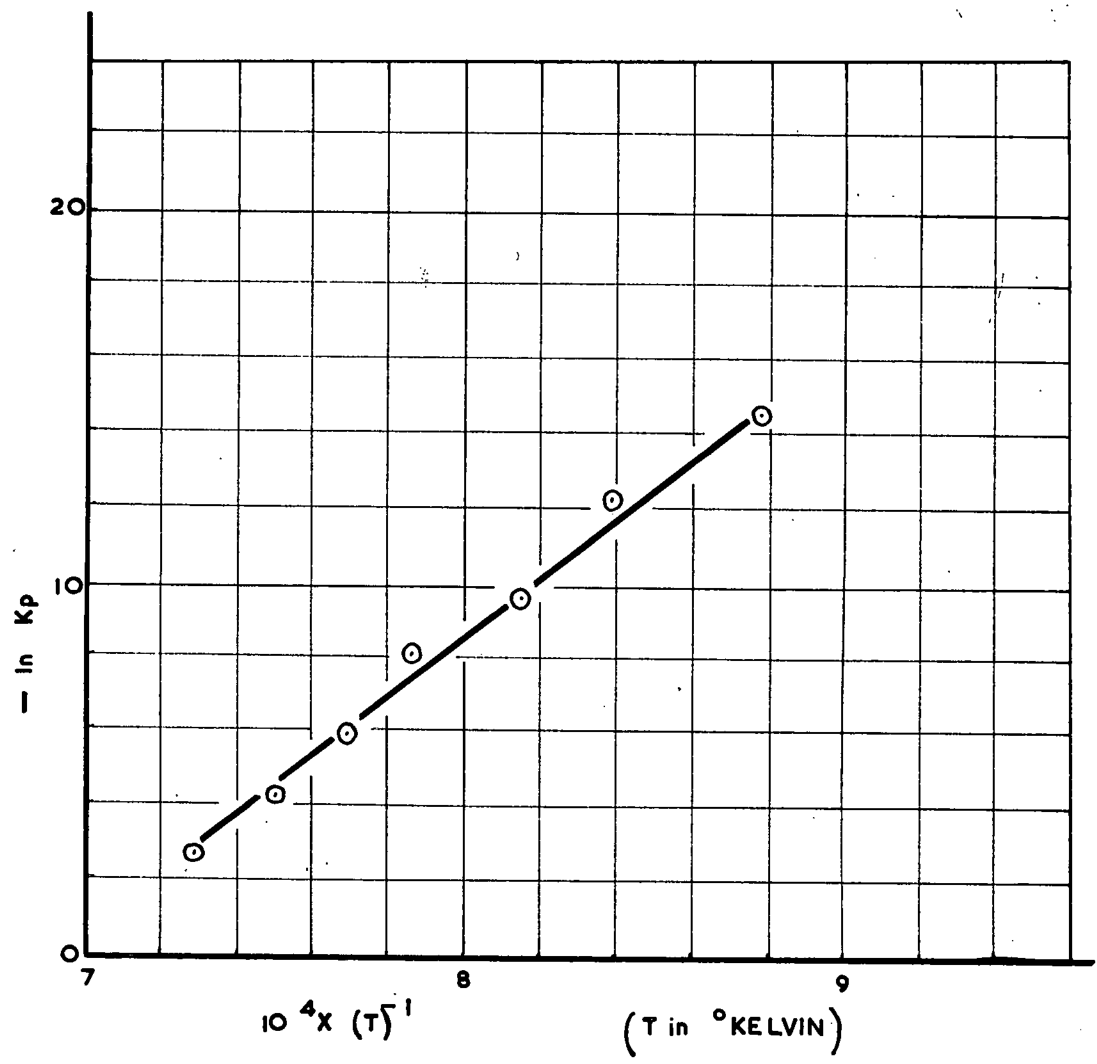

FIGURE A5

CHLORINATION OF FERRIC OXIDE.

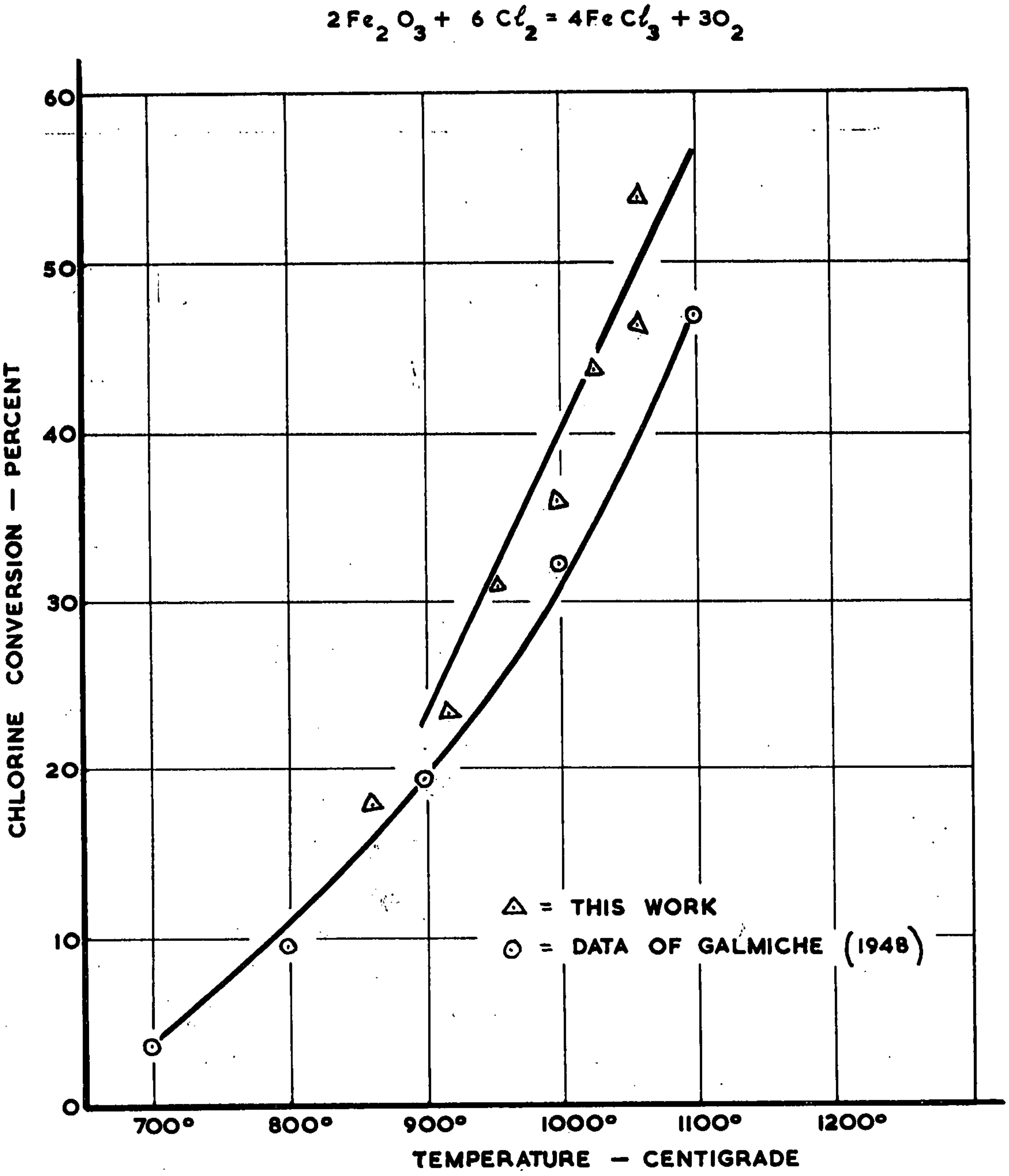

FIGURE A6

CHLORINATION OF OXIDISED ILMENITE.

$2Fe_2O_3\ TiO_2 + 6Cl_2 = 4FeCl_3 + 3O_2 + 2TiO_2$

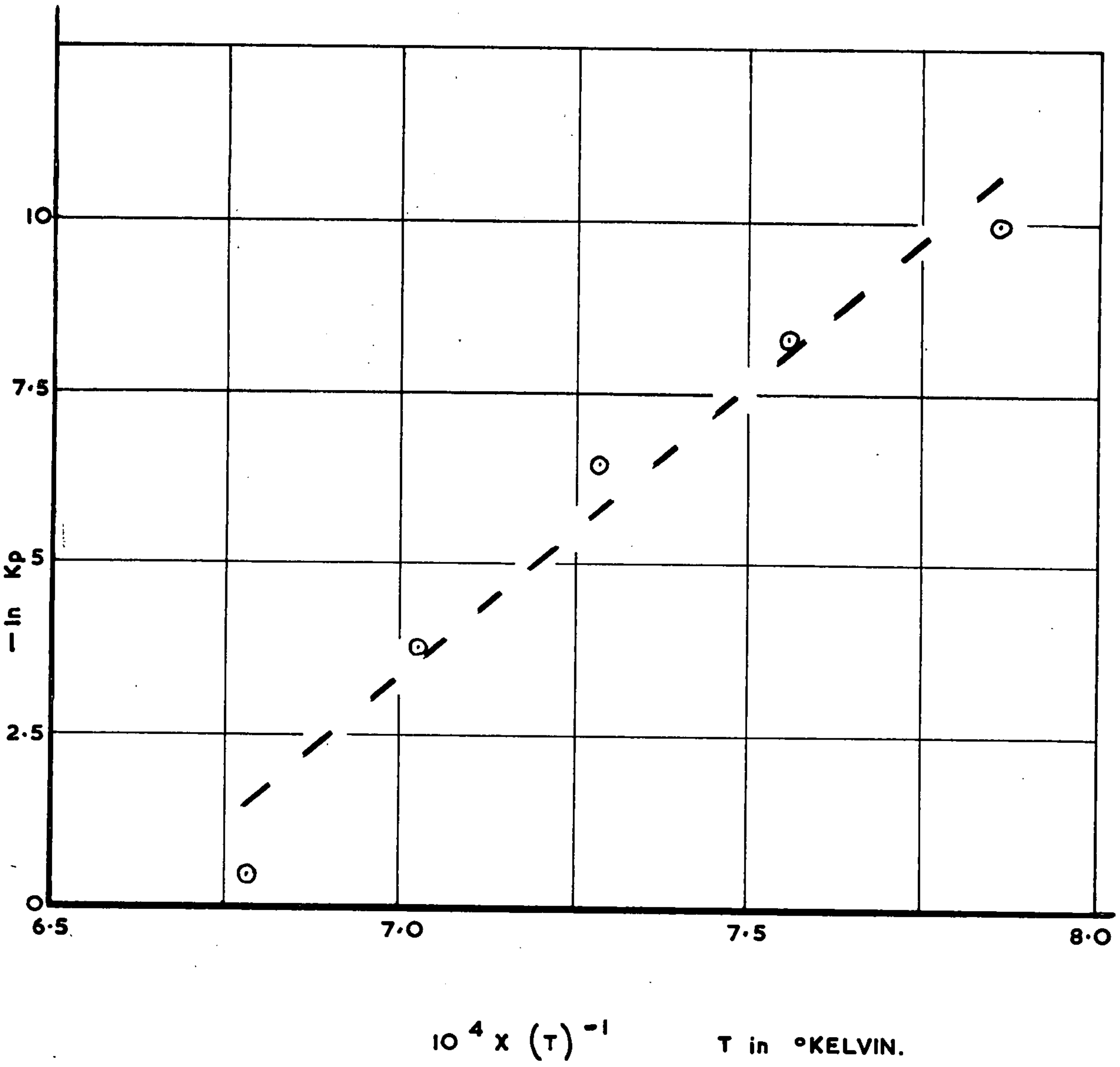

FIGURE A7

CHLORINATION OF OXIDISED ILMENITE.

$$2Fe_2O_3\,TiO_2 + 6Cl_2 = 4FeCl_3 + 3O_2 + 2TiO_2$$

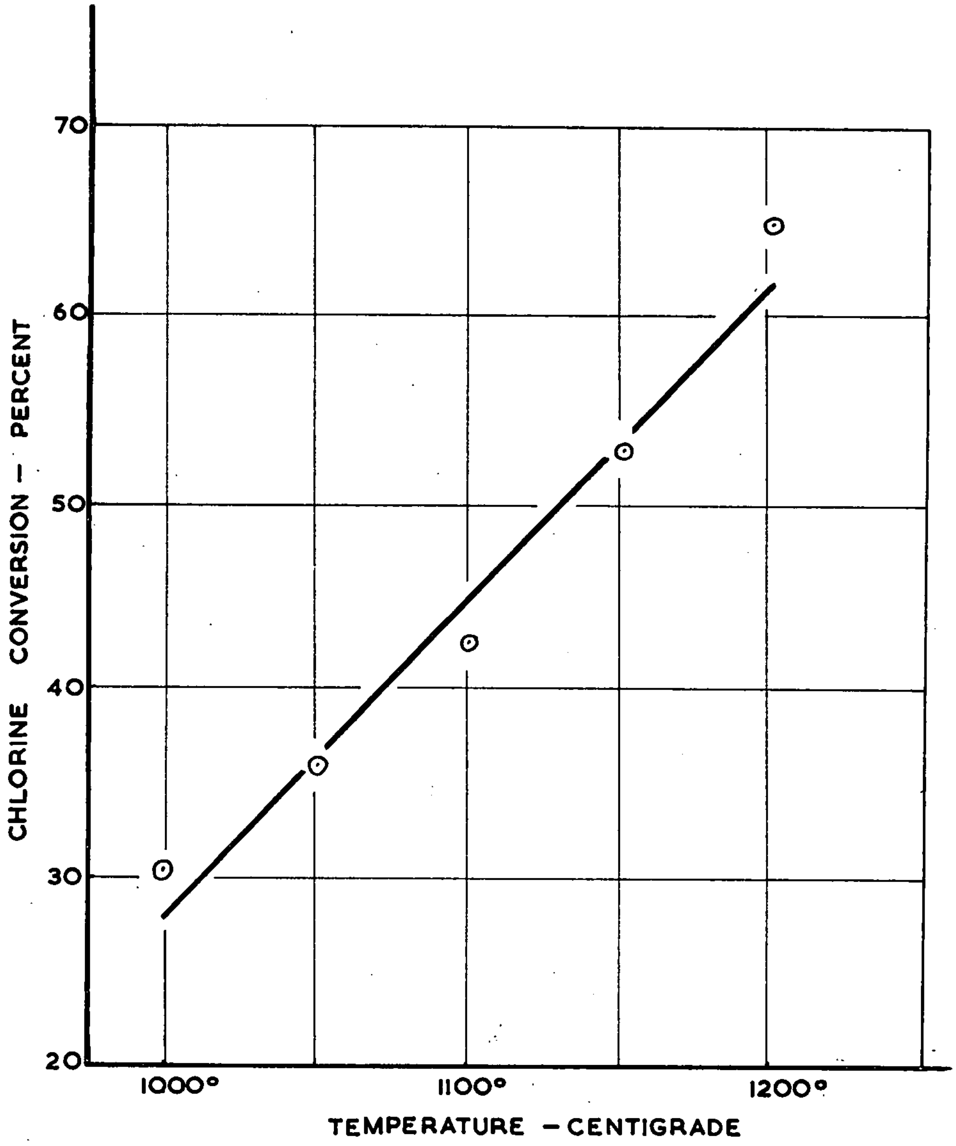

FIGURE A8

CHLORINATION OF FERRIC OXIDE.

$$4Fe_2O_3 + 6Cl_2 = 4FeCl_3 + 3O_2$$
$$4Fe_2O_3 + 4Cl_2 = 4FeCl_2 + 3O_2$$

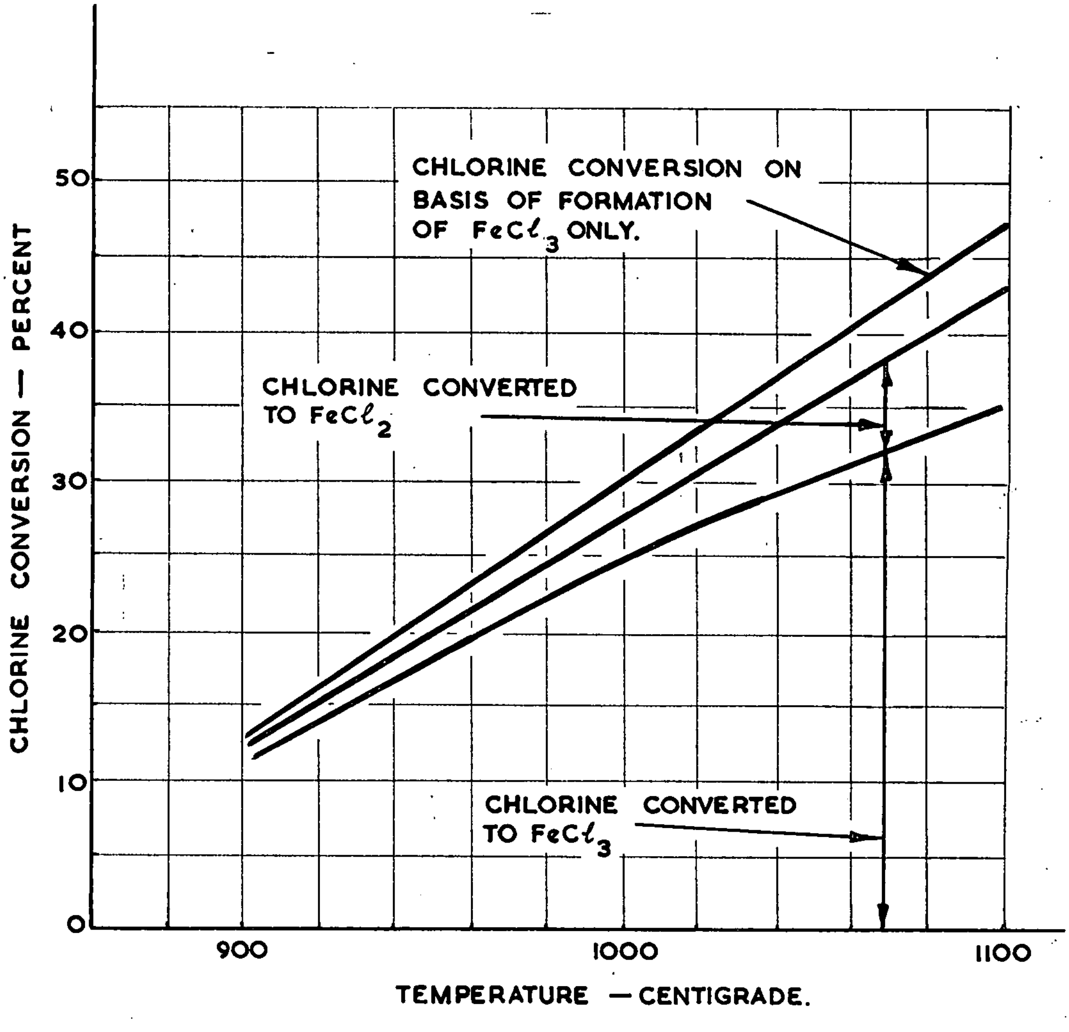

FIGURE A9

VAPOUR PRESSURE OF FERROUS CHLORIDE

● = PARTIAL PRESSURE OF FERROUS CHLORIDE IN THE GASES FORMED BY CHLORINATION OF OXIDISED ILMENITE WITH CHLORINE AT 1100°C.