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Note

Kinetics of reduction of Fe_2O_3 to Fe_3O_4 by the constant temperature differential thermal analysis method

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The direct reduction of ferric oxide by gaseous reductants is an industrially important reaction. The reaction proceeds through the formation of Fe_3O_4 if the temperature is below 575°C as the wustite phase is unstable under these conditions.

In the reaction sequence

$$Fe_2O_3 \xrightarrow{\text{I}} Fe_3O_4 \xrightarrow{\text{II}} Fe$$

both reduction steps are endothermic if carbon monoxide is used as the reductant, while the first step is exothermic and the second reaction is endothermic if the reduction is carried out with hydrogen[1].

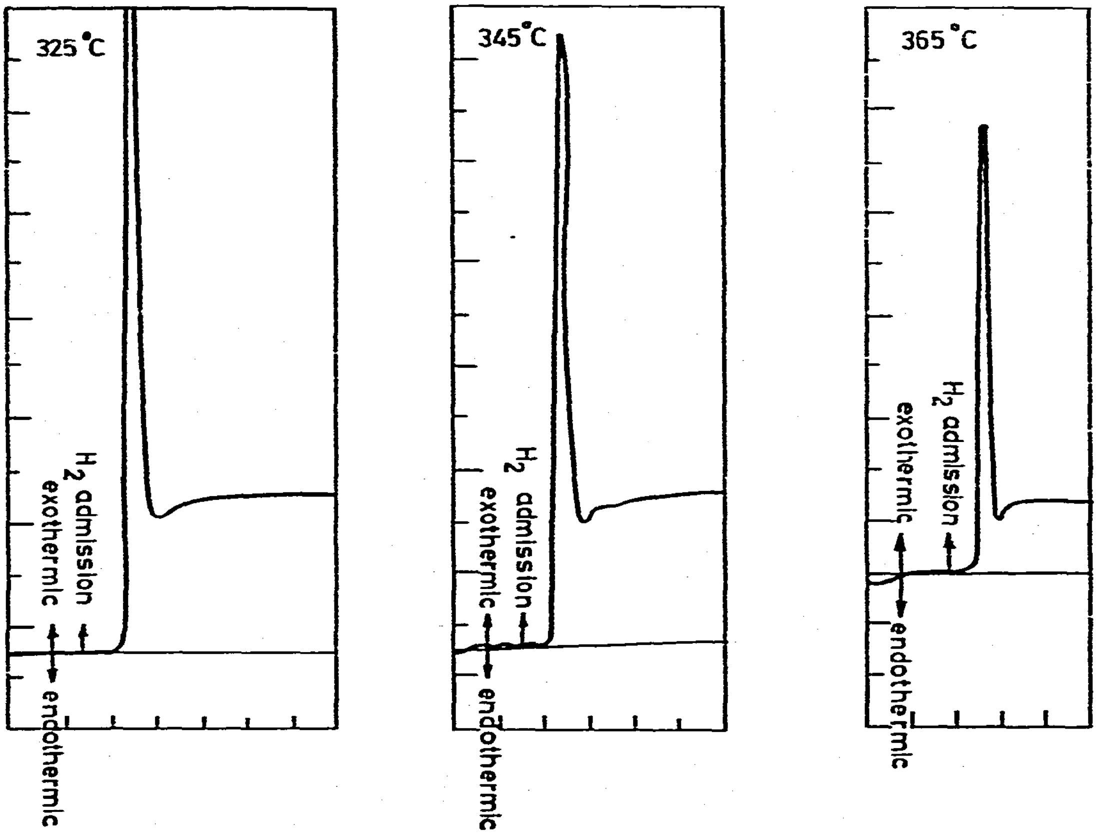
The differential thermal analysis technique has been employed by many authors[2,3] in order to follow the course of reduction of iron oxides. By independent kinetic studies, it has been established that the reduction of pure α-Fe_2O_3 follows a consecutive mechanism[4]. This result has been further supported by the observation of an exothermic peak corresponding to the reduction of Fe_2O_3 to Fe_3O_4 followed by a diffused endotherm in the DTA of the reduction of Fe_2O_3[5]. Since the exothermic peak obtained is due solely to the reduction of Fe_2O_3 to Fe_3O_4 it was thought of interest to follow the heat changes of this reaction at constant temperatures by the DTA method as a function of time so that a comparison of kinetic data obtained by this method with that obtained from the weight-loss measurements can be made. The aim of the present investigation is to establish the suitability of the isothermal DTA method for the study of the kinetics of reactions.

EXPERIMENTAL

Pure α-Fe_2O_3 was obtained by decomposing AnalaR (Baker analysed) ferric nitrate at 475°C for 8 h. The reduction kinetics of this oxide was followed gravimetrically by recording the weight changes as a function of time using a quartz spiring microbalance. The differential thermal analysis studies were carried out using a Netzsch differential thermal analyser (Netzsch Gerätbau GmbH, Selb, West Germany) in flowing hydrogen atmosphere (280 ml min^{-1}) using ignited alumina as reference. The DTA experiments at constant temperature were carried out by heating 200 mg of the sample in situ in the apparatus in flowing nitrogen. After stabilisation at the desired temperature, the nitrogen flow was changed to hydrogen flow and the heat changes accompanying the reaction were followed as a function of time, keeping the temperature constant at 325, 345 and 365°C. The DTA plots were corrected for change of ambient gas from nitrogen to hydrogen by carrying out blank experiments without the Fe_2O_3 sample.

RESULTS AND DISCUSSION

The isothermal DTA plots obtained at the three temperatures are shown in Figs. 1a–c. An exothermic peak is observed immediately after admission of hydrogen. The intensity of this peak decreases with increase of temperature. From the calculated values of heat changes at different temperatures given in Table 1, it can be concluded that there should be an *increase* in the intensity of the exothermic peak with temperature. Hence, the decrease observed cannot be due to differences in the values of heat



(a) (b) (c)

Fig. 1. DTA plot for the reduction of pure α-Fe_2O_3 (200 mg) in flowing hydrogen (280 ml min^{-1}) at (a) 325°C; (b) 345°C; and (c) 365°C.

content at different temperatures; it can only be due to the overlap of the endothermic second step with the primary exothermic process. This overlap will increase with increase of temperature, thus accounting for the decrease in the intensity of the exothermic peak with temperature.

TABLE 1

VALUES OF HEAT CHANGES (ΔH) AT DIFFERENT TEMPERATURES FOR THE TWO STEPS

Temp. (K)	*ΔH (kcal mol^{-1})* $3Fe_2O_3+H_2 \rightarrow 2Fe_3O_4+H_2O$	*ΔH (kcal mol^{-1})* $Fe_3O_4+4H_2 \rightarrow 3Fe+4H_2O$
598	−16.7	+89.9
618	−18.5	+91.6
638	−21.5	+93.4

If the exothermic peak were due to the reduction of Fe_2O_3 to Fe_3O_4, the total/partial heat changes observed as a function of time should yield kinetic data which should be comparable with the kinetic data obtained from weight-loss measurements. From the analysis of the products by X-ray, it has been established that the Fe_3O_4 formation is complete before the formation of Fe and, corresponding to this change in the reduction process, there is a break in the kinetic plots (Fig. 2). To establish that the kinetic data obtained upto the break in Fig. 2 pertain to the reduction of Fe_2O_3 to Fe_3O_4, a comparison of these data with the kinetic data cbtained from DTA experiments had been made and the typical reduced plots obtained are shown in

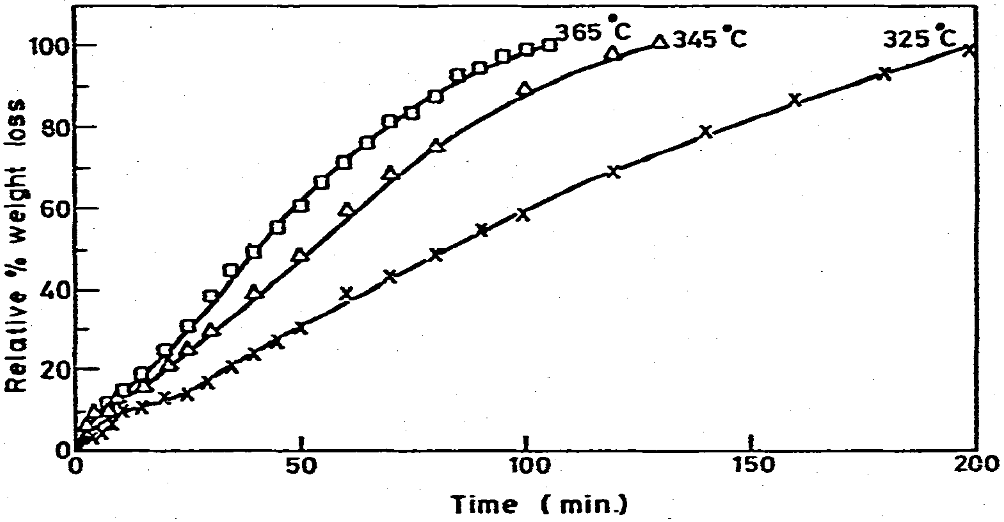
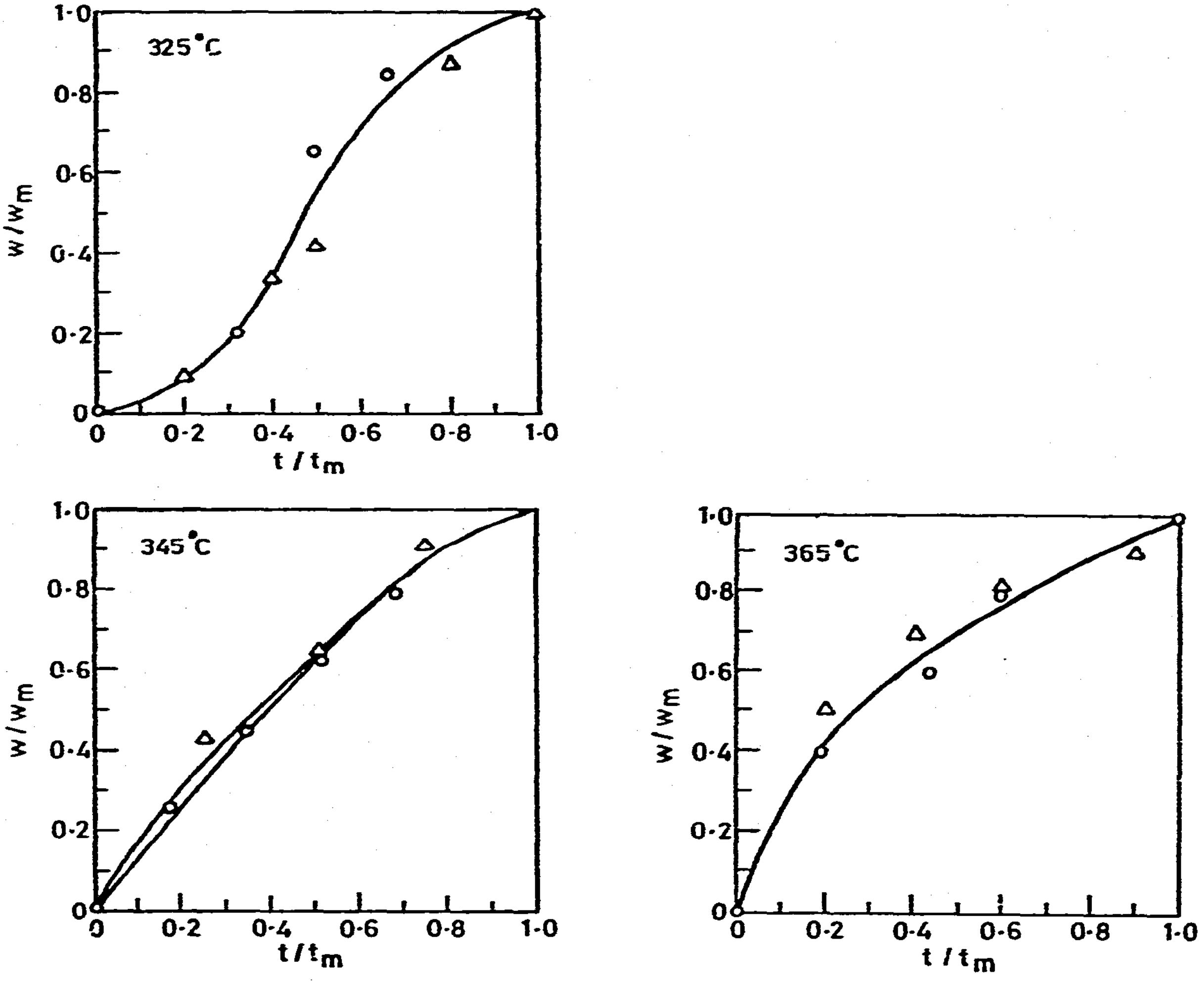


Fig. 2. The reduction kinetics of pure α-Fe_2O_3 at different temperatures in flowing hydrogen (280 ml min^{-1}).

Fig. 3, wherein the fraction reduced is plotted against the fractional time required for the reduction. It is seen that the kinetic data obtained from both methods can be represented by a single smooth curve.



(a–b) (c)

Fig. 3. Comparison of isothermal kinetic data with the data obtained from isothermal DTA at (a) 325°C; (b) 345°C; and (c) 365°C. O, points from regular kinetics; Δ, points from isothermal DTA.

The results of this study show that the isothermal DTA method can be used under favourable conditions for the evaluation of kinetics of reactions and confirm in particular that the reduction of iron oxide by hydrogen proceeds by a step-wise mechanism.

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