

## REDUCTION OF IRON ORE UNDER RISING TEMPERATURE AND FLUCTUATING TEMPERATURE CONDITIONS

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(Received 1 July 1986)

### ABSTRACT

Reduction of iron ore lumps by coal and carbon monoxide was investigated under a variety of temperature–time schedules. The rate law has been established using isothermal experiments in the range 800–1000°C. Non-isothermal experiments were carried out with constant and variable heating rates using large samples. Some additional experiments have been carried out under fluctuating temperature conditions. It is shown that non-isothermal kinetic data can easily be analysed to obtain values of kinetic parameters even when the rate of heating is not constant. The course of a reaction under any temperature–time schedule can be predicted provided the kinetic parameters are first evaluated through some test runs.

### INTRODUCTION

Non-isothermal kinetic studies are generally restricted to studies employing thermal analysers where the sample size is small and the temperature is made to increase at constant rates. The importance of studies under increase of temperature at variable rates or under fluctuating temperatures cannot be over emphasized. There can be two main aims of such studies. Firstly, kinetic data generated under arbitrary temperature variation conditions may be examined and analysed for evaluation of the kinetic parameters. Secondly, having evaluated these parameters through some test runs, one may try to predict the course of the reaction under different temperature–time schedules. Some previous publications [1,2] from this laboratory have been concerned with these problems.

In this paper, the theory has been applied to analyse rising temperature kinetic data on the reduction of iron ore by carbon and carbon monoxide to evaluate the kinetic parameters. The parameters so evaluated have been used in the prediction of values of the degree of reduction ( $\alpha$ ) as a function of

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time ( $t$ ) under fluctuating temperature conditions. The influence of particle size and ore/coal ratio on reduction rates has also been studied. A special experimental technique, called the moving bed technique, has been used to generate non-isothermal kinetic data under rising temperature conditions using large samples.

## THEORY

Numerous publications have reviewed from time to time the mathematical approaches that can be employed in the analysis of kinetic data obtained under temperature variations at a constant rate. As is well known, the basic equation of non-isothermal kinetic equation is derived by combining three equations.

(a) The differential form of the kinetic equation

$$d\alpha/dt = kf(\alpha) \quad (1)$$

where  $\alpha$  denotes the degree of reaction;  $t$ , the time and,  $k$ , the rate constant.  $f(\alpha)$  is an appropriate function which equals  $1/g'(\alpha)$  when the isothermal kinetic equation is given by

$$g(\alpha) = kt \quad (2)$$

(b) The Arrhenius type relationship

$$k = A \exp(-E/RT) \quad (3)$$

where  $A$  and  $E$  are kinetic parameters as defined and  $T$  is the temperature.  $R$  is the gas constant.

(c) The equation representing the variation of temperature with time

$$T = f_1(t) \quad (4)$$

where  $f_1(t)$  is an appropriate function. In the case of a constant heating rate ( $B$ ), eqn. (4) has the differential form

$$dT/dt = B \quad (5)$$

The basic kinetic equation for TG data obtained by thermal analysers is obtained by combining eqns. (1), (3) and (5) and then integrating. This subject has been thoroughly discussed in the literature. Here we are mainly concerned with situations where  $B$  is variable.

There is some literature on the derivation of the kinetic equation when temperature variation follows some specific non-linear equations, for example, those describing reciprocal temperature rise [3], exponential temperature rise [4], or some other non-linear types [5].

In real industrial situations, however, the temperature can vary in a rather complex manner and it may not be possible to write the kinetic equation in the integrated form. In such cases a simple differential approach should be

preferable. If during the temperature variation or fluctuation the reaction is assumed to be iso-kinetic and the kinetic parameters are assumed to retain fixed values, then it is possible to analyse or, alternatively, to predict the kinetic data.

From eqns., (1) and (3) we have

$$d\alpha/dt = A \exp(-E/RT)f(\alpha) \quad (6)$$

For general variation of temperature as given by eqn. (4)

$$dT/dt = f_1'(t) \quad (7)$$

Combining the preceding two equations

$$\left[ \frac{d\alpha/dt}{f(\alpha)} \right] = \left[ \frac{(d\alpha/dT)f_1'(t)}{f(\alpha)} \right] = A \exp(-E/RT) \quad (8)$$

Therefore a plot of either  $\ln \left[ \frac{d\alpha/dt}{f(\alpha)} \right]$  or  $\ln \left[ \left( \frac{d\alpha}{dT} \right) f_1'(t) / f(\alpha) \right]$  against reciprocal temperature should give a straight line. The kinetic parameters  $E$  and  $A$  should be obtainable from, respectively, the slope and the intercept.

#### *Prediction of $\alpha$ - $t$ plots*

To predict the course of a reaction for a known temperature-time schedule, one must first evaluate the kinetic parameters using some test runs where not only the temperature time history should be known but  $\alpha$  values must be determined at close time intervals experimentally. We have,

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = A \int_0^t \exp(-E/RT) dt \quad (9)$$

The right hand side (RHS) integral is obtained by first plotting  $\exp(-E/RT)$  values at instantaneous values of time and then by graphical integration of the area covered on the  $t$  axis using the procedure discussed. The result is multiplied by  $A$  to get the  $g(\alpha)$  value from which  $\alpha$  for the given  $t$  value is calculated. These treatments assume that the kinetic parameters remain unchanged during the entire period of reaction.

#### GRAPHICAL INTEGRATION: SIMPSON'S ONE-THIRD RULE

The graphical integration for calculation of the area covered by  $\exp(-E/RT)$  values on the time axis is conveniently carried out by Simpson's one-third rule which is now discussed.

Consider the variation of a quantity  $y$  as a function of the independent variable  $x$  and a plot of  $y$  between the limits  $x_0$  and  $x_{\max}$ . Let us divide the total  $x$  interval into  $n$  equidistant intervals of width  $h$  (i.e.,  $h = \Delta x$ ). The

limits are then,  $x_0$  and  $x_{0+nh}$ . According to Simpson's one-third rule [6] for even values of  $n$ .

$$\int_0^{x_{0+nh}} y dx = \frac{h}{3} [y_0 + 4(y_1 + y_3 + \dots + y_{n-1}) + 2(y_2 + y_4 + y_{n-2}) + y_n] \quad (10)$$

where  $y_0, y_1, y_2$  are values of  $y$  at  $x$  values of  $x_0, x_{0+h}, x_{0+2h}$  respectively. In the present case,  $y$  equals  $\exp(-E/RT)$  and  $x$  is time and, therefore, the desired area of the curve, which gives the value of  $g(\alpha)/A$ , is easily evaluated by splitting the time axis into  $n$  equal intervals, with  $n$  being an even number. The area multiplied by  $A$  gives  $g(\alpha)$  value from which  $\alpha$  is evaluated.

## EXPERIMENTAL

The analysis of ore and coal samples used in the present work is given in Table 1. These materials were all dried in an oven and kept stored in desiccators. The CO-N<sub>2</sub> mixture used in gaseous reduction was prepared by passing CO<sub>2</sub> over a heated coke bed at  $1000 \pm 10^\circ\text{C}$  at a flow rate of  $15 \text{ l min}^{-1}$ . The gas analysed approximately 30% CO and 70% N<sub>2</sub>.

Three experimental methods were used in reduction studies. These methods, in all of which the sample size was large (30–1360 g) are discussed briefly.

### (a) Standard reducibility set up

Figure 1 shows schematically the set up which was used for some

TABLE 1

Analysis of ore and coal used

Iron ore (chemical composition, %)		Non-coking coal (approximate analysis (%) at 60% RH and 40°C)	
Barajamda (Bihar, India)	Kiriburu (Orissa, India)	Raniganj (Bihar, India)	
Fe <sub>T</sub>	68.8	63.84	
Fe <sub>2</sub> O <sub>3</sub>	92.7	88.05	Moisture
FeO	5.07	3.64	Ash
SiO <sub>2</sub>	1.10	1.78	Volatile matter
Al <sub>2</sub> O <sub>3</sub>	—	2.14	Fixed carbon
CaO	0.81	0.24	
MgO	0.07	0.11	
LOI	0.60	4.01	
S	Traces	Traces	
P	0.023	0.03	

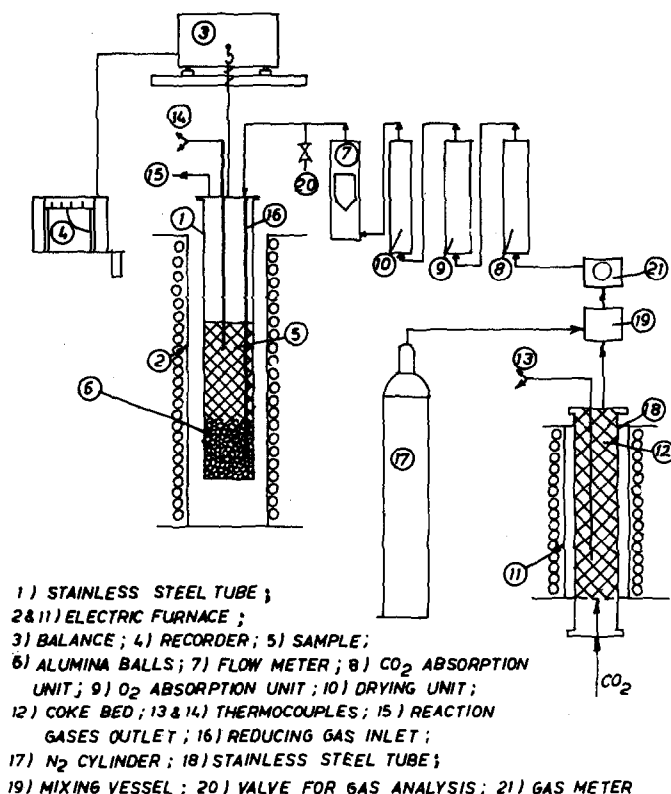


Fig. 1. Schematic diagram of the conventional reducibility determination set up.

reduction studies. The set up, described in detail elsewhere [7], is mainly for isothermal reduction of iron ore by CO-N<sub>2</sub> (30:70) mixture. However, it can also be used to study reduction by coal and to study non-isothermal reduction by gaseous and solid reductants by controlling the current input into the furnace to control the temperature.

For isothermal gaseous reduction, 500 g of ore sample in the size range (-12 + 10 mm) was heated first in a stream of nitrogen to the desired temperature and then the reducing gas was switched on at the rate of 15 l min<sup>-1</sup>. The loss of weight with time was measured at short intervals. For non-isothermal reduction the system was kept under flowing CO-N<sub>2</sub> mixture from the beginning and the temperature was raised through manual control of the variac. In either case the degree of reaction was obtained from the weight loss data which gave directly the weight of oxygen lost from the ore mass.

In the case of reduction of an ore-coal mixture, overall loss of weight is due to loss of both carbon and oxygen and these components cannot be delineated easily. However, the course of reaction may be expressed in terms

of a pseudokinetic parameter [8] termed as the fraction of reaction,  $f$ . This fraction is defined by the equation

$$f = \frac{\text{weight loss at time } t}{\text{maximum possible weight loss}} \quad (11)$$

In the present case the denominator in the RHS can be calculated from the total volatile matter and fixed carbon in the coal and the total oxygen in the ore mass. For 1 : 0.8 mixture of ore and coal this value comes to 265.23 g for a total sample weight of 500 g.

*(b) Muffle furnace arrangement*

Reduction by coal under isothermal and fluctuating temperature conditions were also carried out by using 30 g of ore-coal mixture in nickel crucibles (50 ml) and heating them in a muffle furnace ( $\pm 10^\circ\text{C}$ ) using different temperature time schedules. Several samples were introduced in the muffle furnace and these were removed one by one at predetermined intervals and immediately quenched. The reacted mass was then analysed, chemically, to determine the degree of reduction  $\alpha$  which is a true kinetic parameter. It should be noted that reaction kinetics expressed in terms of  $\alpha$  is theoretically sound. However, all treatments become approximate when the course of reaction is expressed in terms of  $f$ .

It has been shown previously [9] that the degree of reduction of partially reduced ore mass can be obtained from the total iron analysis if it is assumed that all loss of weight of the ore is due to removal of oxygen only. In the present case the ore samples used were all preheated to eliminate volatiles and, therefore, the reduced ore particles collected from the quenched sample were analysed for total iron only and  $\alpha$  values obtained on the basis of this analysis using the equation

$$\alpha = 100K \left[ \frac{\%Fe_T^r - \%Fe_T^0}{\%Fe_T^r \times \%Fe_T^0} \right] \quad (12)$$

where  $\%Fe_T^r$  = total iron analysis in the reduced mass;  $\%Fe_T^0$  = total iron analysis in the original mass;  $K$  = ratio of weight of iron to oxygen in the ore. This formula has been used successfully by Mookerjee et al. [10].

*(c) The moving bed technique (MBT)*

The special experimental set up, called the moving bed technique (MBT) was used to impose rising temperature conditions on relatively large volume elements of a reaction mixture. The principle of MBT has been discussed in detail elsewhere [4,11]. Figure 2 shows a schematic diagram of the set up.

The MBT set up employed a stainless steel cage containing ore-coal

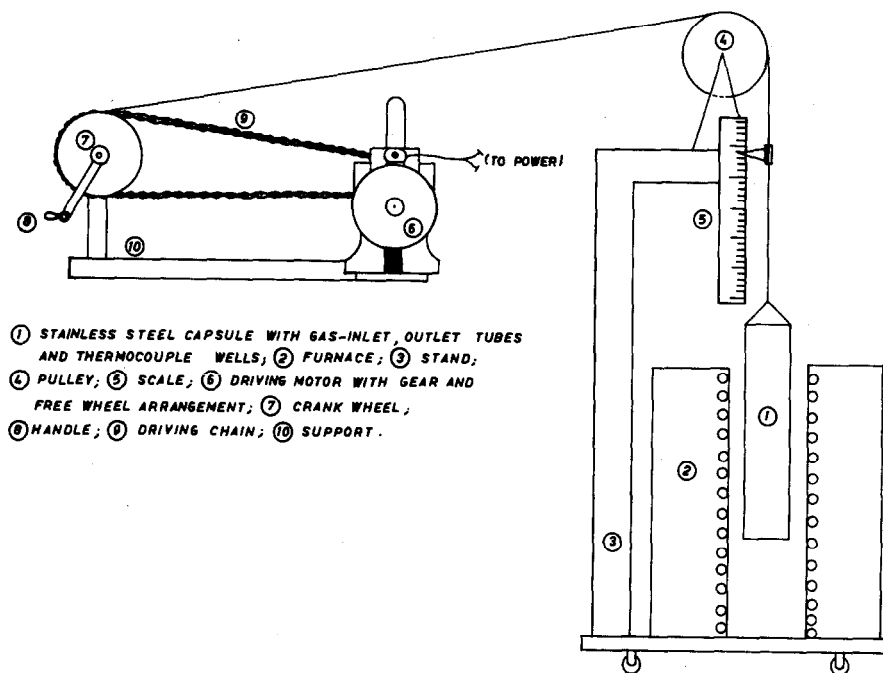


Fig. 2. Schematic diagram of the moving bed technique.

mixture. The cage itself was enclosed in a stainless steel capsule of 75 mm diameter and 360 mm length (Fig. 3). This capsule was lowered into the furnace hot zone at a fixed predetermined speed from an initial rest position when the bottom of the capsule rested just at the furnace mouth. The capsule was provided with outlets for volatiles and with thermocouple wells.

The movement of the capsule to the furnace interior simulated material flow and gradual exposure of a series of volume elements to the hot zone. When the capsule was fully inside the furnace, i.e., its top came to the same level as the furnace mouth, it was quickly withdrawn and then quenched by nitrogen gas. The reacted mass then showed the state of the system at different time intervals from a maximum near the leading edge to a time zero at the trailing edge. The distance of volume element from the capsule top represented the exposure time.

Any volume element entering the hot zone of the furnace gets heated up gradually and all successive volume elements get heated up in essentially the same manner because heat flux is mostly radial and not along the packed bed [11]. The analysis of samples from different locations, therefore, yields comprehensive non-isothermal kinetic data under the existing mode of heating. The actual variation of temperature with time was measured using thermocouples inserted in the reaction mass. The degree of reaction at various depths was obtained from the analysis of total iron in the samples

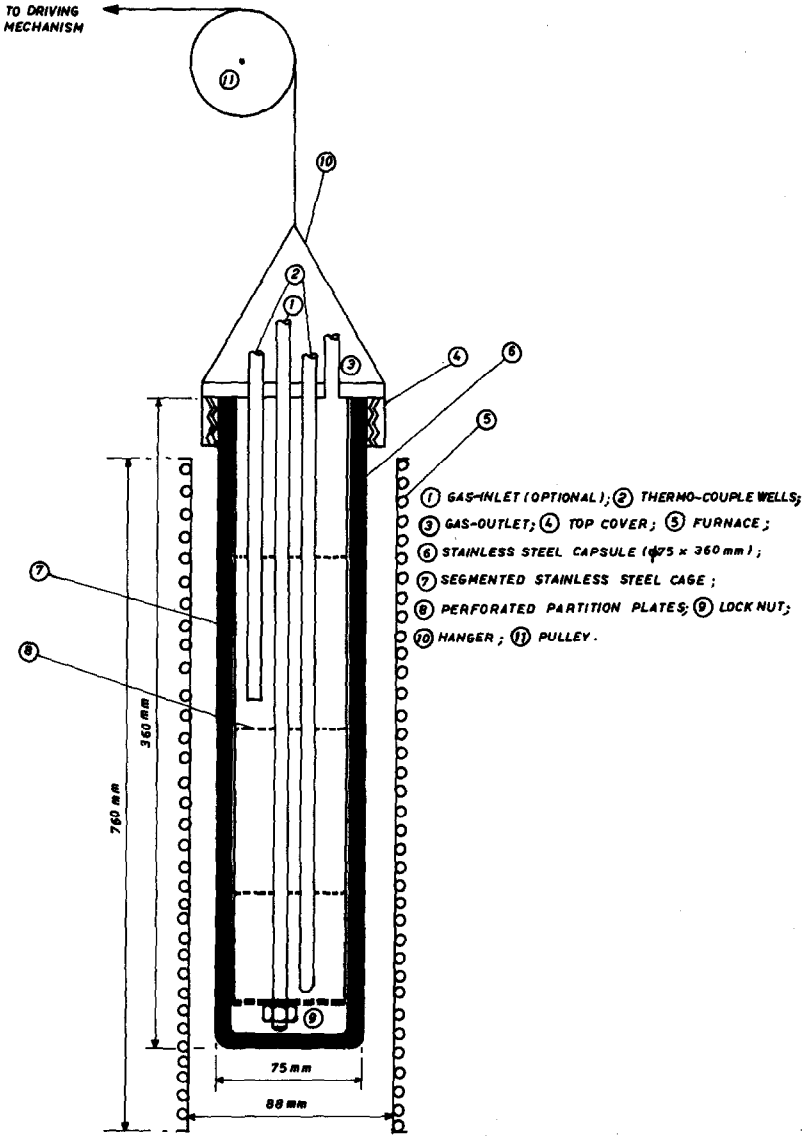


Fig. 3. Schematic diagram of stainless steel capsule.

collected using eqn.(12) mentioned earlier. Further details of MBT are available elsewhere [12].

RESULTS AND DISCUSSION

*Isothermal reducibility by coal*

Figure 4 shows some data on isothermal reduction of ore by coal at temperatures of 800, 900 and 1000°C ( $\pm 10^\circ\text{C}$ ) in the reducibility set up. It



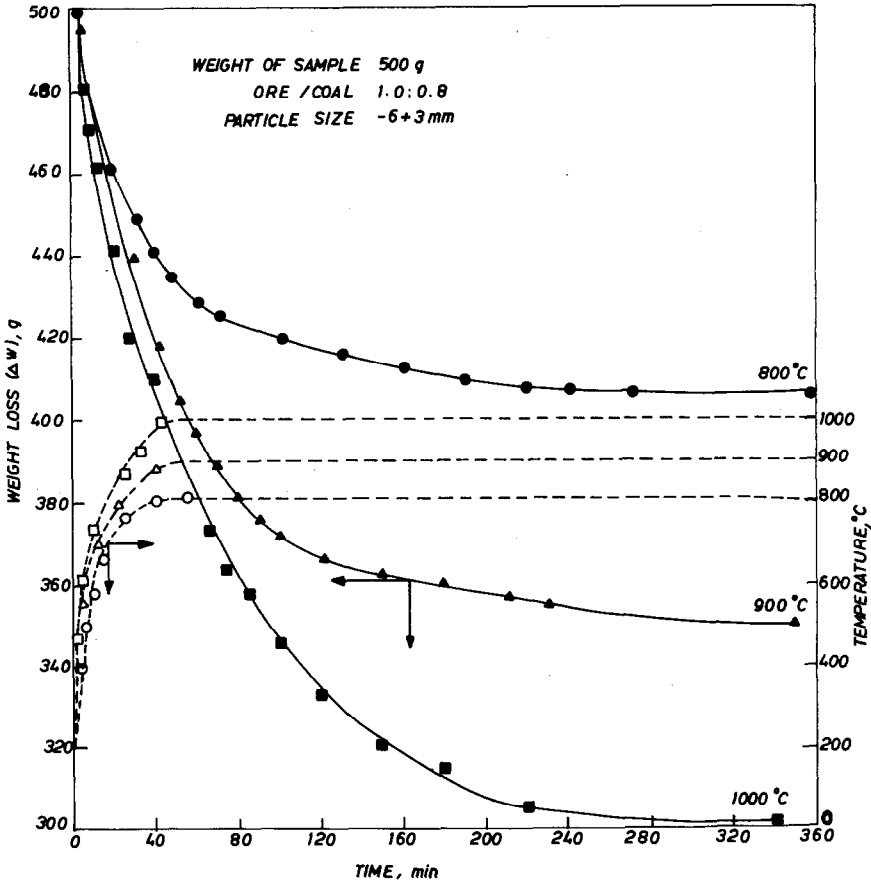


Fig. 4. Plots of temperature variation and weight loss with time during isothermal reduction of Barajamda iron ore by Raniganj non-coking coal.

shows plots of total weight loss with time and also the temperature variation. It is seen that the reaction mass took 30–40 min to attain the preset temperatures. Figure 5 shows the pseudo kinetic plots in terms of the fraction of reaction. While Fig. 5(a) shows a plot of  $f$  values against  $t$ , Fig. 5(b) shows that the values fit into the well known Ginstling–Brounshtein equation (GB equation). Figure 6 shows the different plots that have been used to evaluate the kinetic parameters from the data presented in Fig. 5. It is well known that a given set of kinetic data can often be fitted into more than one kinetic rate equation. To ensure that the model chosen is correct, the kinetic data should be evaluated by both integral and differential methods. Figure 6(a) shows the Arrhenius type plots based on the  $k$  values given by the GB plots (Fig. 5b). This is an integral approach. The kinetic parameters can also be evaluated by using the differential form of the kinetic law [13] which is given by eqn. (6).

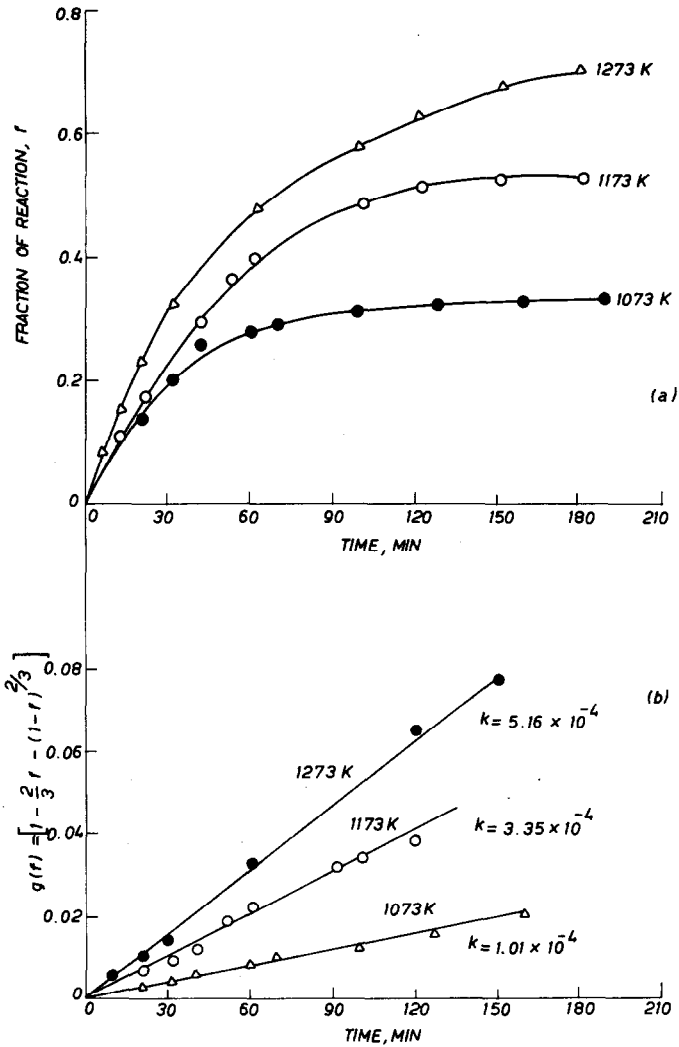


Fig. 5. Kinetic plots in terms of fraction of reaction for solid reduction for the data shown in Fig. 4.

For any fixed value of  $\alpha$  we have

$$\ln \left[ \frac{d\alpha}{dt} \right]_{\alpha} = \text{const} - E/RT \tag{13}$$

$$\text{and } \ln t_{\alpha} = \text{const} + E/RT \tag{14}$$

Where  $d\alpha/dt|_{\alpha}$  designates the slope of the  $\alpha - t$  plot at the given value of  $\alpha$  and  $t_{\alpha}$  the time at the given value of  $t$  for a given isothermal run.

Figures 6(b) and 6(c) show plots for three levels according to eqns. (13) and (14), respectively. Here,  $\alpha$  has been replaced by the pseudokinetic parameter  $f$ . The values of  $E$  obtained from the slopes of the linear plots are

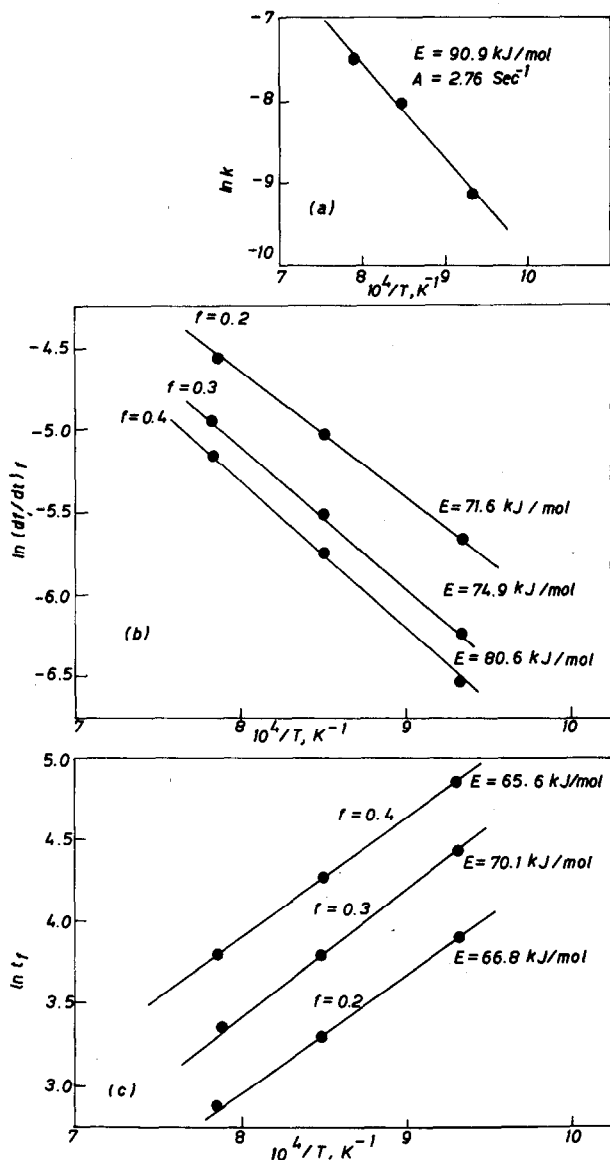


Fig. 6. Evaluation of kinetic parameters, using different approaches in the case of solid reduction for the data shown in Figs. 4 and 5.

all indicated in the figure. Since the  $E$  values obtained using integral and differential approaches are similar one may conclude that the GB equation is the correct rate equation. However, it should be remembered that the preceding analysis was made on the basis of fraction of reaction and, therefore, necessarily approximate.

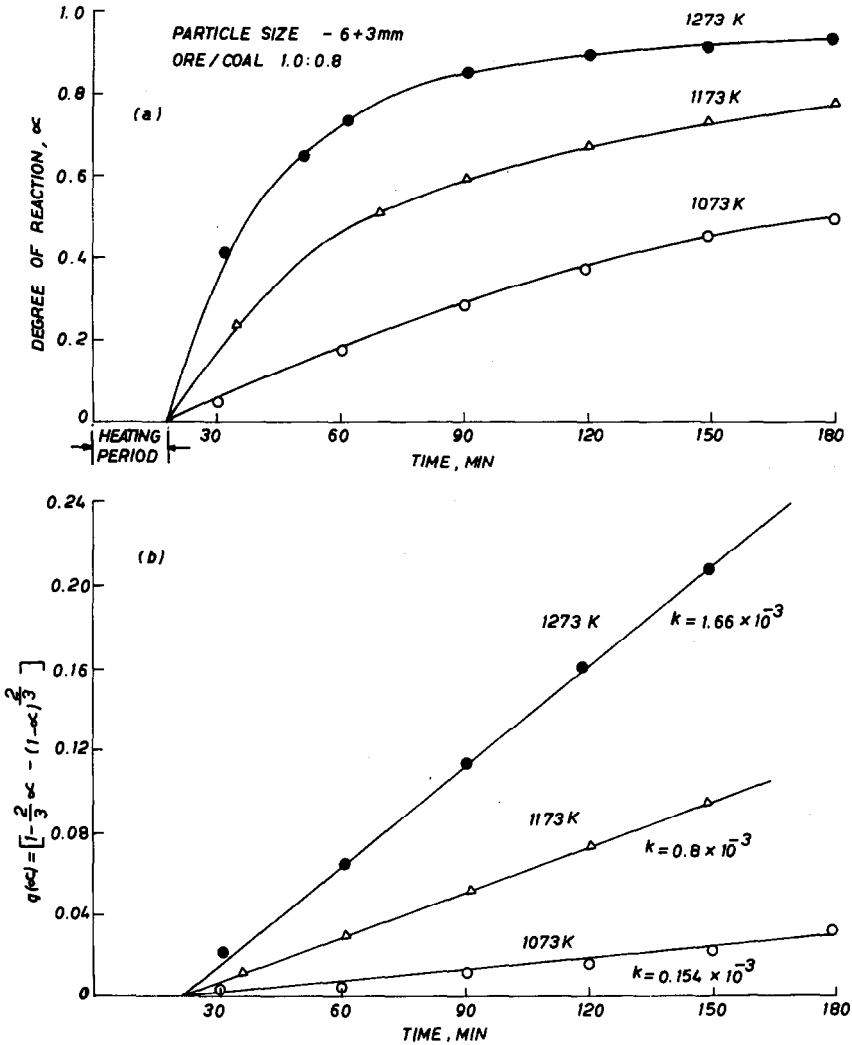


Fig. 7. Kinetic plots for the isothermal reduction of Barajamda iron ore by Raniganj non-coking coal in terms of degree of reaction.

Figure 7 presents some more data on the same system which may be considered more reliable. In these experiments, carried out with the crucible in a muffle furnace, the reacted mass was analysed for total iron at the end of each run to determine the degree of reduction,  $\alpha$ . Primarily kinetic data (Fig. 7a) which indicate a short heating period, fits the GB rate equation (Fig. 7b). The rate constants determined from the GB plots fit into an Arrhenius type plot (Fig. 8a) which gives a value of  $111.3 \text{ kJ mol}^{-1}$  for the apparent activation energy. The differential plots (Fig. 8b) give comparable

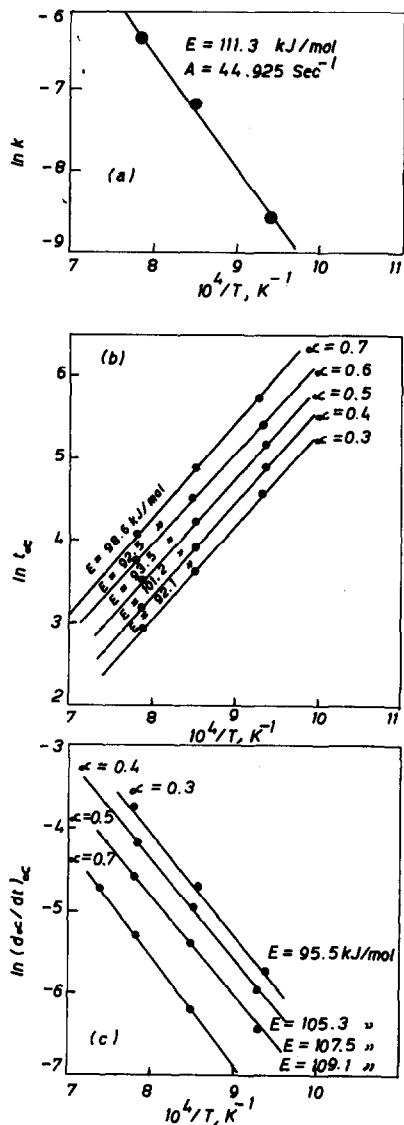


Fig. 8. Evaluation of kinetic parameters, using different approaches in the case of solid reduction for the data shown in Fig. 7.

values of  $E$ . We may conclude that, for coal reduction the GB rate equation is valid for which the form of  $f(\alpha)$  is given by

$$f(\alpha) = \frac{1}{g'(\alpha)} = \frac{3}{2} \left[ (1 - \alpha)^{-1/3} - 1 \right]^{-1} \quad (15)$$

*Isothermal reduction by carbon monoxide*

Some results of the isothermal reduction of Kiriburu iron ore by a CO-N<sub>2</sub> mixture carried out in the reducibility set up are plotted in Fig. 9. Figure 9(a) shows the primary  $\alpha-t$  plots which have been linearized in Fig. 9(b) using the GB equation.

Figure 10 shows three different sets of plots drawn for the evaluation of the kinetic parameters, while Fig. 10(a) shows the Arrhenius type plot and

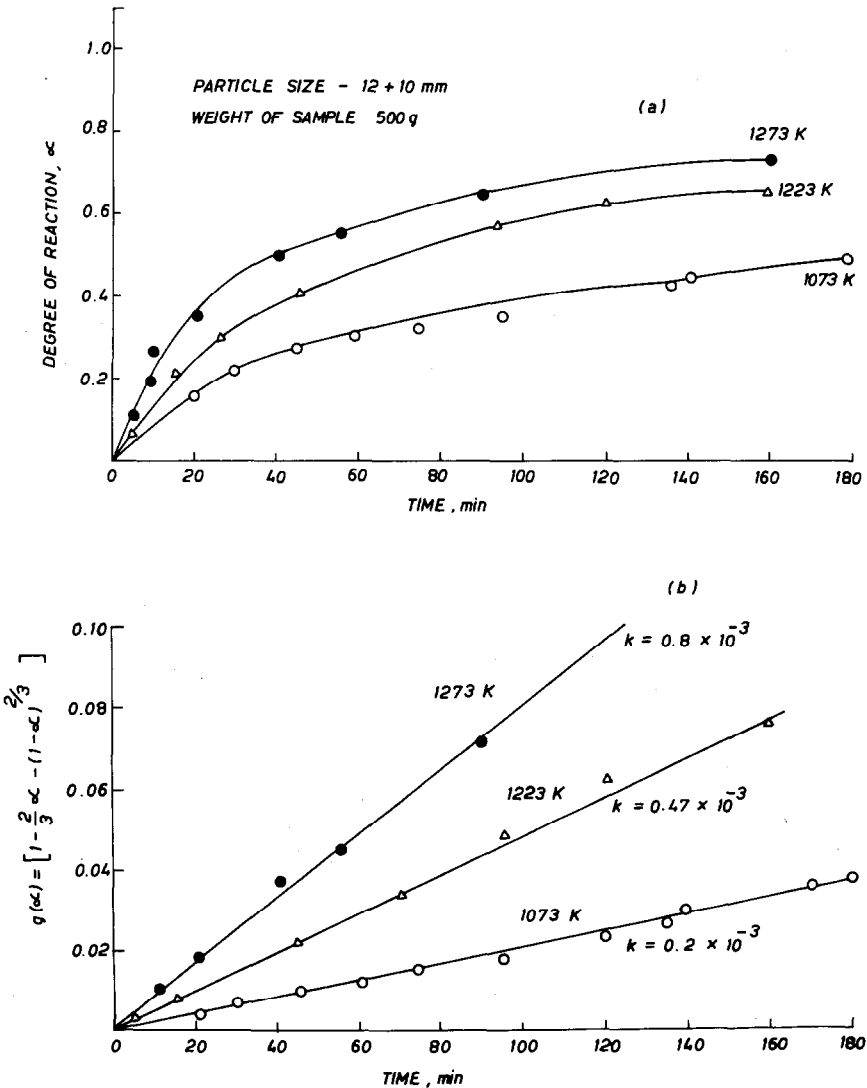


Fig. 9. Kinetic plots for the isothermal reduction of Kiriburu iron ore by reducing gas (CO-N<sub>2</sub> = 30:70).

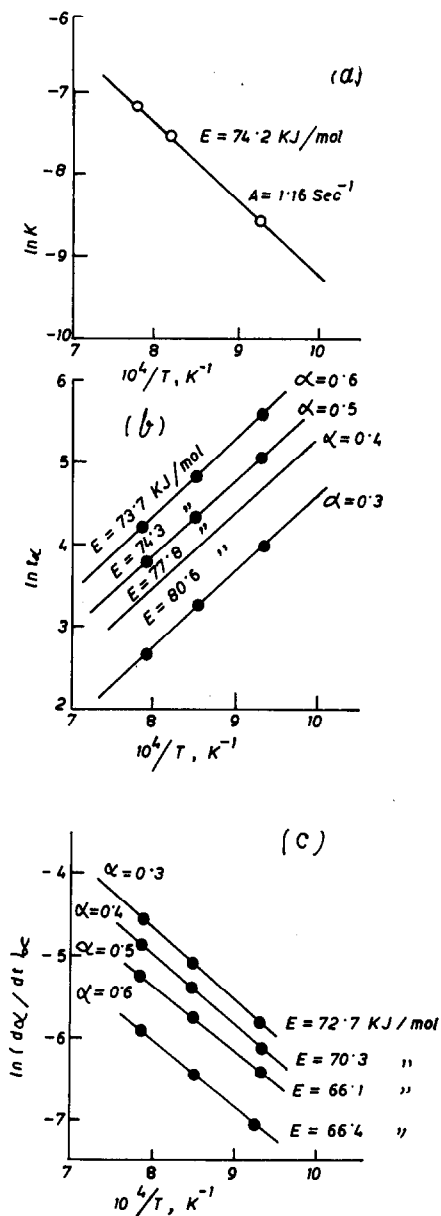


Fig. 10. Evaluation of kinetic parameters, using different approaches, for gaseous reduction for the data shown in Fig. 9.

Figs. 10(b) and 10(c) show the differential plots. The similarities of  $E$  values may be taken as a support of the GB rate equation used. It may be noted that the gaseous reduction is characterised by activation energy values which are somewhat lower than that for reduction by coal.

### Studies under rising temperature conditions

The bulk of the rising temperature reduction experiments were carried out using the moving bed technique (MBT), where the rate of heating is not constant. Figure 11 presents some data for a typical study to show how a volume element gets heated up as it moves into a given hot zone, i.e., furnace temperature profile. Heating data for two capsule speeds are given.

The temperature rise was recorded by having a thermocouple placed near the leading edge of the capsule. Obviously, a higher speed allows the given volume element to be exposed to higher furnace temperatures sooner and, therefore, its rate of heating is faster. The course of reaction in this volume element is governed by the heating schedule it undergoes as well as some other factors such as the ore/coal ratio, the particle size, etc.

It should be noted that during the downward movement of the capsule the temperature is not uniform across a section of the reaction mixture at a given level. A volume element near the periphery would obviously be at a higher temperature as compared to an element near the centre. Some experiments were, therefore, carried out by placing one thermocouple centrally and another near the periphery at the same level. Figure 12 shows the temperature data. To eliminate uncertainties regarding the rate of heating, all samples were collected from the centre of the reaction mixture in the capsule and the temperature variation was also measured by placing the thermocouple in this central region.

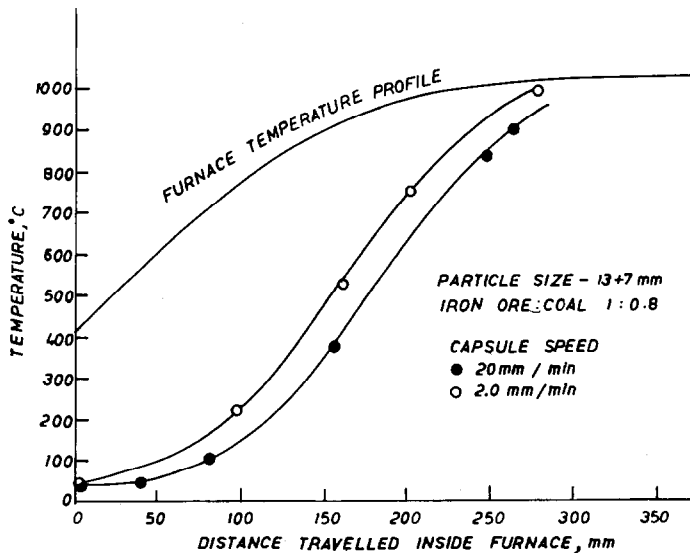


Fig. 11. Variation of temperature of a volume element with capsule speed during the moving bed experiment.



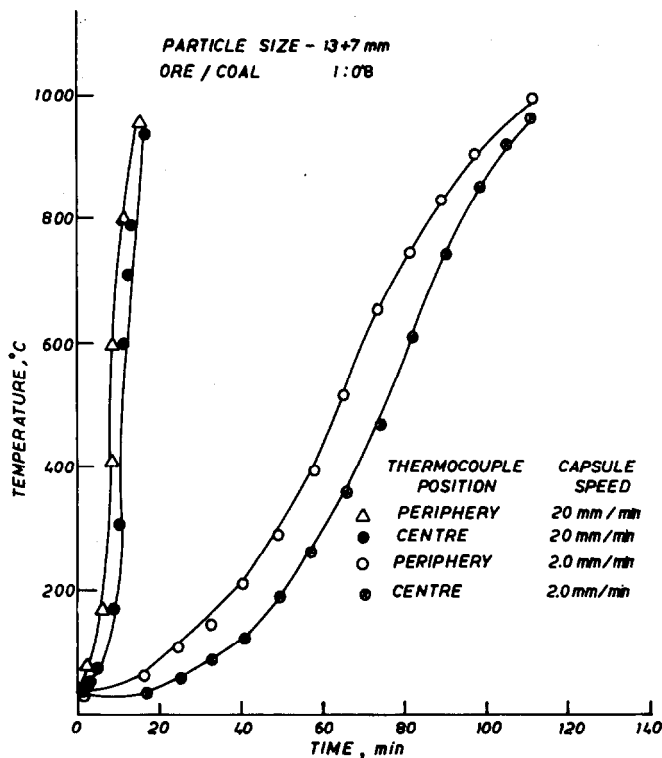


Fig. 12. Temperature lag between a volume element at the capsule centre and another near the capsule periphery during movement of the capsule into the furnace hot zone.

Ray and Kundu [13,14] have recently reported some thermogravimetric studies on the non-isothermal reduction of iron oxides by a reducing gas. They have shown that, under rising temperature conditions, the reduction takes place in distinct stages. However, these stages overlap when the system is suddenly exposed to high temperatures, in which case only an overall average value of the apparent activation energy can be determined. In the MBT the volume elements are exposed to higher temperatures suddenly and the initial heating is rapid. Therefore, one may not be able to detect the stage-wise reduction.

Figures 13 and 14 summarize some non-isothermal kinetic data generated by the MBT for three ore/coal mixtures in two size ranges. Each figure shows (top) the temperature variation and change of  $\alpha$  with time and (bottom) the plot in  $\ln[(d\alpha/dt)/f(\alpha)]$  against reciprocal temperature. For the latter plots the form of  $f(\alpha)$  has been taken from the results of the isothermal experiments, i.e., those given by eqn. (15). The plots are linear as predicted by eqn. (8). The apparent activation energy values, obtained from the slopes of the straight lines, are indicated in the figures.

It is found that in either figure the apparent activation energy is about

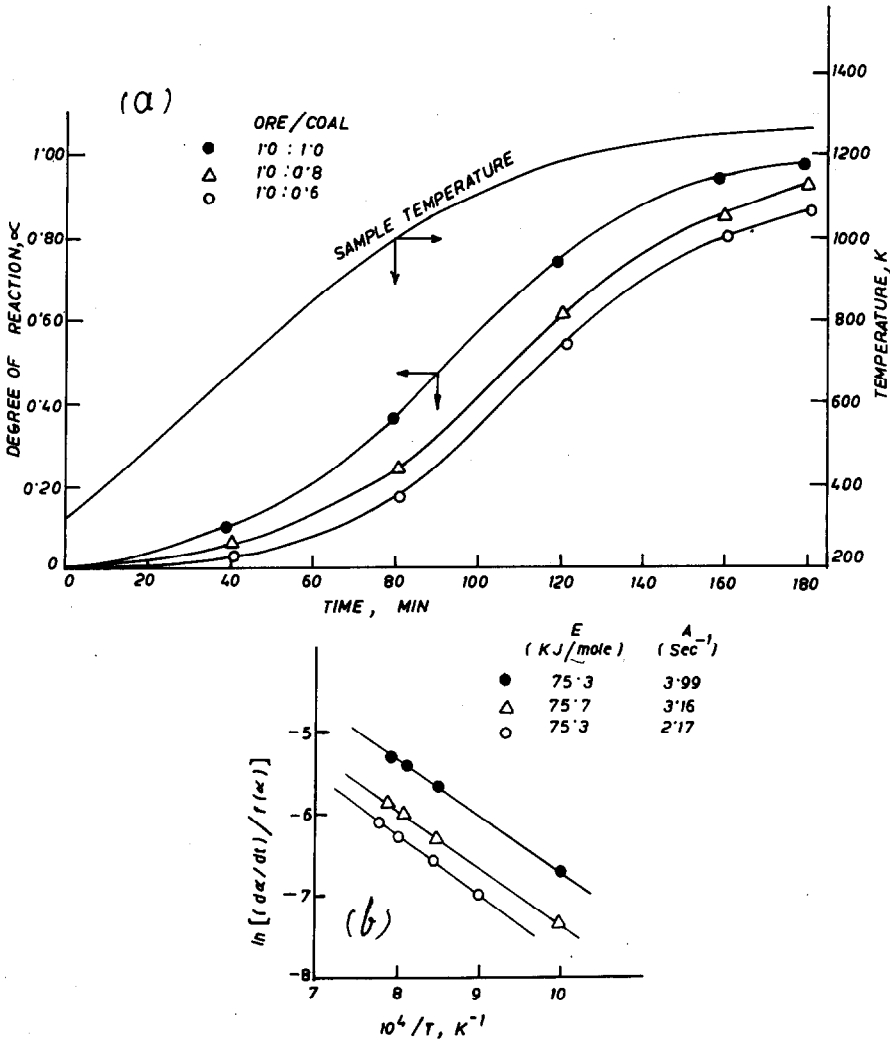


Fig. 13. Non-isothermal kinetic data for the reduction of Barajamda iron ore by Raniganj non-coking coal (particle size  $-3+1$  mm).

TABLE 2

$E$  and  $A$  values for different particle size and ore/coal ratios

Particle size (mm)	$-6+3$			$-3+1$		
	1:1	1:0.8	1:0.6	1:1	1:0.8	1:0.6
$E$ (kJ mol <sup>-1</sup> )	73.7	73.9	74.8	75.3	75.7	75.3
$A$ (s <sup>-1</sup> )	3.44	2.47	2.13	3.99	3.16	2.17

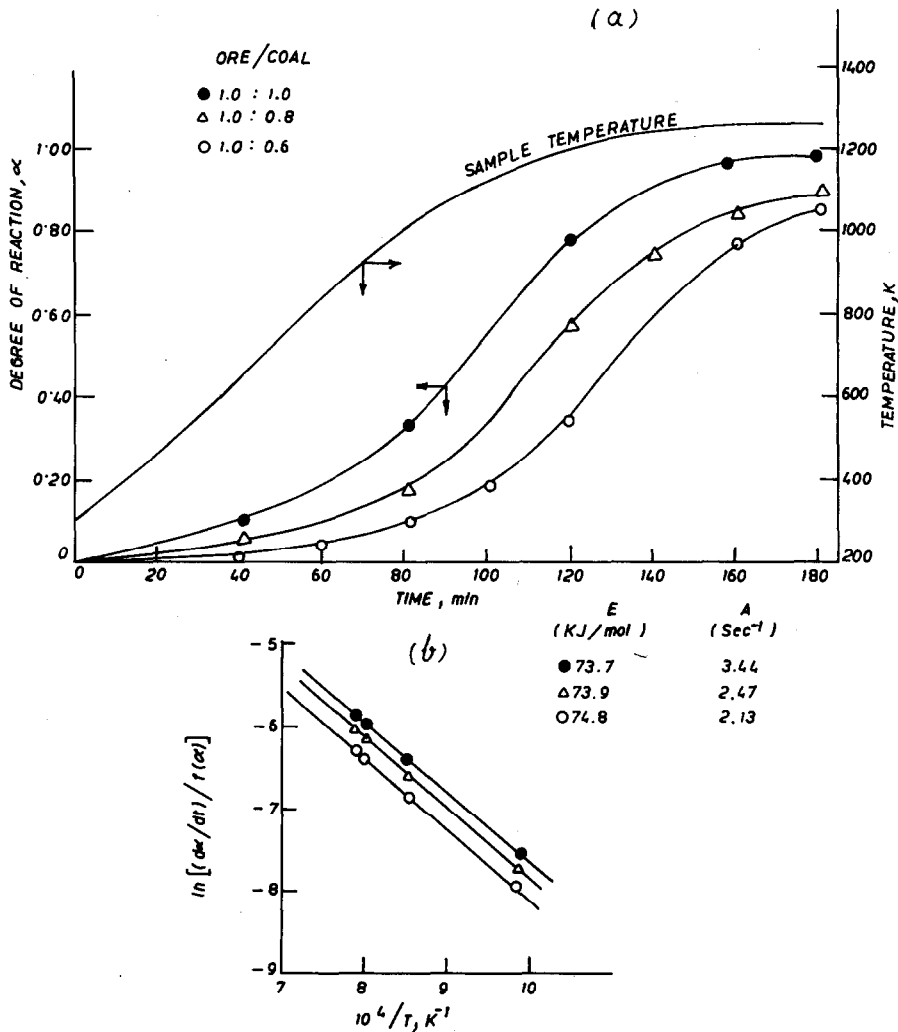


Fig. 14. Non-isothermal kinetic data for the reduction of Barajamda iron ore by Raniganj non-coking coal (particle size  $-6+3$  mm).

$75 \text{ kJ mol}^{-1}$  for all ore/coal ratios. The value is near the isothermal value given earlier. The  $E$  and  $A$  values are given in Table 2.

Assuming that kinetic parameters, as determined by the MBT, are operative during the non-isothermal conditions in general and that the form of  $f(\alpha)$  is as established by the isothermal experiments, one can predict the course of reduction reactions under fluctuating temperatures.

#### Prediction of $\alpha$ - $t$ plots

Figure 15 shows some data obtained in a special experiment where the temperature of three reaction mixtures containing Barajamda ore and

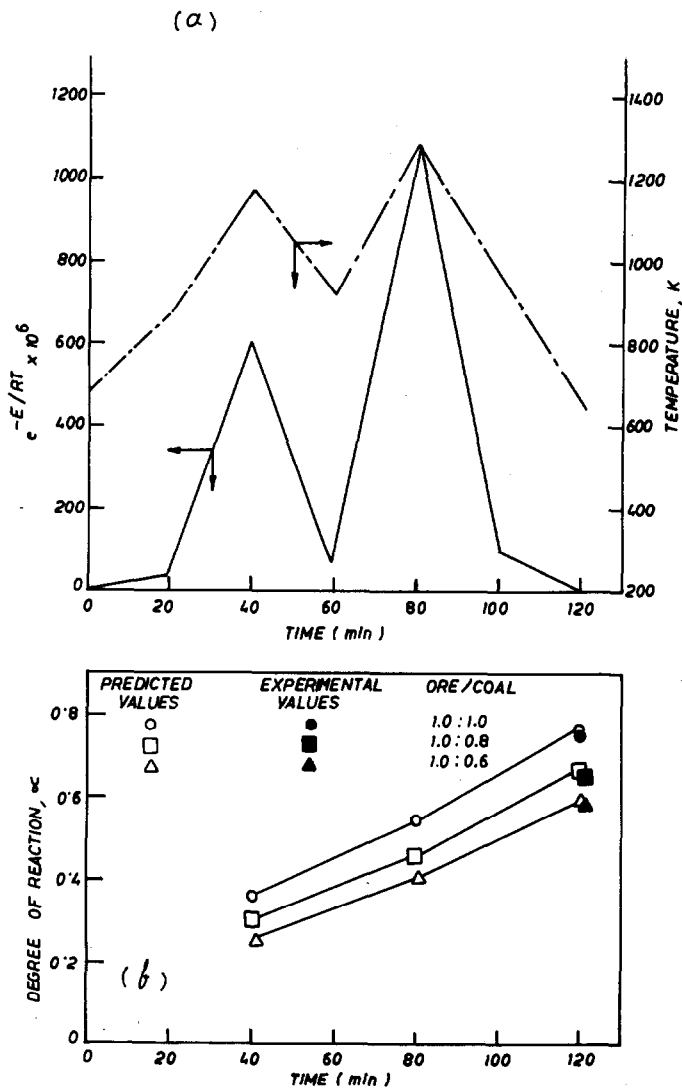


Fig. 15. Experimental and predicted values for the reduction of Barajamda ore by Raniganj coal under fluctuating temperatures.

Raniganj non-coking coal were varied in the manner shown in the figure. The total mass of each sample was 30 g and they were kept in a muffle furnace whose temperature was manipulated. Figure 15(a) shows the  $T$  vs.  $t$  plot as well as the plot of  $\exp(-E/RT)$  values against time. The area covered by the latter has been graphically integrated using time intervals shown. Figure 15(b) shows the theoretical  $\alpha$  vs.  $t$  plots obtained by using values of kinetic parameters as shown. It also shows the  $\alpha$  values determined

experimentally at the end of each run. The agreement between the theoretical and experimental values is very close.

Some experiments were also carried out to predict the course of gaseous reduction under fluctuating temperatures. We have already presented some data on isothermal reduction which were used to establish the rate equation.

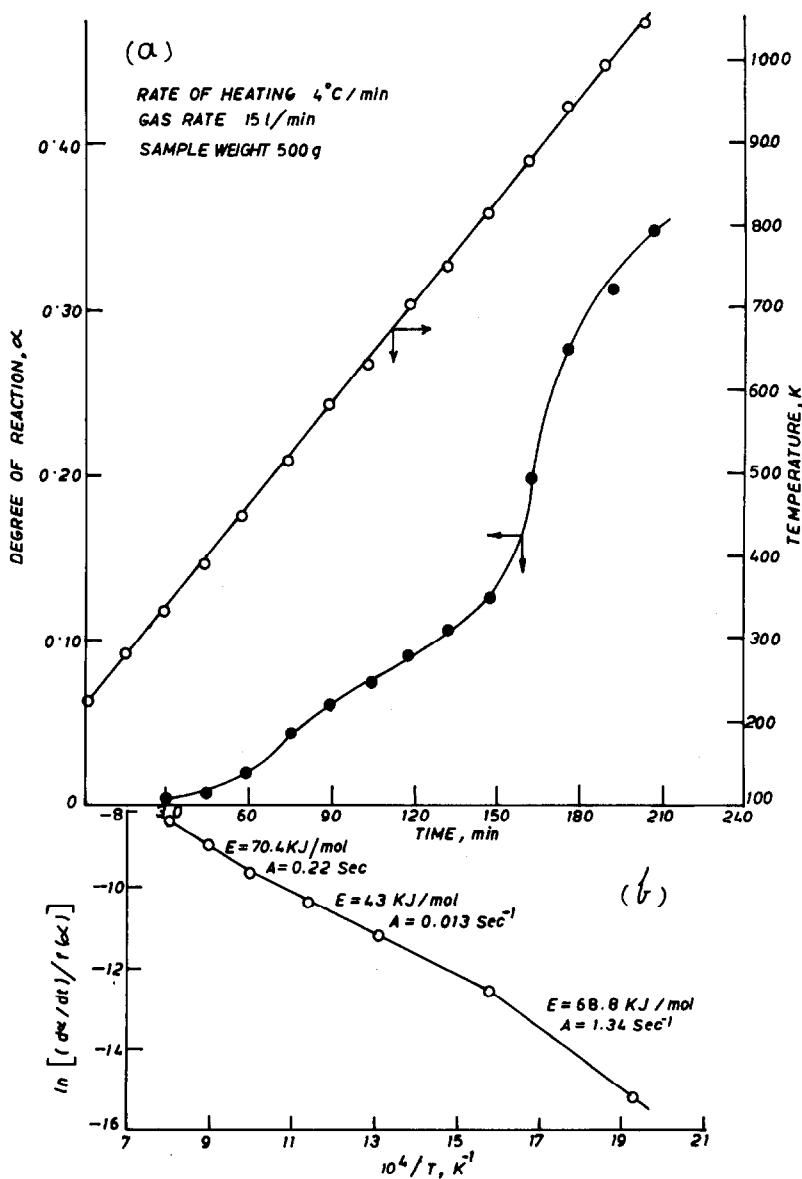


Fig. 16. Gaseous reduction of Kiriburu iron ore by  $\text{CO-N}_2$  (30:70) under rising temperature condition (particle size  $-12+10\text{ mm}$ ).

It is, however, not advisable to use the isothermal kinetic parameters in the predictions for non-isothermal conditions. Therefore, some test runs were carried out to evaluate the kinetic parameters for non-isothermal conditions. Figure 16(a) presents the results of some experiments in the reducibility set up where Kiriburu iron ore was reduced by a flowing CO-N<sub>2</sub> mixture while the temperature was raised linearly as shown.

The  $\alpha$  vs.  $t$  plot as determined from the weight loss data (also shown in the figure) shows stagewise reduction. Figure 16(b) shows the plot of  $\ln[(d\alpha/dt)/f(\alpha)]$  against reciprocal temperature. This plot also shows vari-

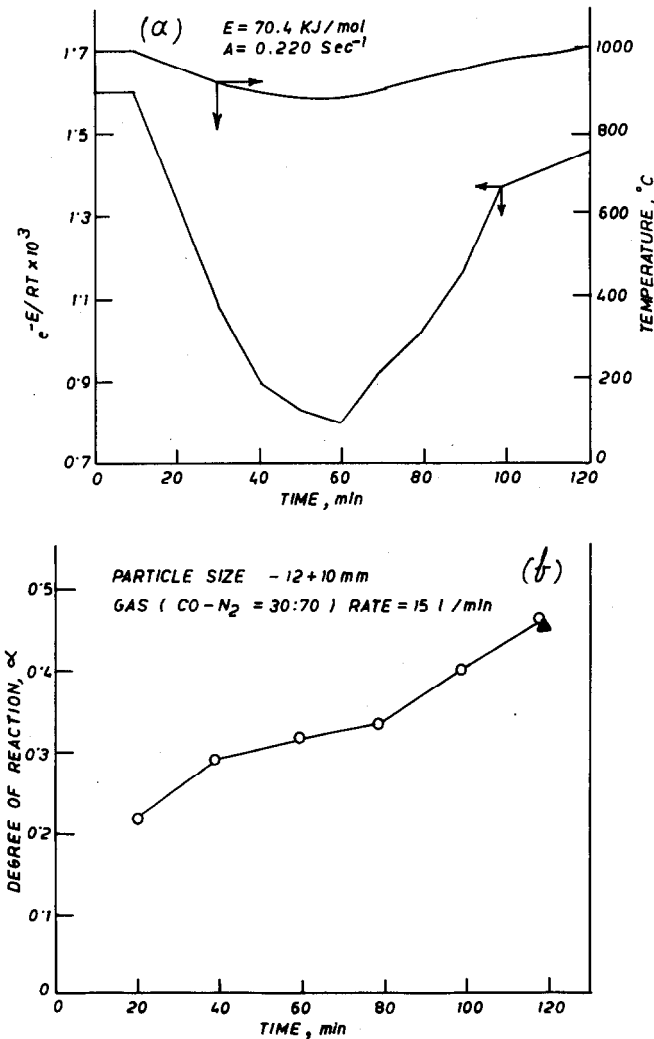


Fig. 17. Experimental and predicted values for gaseous reduction of Kiriburu iron ore under fluctuating temperatures.

ations in the values of the kinetic parameters with change of temperature; for prediction only the values for the final stages are to be used.

Figure 17(a) shows how the temperature of the sample was varied in the reducibility set up. It also shows the plot of  $\exp(-E/RT)$  values against time. The area thus enclosed gives the value of  $g(\alpha)$  when it is multiplied by the value of  $A$ . The final experimental  $\alpha$  value is compared in the light of the theoretically predicted  $\alpha$  vs.  $t$  plot in Fig. 17(b); again the agreement is very good.

## CONCLUSIONS

Isothermal reduction experiments show that reduction of ore particles by both coal and a CO-N<sub>2</sub> mixture follow the Ginstling-Brounshtein rate equation. Kinetic parameters can be evaluated from  $\alpha$  vs.  $t$  plots generated under known temperature time programs, both linear and non-linear. If these parameters are first evaluated through some test runs carried out under non-isothermal conditions then one can predict the complete  $\alpha$  vs.  $t$  plots for any arbitrary temperature time schedule provided this schedule is known accurately.

## ACKNOWLEDGEMENTS

The authors are grateful to Professor S. Banerjee, Director, National Metallurgical Laboratory for providing facilities for the experimental work. They also wish to thank Mr. K.N. Gupta, Scientist 'F' for helpful suggestions and discussions.

## REFERENCES

- 1 H.S. Ray and S. Chakraborty, *Thermochim. Acta*, 101 (1986) 131.
- 2 H.S. Ray, S. Chakraborty and S. Prakash, Proc. Fifth National Symposium on Thermal Analysis, Indian Institute of Technology, Kharagpur, India, December 1985, 2.1.
- 3 S.K. Dixit and H.S. Ray, *Thermochim. Acta*, 54 (1982) 245.
- 4 H.S. Ray and D.P. Duttachaudhary, *Thermochim. Acta*, 101 (1986) 119.
- 5 J. Blazejowski, *Thermochim. Acta*, 76 (1984) 359.
- 6 A.C. Bajpai, J.M. Calus and J.A. Fairley, *Numerical Methods for Engineers and Scientists*, Wiley, New York, 1978, p. 258.
- 7 V.A. Altekar, Proc. Symposium on Direct Reduction Process in Iron and Steel-making, 36th ATM and 20th NMD Celebrations, Rourkela, India, Nov. 1982, p. 177.
- 8 S. Mookherjee, H.S. Ray and A. Mukherjee, *Thermochim. Acta*, 95 (1985) 247, 257.
- 9 A.M. Chernyshev, N.K. Karnilova and Yu.V. Tarasenko, *Steel U.S.S.R.*, 7(3) (1977) 133.
- 10 S. Mookherjee, A. Mukherjee, B.K. Dhindaw and H.S. Ray, *Trans. ISI, Jpn.*, 26 (1986) 101, 119.

- 11 S. Prakash, H.S. Ray and K.N. Gupta, *Iron-making Steel-making*, 13(2) (1986) 76.
- 12 H.S. Ray and P.A. Sewell, *Proc. Int. Conf. on Advances in Chemical Metallurgy (ICMS-79)*, Bhabha Atomic Research Centre, Bombay, India, Vol. II, 1979, 43/I/1.
- 13 H.S. Ray and N. Kundu, *Thermochim. Acta*, 101 (1986) 247.
- 14 N. Kundu, *Isothermal and Non-isothermal Kinetic Studies on the Initial Stages of Iron Ore Reduction*, M. Tech. Thesis, Indian Institute of Technology, Kharagpur, India, 1984.