Thermochimica Acta, 101 (1986) 107–118
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

THERMAL ANALYSIS STUDIES ON THE INITIAL STAGES OF IRON OXIDE REDUCTION

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(Received 30 September 1985)

ABSTRACT

Initial stages of reduction of Fe_2O_3, leading to the formation of wustite, have been investigated using thermal analysis. Isothermal TG experiments were carried out at temperatures of 826, 900 and 1020°C ensuring that the reduction did not go beyond the wustite stage. The activation energy for isothermal reduction is an overall average for overlapping reactions. This isothermal E value is almost the average of the non-isothermal E values for the two individual stages which are clearly delineated in rising temperature TG studies.

INTRODUCTION

An enormous amount of work has been carried out on iron oxide reduction. In addition to numerous papers on the subject, many reviews and monographs are also available. However, most of these mainly deal with isothermal reduction of wustite to metallic iron, i.e., the final stage of reduction.

In recent years some thermal analysis studies, under rising temperature conditions, have been reported in the literature on reduction of iron oxides by gaseous and solid reductants. Most of these, however, are rather qualitative. Szendrei and Van Berge [1] used TG and EGA to study the kinetics of mixtures of iron oxides and carbon powders with or without addition of catalysts such as Na_2CO_3 which is known to catalyse the gasification of carbon. They found distinct peaks in the rates of weight change and generation of CO and CO_2, the steps clearly showing the multistage nature of the reaction. Dobovisek [2] also studied the effect of catalysts on the reduction of iron oxide by petrol coke in a thermal analyser. He also found the reaction to be distinctly multistep and he used the position of the characteristic DTA peak of reduction of FeO to metallic iron to interpret the results. Both studies found that the overall reduction reaction was catalysed by carbonate which indicated the importance of the carbon gasification step in controlling the reaction rate.

0040-6031/86/$03.50

Thermal analysis studies on the oxide–carbon system have been carried out not only to study the reduction reaction but also to investigate the effect of the oxide on pyrolysis of coal. Cypres and Soudan-Moinet [3], in their studies on pyrolysis, found that the yield of tar and gaseous hydrocarbons decreases but the production of methane increases in presence of iron oxides. They found that even small iron oxide additions had a catalytic effect on pyrolysis.

Reduction of Fe_2O_3 by a reducing gas is made up of individual subsidiary processes occurring successively. The slowest step in the reaction sequence is supposed to be rate controlling. In the reduction of ores where the temperature, composition of reducing gas, rate of gas flow, pore structure of the solid, particle size, etc., are all variable, various sub-processes may be rate determining. Formulation of the kinetic law and determination of the activation energy help in identifying the rate controlling step. A detailed discussion on possible rate controlling steps is available elsewhere [4,5].

During reduction, those phases which can coexist with one another, i.e., Fe/Fe_xO, Fe/Fe_3O_4, Fe_xO/Fe_3O_4, Fe_3O_4/Fe_2O_3, are always in direct contact with one another. Which of the reduction products at any given instant during the reduction lie on the surface of the oxide and are in contact with the gas phase depends not only on the corresponding equilibria but is also determined by the rates of removal of oxygen on the one hand and by the diffusion processes in the oxide on the other. The overall rate of reduction can be effected by diffusion only in the outermost of the layers of metal or lower oxides which are being formed. Diffusion in the inner layers is a subsequent and subordinate process which has no direct effect on the course of the reaction. In wustite and magnetite it is almost exclusively the iron which diffuses [5], the oxygen being, by comparison, immovable. Wustite is reduced through removal of oxygen by H_2 or CO whereas Fe_3O_4 or Fe_2O_3 is reduced through reaction with iron diffusing inward. The activation energy for the final stages of reduction as well as the overall reaction is generally given in the range 35–60 kJ mol^{-1}, the suggested rate determining process varying from one work to another.

The present work is mainly aimed at studying the first two stages of reduction leading to wustite and magnetite and evaluating the activation energy of the steps individually as well as when they are allowed to overlap.

EXPERIMENTAL

Two samples of ferric oxide were used. One was a laboratory grade reagent given as 97% Fe_2O_3, the rest being nonvolatile impurities, mainly SiO_2. The second was hematite ore from Noamundi Mines, Bihar (India). Chemical analysis of the ore is shown in Table 1. It contained about 7 wt.% moisture and was, therefore, heated to 600°C and then stored in a desiccator prior to use.

TABLE 1

Chemical analysis of hematite ore

Item	Weight percent
Fe_T	65.28
Fe^{2+}	2.0
SiO_2	1.8
Al_2O_3	4.8
C, S	trace

The laboratory grade reagent was reduced by an N_2–CO (70%) mixture from a cylinder using a Stanton-Redcroft thermobalance (Model TG-770). There was also a unit for direct continuous recording of the derivative curve, i.e., a rate of weight loss versus temperature curve. The gas mixture, which was not purified, was passed at a rate of about 10 ml min^{-1}.

In the second case, simultaneous TG/DTA, under both isothermal and non-isothermal conditions, was carried out on the iron ore using a Stanton-Redcroft thermal analyser (Model STA-780). The reducing gas used was made in the laboratory via reaction between formic acid and sulphuric acid. It was passed through a series of alkaline pyrogallol bottles and then stored in a cylinder. The analysis of the gas, as determined using an Orsat apparatus is shown in Table 2. Preliminary weight loss experiments showed that this gas was sufficiently reducing to 1000°C to reduce Fe_2O_3 to the wustite phase.

All experiments were carried out using a sample size of 20–50 mg in flowing gas ($\sim$ 10–20 cm^3 min^{-1}). For isothermal experiments the sample was maintained initially under flowing nitrogen until the furnace achieved a predetermined temperature and the temperature stabilized when the reducing gas was allowed to flow. Rising temperature experiments, however, were carried out with reducing gas being allowed to pass from the very beginning.

TABLE 2

Analysis of reducing gas

Item	Volume percent
CO	91.0
O_2	7.0
CO_2	0.7
other gases	rest

RESULTS AND DISCUSSION

Reduction of laboratory grade Fe_2O_3

Figure 1 shows TG plots for reduction of Fe_2O_3 by $CO-N_2$ mixtures for three different heating rates. These plots were obtained from the preliminary weight loss versus temperature plots given by the thermobalance on the basis of 97% Fe_2O_3 in the sample.

The curves indicate various changes of slopes at different temperatures, the changes becoming more prominent at lower heating rates. These are indicative of sequential reactions. The DTG curves for the two lower heating rates are shown in Fig. 2. These curves indicate the variation of the slopes of two plots shown in Fig. 1 as a function of temperature.

The first rise in a DTG plot corresponds to the beginning of the weight loss reaction, indicating formation of Fe_3O_4 from Fe_2O_3. The second peak perhaps indicates reduction of Fe_3O_4 of iron. Beyond 560°C, wustite (Fe_xO)

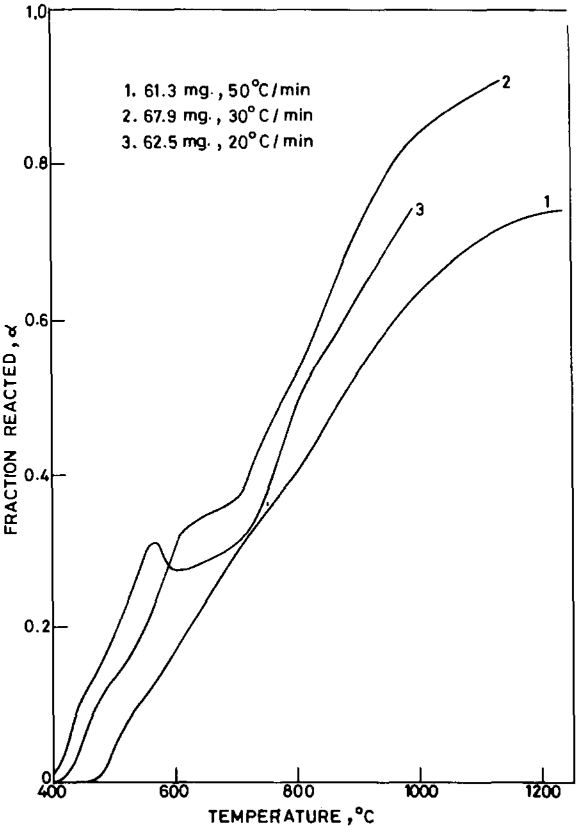

Fig. 1. TG plots for reduction of Fe_2O_3 by $CO-N_2$ mixture.

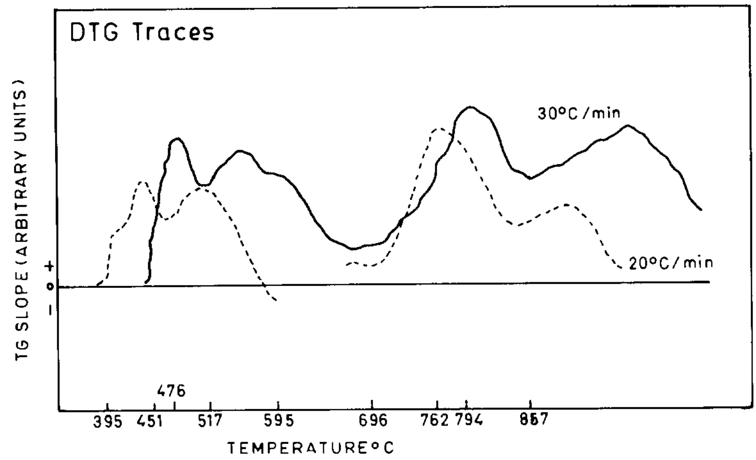

Fig. 2. DTG plots for two TG curves of Fig. 1.

becomes stable and reduction of Fe_3O_4 to iron must stop. At temperatures around 600°C, however, this sequential reduction reaction is characterised by many complications.

The fact that finite layers of Fe_3O_4 and/or Fe_xO exist during reduction of Fe_2O_3 shows that the formation of these layers is a faster process than the reaction at the Fe_xO/Fe interface. Kinetically it is simple to consider the reduction as a simple two phase system, oxide/metal [6]. It has been shown [6,7] that the gas–solid type of reaction takes place only at the Fe_xO/Fe interface and is often described by the topochemical reaction model. There is, however, evidence in the literature to suggest that the rate controlling mechanism may change with temperature, among other factors.

Many workers have noted higher reaction rates just below 600°C than at temperatures in the range 600–800°C. Several reasons have been proposed for the occurrence of a rate minimum [8]. These include sintering of the iron product and formulation of wustite in very dense forms which reduce diffusion of the reductant and the product gas to and from the reaction interface.

The rate minimum phenomenon is clear in runs 2 and 3 shown in Fig. 1. To explain the shape of these curves more clearly, one must also consider the Boudouard reaction which tends to deposit carbon

$$2CO = CO_2 + C \qquad (1)$$

It is well known that at temperatures above 710°C all iron oxides can be reduced by mixtures of CO/CO_2 at a total pressure of 1 atm. At lower temperatures only those mixtures which are supersaturated with carbon and which, therefore, must react towards carbon deposition, have a reducing action on Fe_xO.

In the present case CO from the cylinder does not decompose initially since decomposition in the homogeneous gas phase or at the surface of any carbon particle is negligible [5]. However, CO begins to decompose with reduction of iron oxides, the reaction products, particularly iron acting as catalyst [5,9]. The lower temperature limit for perceptible reduction and, therefore, carbon deposition would vary from ore to ore and would set in after a clearly marked incubation period.

Deposition of carbon, of course, would affect the shape of the weight loss curve. The rate may be lowered or even made negative. Therefore, it is essential to estimate the uncertainty involved in the light of data on carbon monoxide dissociation available in the literature [5,10].

Von Bogdandy and Engell [5] have given some typical values for rates of carbon deposition at different temperatures for a given sinter (50 g, 2.5–5 mm size) being reduced by carbon monoxide in a given tube (41 mm diameter). The gas flow rate of CO was 1 l min^{-1}. The data show almost no deposition until 300°C and then an increasing rate of deposition until a maximum is reached at about 500°C beyond which the rate falls rapidly. In the present case it takes 40 min to reach 800°C at a rate of 20°C min^{-1}. If 20 min is given for incubation then only 20 min is available for appreciable deposition in the range 400–800°C. It is estimated that the weight deposited would be around 5% or less of the sample weight. This, of course, would be lower for a higher heating rate. Figures 1 and 2 show that there is a region beyond 600°C where the rate of reduction falls appreciably. In this range the TG plot showed an apparent weight gain in one plot (curve 3) presumably because of some carbon deposition.

Isothermal reduction of iron ore fines

Figure 3 shows some kinetic plots based on results of isothermal TG experiments at three temperatures. In these experiments iron ore fines were reduced by the laboratory-made reducing gas and the final state was wustite

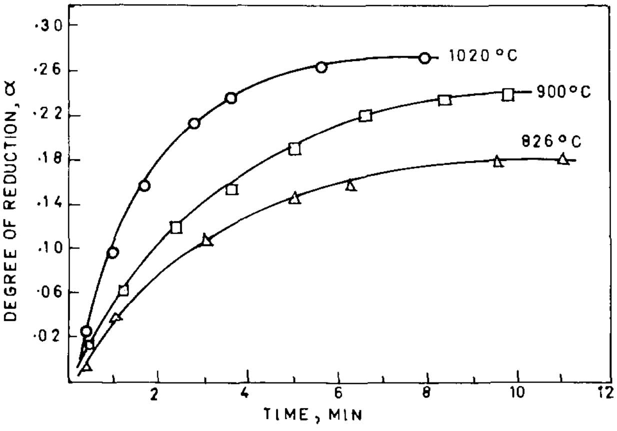

Fig. 3. Kinetic data for isothermal reduction of iron ore.

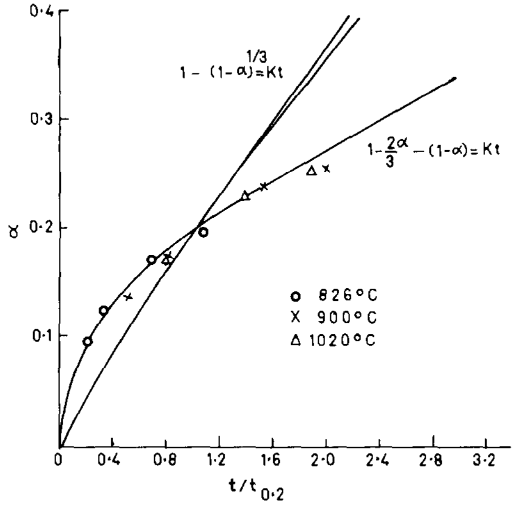

Fig. 4. Reduced time plots for isothermal kinetic data.

only. The plots indicate a time delay for the onset of reaction. This may be attributed to the time required for switching over from inert gas to the reducing atmosphere used for the experiments. These data were examined against standard reduced-time plots [11] for three kinetic models (Fig. 4) which have been found appropriate in various studies on iron ore reduction. For these plots the time values were corrected taking into account the "delay". The figure clearly identifies the Ginstling–Brounshtein model, for reaction controlled by product layer diffusion, to be the correct one in the present case. Plots of the Ginstling–Brounshtein equation, accordingly, are linear as shown in Fig. 5. The slopes of the linear plots yield values of the rate constant, k, at different temperatures. The Arrhenius type plot of these k values, which is also linear as shown in Fig. 6, yield, for the activation energy, a value of about 74 kJ mol^{-1} for the given temperature range.

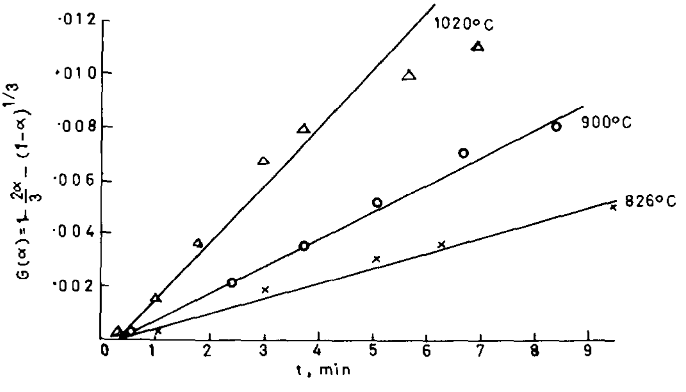

Fig. 5. Ginstling–Brounshtein plots to linearise kinetic data.

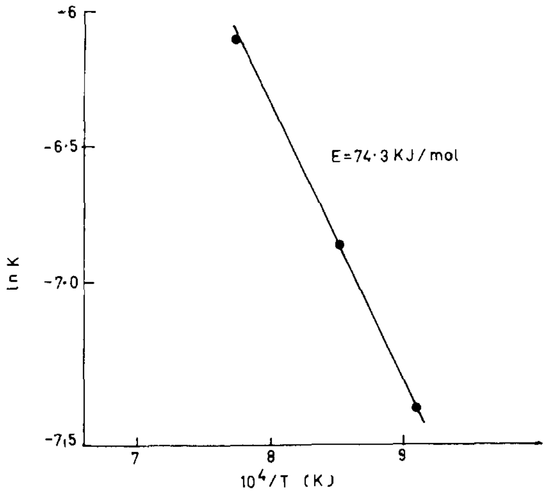

Fig. 6. Arrhenius plot for rate constant values.

It should be noted that in the isothermal experiments just discussed all stages prior to reduction of wustite were involved and they were allowed to overlap. The E value, therefore, gives an overall average only.

The E value can also be calculated using differential approaches without reference to any particular kinetic model. We note that the rate of reaction is related to temperature (T) and degree of reduction (α) by the differential equation

$$\frac{d\alpha}{dt} = A\exp(-E/RT)f(\alpha) \tag{2}$$

considering a fixed value of α one gets

$$\ln\left(\frac{d\alpha}{dt}\right)_\alpha = \ln A + \ln f(\alpha) - E/RT \tag{3}$$

Since ln f(α) has a fixed value for a fixed α it follows that a plot of the left-hand side against reciprocal temperature would be a straight line, the slope of which should yield the value of E/R.

Again, eqn. (2) can be rewritten as

$$\frac{1}{A\exp(-E/RT)}\int\frac{d\alpha}{f(\alpha)} = \int dt \tag{4}$$

$$t_\alpha = \frac{\text{const}}{A}\exp(E/RT) \tag{5}$$

i.e., t_α, the time required for a fixed value of α, is directly proportional to exp(E/RT). Therefore, a plot of ln t_α against reciprocal temperature should be a straight line and the slope should yield the value of E.

Figure 7 shows plots of $\ln(d\alpha/dt)_\alpha$ against reciprocal temperature for three values of α and Fig. 8 shows plots of ln t_α against reciprocal tempera-

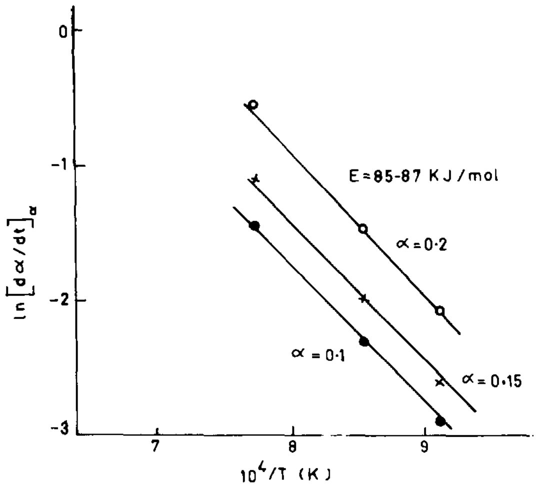

Fig. 7. Plots of $\ln(d\alpha/dt)_\alpha$ against $1/T$ for three levels of α.

ture for the same three levels of α. All plots are linear and the slopes yield E values in the range 85–87 kJ mol^{-1} which is not too different from that obtained earlier using the integral approach based on a given kinetic model.

Non-isothermal reduction of ore fines

Under rising temperature conditions the various reduction steps can appear without overlapping and, therefore, TG data should indicate sequential reactions. The TG plots, reproduced schematically in Fig. 9 indicate, in each case, sequential reactions as steps in the plots of weight loss with

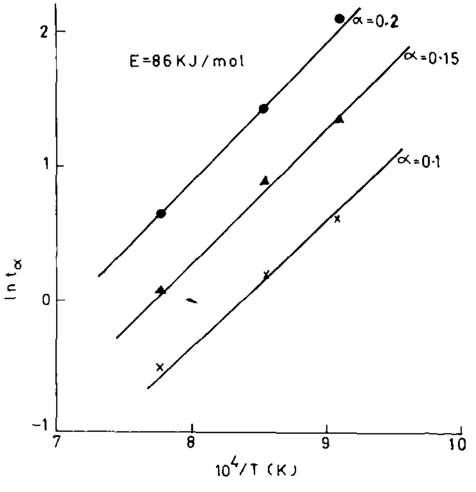

Fig. 8. Plots of t_α against $1/T$ for three levels of α.

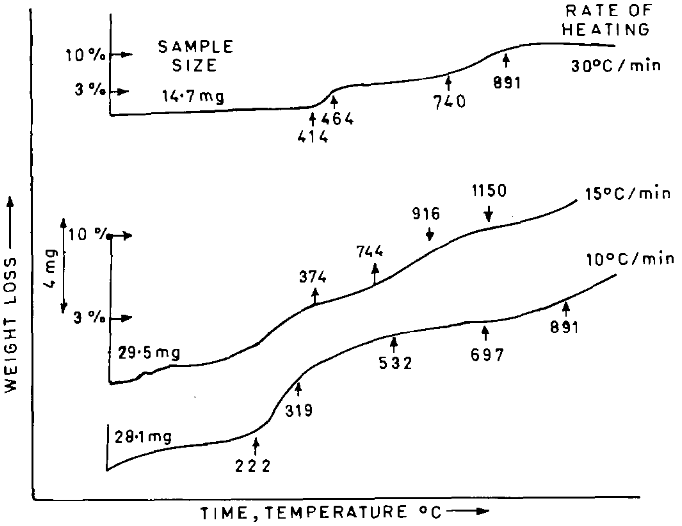

Fig. 9. Non-isothermal TG plots for initial stages of ore reduction.

temperature. The resolution of the steps is better at higher heating rates. It should be noted that the reduction of Fe_2O_3 to Fe_3O_4 is accompanied by a 3.3% weight loss and that to FeO by a 10% weight loss for pure dry Fe_2O_3. These levels of weight loss are approximately indicated in two of the TG plots. The TG data were used to obtain α–t plots in each case. Figures 10 and 11 show, respectively, the plots of the kinetic data corresponding to a heating rate of 15°C min^{-1}, according to equations proposed by Coats and Redfern [12] and Dixit and Ray [13].

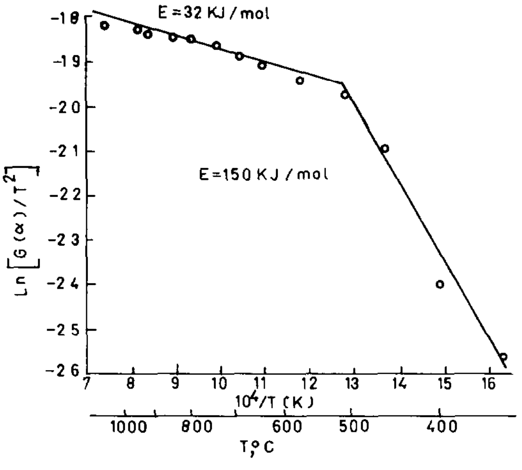

Fig. 10. Coats and Redfern plots for non-isothermal TG data.

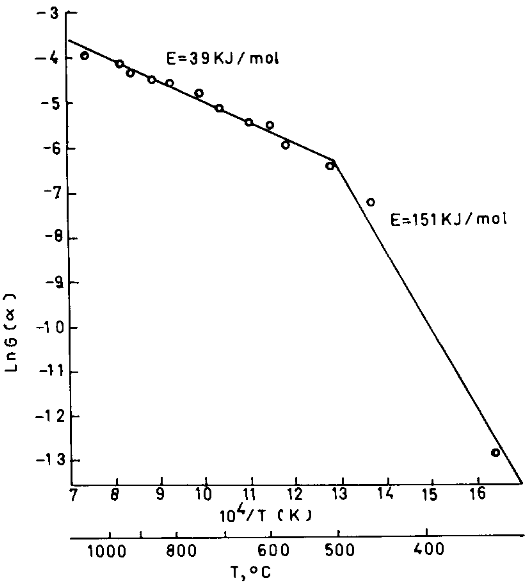

Fig. 11. Non-isothermal plots of TG data according to Dixit and Ray's equation.

Figures 10 and 11 clearly indicate the distinct stages in the reduction reaction, each characterised by a value of the activation energy. The change-over takes place around 500°C. In the very early stages, the apparent activation energy is about 150 kJ mol^{-1} and that in the latter stage is very much less, slightly over 30 kJ mol^{-1}. The average value, i.e., about 90 kJ mol^{-1}, is comparable to that obtained by isothermal experiments. This seems to indicate that during isothermal reduction an average E value prevails and that the isothermal and non-isothermal E averages match rather closely.

CONCLUSIONS

It may be concluded that isothermal reduction studies in the temperature range 800–1000°C show smooth α–t plots because of overlap of reduction stages. The overall reduction to the wustite state is characterised by an activation energy of nearly 90 kJ mol^{-1}. The reaction steps, however, are clearly brought out by rising temperature TG plots. Two clear stages are indicated with apparent E values of 150 and 30 kJ mol^{-1} for the first and second stages, respectively. The isothermal E value represents an average of these values.

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