

# Kinetics of Aluminothermic Reduction of $\text{MnO}_2$ and $\text{Fe}_2\text{O}_3$ : A Thermoanalytical Investigation

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This paper presents the main kinetic parameters for aluminothermic reduction of  $\text{MnO}_2$  and  $\text{Fe}_2\text{O}_3$ . Aluminothermic reduction which in fact is a redox reaction requires an initial input of heat which is obtained through external reaction and/or oxidation of aluminium. In a system where oxidation as well as reduction take place simultaneously it is difficult to predict the kinetics of either reduction or oxidation. The present work aims at to describe the kinetics of reduction of  $\text{MnO}_2$  and  $\text{Fe}_2\text{O}_3$  during aluminothermic reductions using simultaneous DTA/TG technique. If one understand the aluminium oxidation reaction then kinetics for the reduction of  $\text{MnO}_2$  and  $\text{Fe}_2\text{O}_3$  can be obtained from DTA data for the overall reaction.

Using suitable calibration constant a theoretical DTA curve is generated from the TG data to describe oxidation of aluminium. The oxidation data were deducted from the overall DTA data on redox reaction to obtain data on reduction only. The rate of generation of peak area for  $\text{MnO}_2$  and  $\text{Fe}_2\text{O}_3$  thus obtained was a measure of reduction reaction rate.

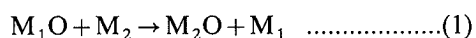
KEY WORDS: kinetics; reduction; aluminothermic; manganese dioxide; ferric oxide.

## 1. Introduction

Heat of reaction of a chemical process is very much important for the related industries. In a metallurgical process particularly not only the heat of reaction but also kinetics of reaction plays a decisive role. As is well known that carbothermic process is one of the most economical and widely used extraction process for ferroalloys. However a reductant carbon has some limitations. (1) high affinity of carbon for many metals such as Co, V, Ti, Cr, Fe and Mn results in the formation of their carbides, (2) inability to reduce many metal oxides at usual operable temperatures. The growing demand for carbon free metals/alloys not obtainable by carbon reduction has resulted in considerable interest in metallothermic reduction of various oxides, sulphides and halides to produce metals and alloys.

In the production of ferroalloys and some common nonferrous metals, metallothermic reduction involves, the reaction between oxides or sulphides of the metal to be reduced and the reducing metals.

The metallothermic reduction of sulphides or oxides is based on the difference in the standard free energy change ( $\Delta G^\circ$ ) of formation of metal oxides/sulphides. The metallothermic reduction which is in general a replacement type can be represented as



Therefore, a careful selection of reducing metal is very

much essential. On the basis of standard free energy of formation reducing metals are so chosen that  $\Delta G^\circ$  value of their oxides or sulphides should be more negative than for the oxides/sulphides to be reduced. The metallothermic reduction is characterised by highly exothermic nature of the reaction involved. Heat evolved in metallothermic reduction should be adequate to form liquid products in order to facilitate the better slag and metal separation. In some cases the reduction of metal oxide generates massive heats such as in the reduction of  $\text{MoO}_2$ ,  $\text{MoO}_3$ ,  $\text{MnO}_2$ ,  $\text{Fe}_2\text{O}_3$  and  $\text{V}_2\text{O}_5$  with aluminium results in the release of 4002.6, 4662, 4863.6, 3649.8 and 4548.6 k·J/kg of reactants/products.<sup>1)</sup> This heat is much excess over the required (2310–2730 k·J/kg) for the proper control of the reaction. Therefore, in such case either these oxides are reduced/roasted to lower oxides or some scrap iron (for ferroalloys) or some metal (for metals) is added as coolant to control the reaction temperature within a safety limit. This is the reason why as in the present investigation simultaneous DTA–TG technique has been used which is in fact is not an adiabatic system and heat dissipation characteristic can not be predicted from theory. It is therefore impossible to predict the ultimate temperature attainable by aluminothermic mixture in a DTA–TG set up.

The problems arising out of using carbon as a reductant can be overcome by using aluminium as a reductant. On the other hand aluminium being a costly reducer it is very much important to know the optimum aluminium

requirement for maximum recovery of alloys.

Of the thermal methods, both differential thermal analysis (DTA) and thermogravimetry (TG) have long been accepted as useful technique for studying the kinetics of solid state thermal reaction. In the present investigation, for kinetics studies thermite mixture of  $\text{MnO}_2$ :Al (1:5 molar) and  $\text{Fe}_2\text{O}_3$ :Al (1:8 molar) were subjected to different heating rates 5, 7, 10 and 15 K/min respectively. Suitable composition of  $\text{MnO}_2$ :Al and  $\text{Fe}_2\text{O}_3$ :Al were selected on the basis of several trial runs. The detailed for the first system  $\text{MnO}_2$ -Al is explained elsewhere.<sup>2)</sup>

For calorimetric measurements in metallurgical system use of DTA is rare, however, in our previous works DTA has been successfully used to determine heats of aluminothermic reduction of several transition metal oxides,<sup>3-5)</sup> heats of decomposition of carbonate materials<sup>6)</sup> and heats of solidification of eutectic alloys.<sup>7)</sup>

The idea of relating DTA peak area to the amount of heat evolved or absorbed during a reaction led to many attempts for using DTA for quantitative heat measurements. Since peak area is preferred as satisfactory criterion for quantitative heat measurement, the rate of generation of peak area can be used in predicting the rate of reduction of oxides provided reliable calibration plots are available.

The present work reports a simultaneous DTA/TG study on the determination of reduction kinetic parameters of  $\text{MnO}_2$  and  $\text{Fe}_2\text{O}_3$ . As aluminothermic reactions are complex process where oxidation and reduction reaction takes place simultaneously, it is very difficult to predict the reduction kinetic alone. However, attempts have been made in the present investigation to predict reduction kinetics of aluminothermic reduction of  $\text{MnO}_2$  and  $\text{Fe}_2\text{O}_3$  using DTA data.

For a differential thermal analysis system where the specimen holders are separated by a low thermal conducting medium such as nitrogen, air *etc.* and the thermocouples are located outside, the peak area is directly proportional to the amount of heat evolved or absorbed in the medium and the properties of the reacting sample do not effect the peak area. Mathematically,<sup>8)</sup>

$$\text{Area} = k_1 \cdot \Delta H \quad \dots\dots\dots(2)$$

where  $k_1$  is an instrument constant obtained from calibration.

About the selection of the reaction mixture, here authors were interested to say that for a temperature of 1673 K, on the basis of thermodynamic calculation of ratio of 1:13.56 for  $\text{Fe}_2\text{O}_3$ :Al and 1:10.34 for  $\text{MnO}_2$ :Al is to be maintained. However, after several trial runs it was found that the reaction necessarily required aluminium in excess was used in keeping the reaction temperature of reaction mixture within a safety limit.

## 2. Experimental

For present investigation a Shimadzu DT-40 thermal analyser consisting of simultaneous DTA-TG modular unit was used. Instrument was calibrated using reagent grade chemical compounds supplied by E. Merck, Ger-

many. Alumina crucibles and  $\alpha$ -alumina supplied by Shimadzu Corporation Japan were used as the specimen holders and reference material respectively. Detail experimental procedure and calibration of DTA are available elsewhere.<sup>8)</sup>

DTA peak areas were determined by cutting the chart paper showing the reaction and weighing it. The area of DTA peak was delineated using the well accepted tangent intercept method recommended by Cunningham and Willbrun<sup>9)</sup> and discussed by Ray and Willburn.<sup>7)</sup> Weight of the chart paper was proportional to the area and hence this was a convenient approach. According to Eq. (2) the apparatus constant  $k$  was given by  $k = \text{Area}/\Delta H$ . The calibration constant  $k_1$  for the range 528-1445 K is given by equation

$$k_1 = A_1 + B_1 T \quad \dots\dots\dots(3)$$

Where  $A_1$  and  $B_1$  are constants with values 4580.0 and -2.4 respectively.  $T$  is in degree Kelvin.

### 2.1. Aluminothermic Reduction

Manganese dioxide, Ferric oxide and aluminium powder were used to prepare thermit mixture of different molar ratios. Preliminary experiments showed that reduction reactions were incomplete in the case of stoichiometric mixture. Therefore, suitable composition for the above two systems  $\text{MnO}_2$ -Al and  $\text{Fe}_2\text{O}_3$ -Al were selected on the basis of some preliminary trial runs. This has been discussed in our previous communication.<sup>2)</sup> It has been found that no reaction took place in argon atmosphere. All experiments were therefore, carried out in static air. It appears that the aluminothermic reduction is triggered in the DTA-TG set up by exothermic heat being made available by oxidation of excess aluminium, which necessarily requires oxygen gas.

## 3. Results and Discussion

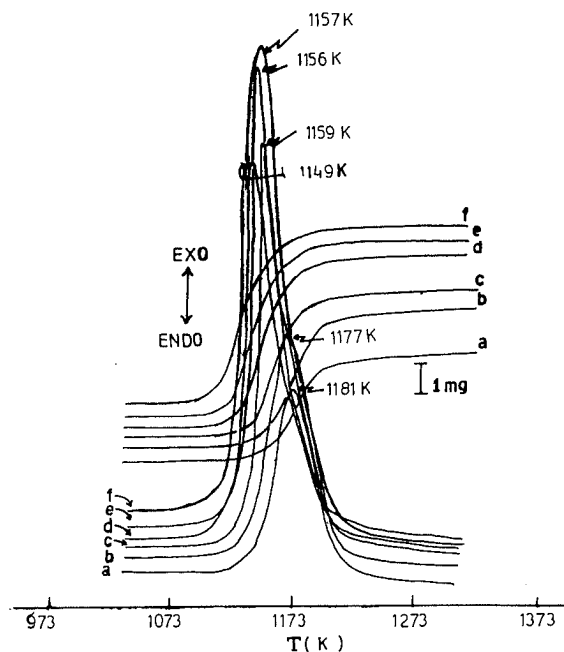
Previously in the text it has been mentioned that thermit mixtures for the two systems  $\text{MnO}_2$ -Al and  $\text{Fe}_2\text{O}_3$ -Al contained excess aluminium. A certain minimum excess is required for the completion of the reduction. A large number of simultaneous DTA-TG runs were carried out in the mixture powder of  $\text{MnO}_2$ ,  $\text{Fe}_2\text{O}_3$  and aluminium with different molar ratios. In every case the following three contributing factors combinedly reflected as a single exothermic DTA peak. However, melting of aluminum shows up as a pre-reaction exothermic dip well below the exothermic peak and thus heat of melting of aluminium does not come in to picture during heat calculation.

- 1) Heat of aluminothermic reduction (exothermic with no mass gain),
- 2) Heat of oxidation of some of the excess aluminium (exothermic with mass gain), and
- 3) Dissolution of metal produced in excess aluminium and formation of intermetallic compounds (exothermic with no mass gain).

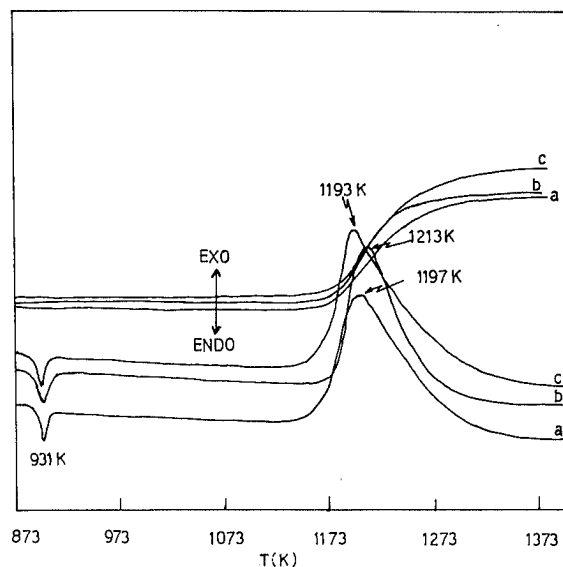
From the heat calculation using simultaneous DTA/TG technique it has been found that reaction is complete when the molar ratio was 1:5 in the case of  $\text{MnO}_2$ :Al and 1:8 in the case of  $\text{Fe}_2\text{O}_3$ :Al. The particle size of

the reaction mixture in case of both the systems were -250 mesh. **Figures 1** and **2** show simultaneous DTA-TG plots for reaction in  $\text{Fe}_2\text{O}_3$ -Al and  $\text{MnO}_2$ -Al system at different molar ratios. From the comparison of theoretically calculated and experimentally determined heat values it has been found that reaction is complete when

the molar ratio was 1:5 and 1:8 molar respectively in the case of  $\text{MnO}_2$ -Al and  $\text{Fe}_2\text{O}_3$ -Al. A detailed study on enthalpy calculation for  $\text{MnO}_2$ -Al system is available in our previous publication.<sup>2)</sup> However, for a better understanding heat values for both systems are summarised in **Tables 1** and **2** respectively.



**Fig. 1.** Simultaneous DTA-TGA plots for different  $\text{Fe}_2\text{O}_3$ : Al molar ratios.



**Fig. 2.** Simultaneous DTA-TGA plots for different  $\text{MnO}_2$ : Al molar ratios.

**Table 1.** Heat of aluminothermic reduction of  $\text{MnO}_2$ .

Expt. No.	$\text{MnO}_2$ : Al molar ratio	DTA peak temp. (K)	Mass gain (mg)	Total DTA peak area ( $\text{kg} \times 10^{-4}$ )	DTA peak area due to reduction ( $\text{kg} \times 10^{-4}$ )	Theoretical heat value (kJ/mol)	Experimental heat value (kJ/mol)	Remarks
1	1:2	1205	4.0	2.342	0.660	501.82	349.24	Incomplete
2	1:3	1197	4.1	2.402	0.310	501.60	198.00	Incomplete
3	1:3	1193	5.1	3.012	0.713	503.30	444.26	Incomplete
4	1:4	1213	3.8	2.173	0.462	499.64	343.65	Incomplete
5	1:5	1187	5.8	3.448	0.610	502.82	498.74	Complete
6	1:5	1183	5.8	3.467	0.613	503.23	497.20	Complete
7	1:5	1183	5.8	3.467	0.613	503.23	497.20	Complete
8	1:5	1183	5.8	3.467	0.613	503.23	497.20	Complete

Quantity of the sample taken for each set of experiment =  $0.15 \times 10^{-4}$  kg.

**Table 2.** Heat of aluminothermic reduction of  $\text{Fe}_2\text{O}_3$ .

Expt. No.	$\text{Fe}_2\text{O}_3$ : Al molar ratio	DTA peak temp. (K)	Mass gain (mg)	Total DTA peak area ( $\text{kg} \times 10^{-4}$ )	DTA peak area due to reduction ( $\text{kg} \times 10^{-4}$ )	Theoretical heat value (kJ/mol)	Experimental heat value (kJ/mol)	Remarks
1	1:2	1200	1.20	0.9726	0.24828	877.011	208.343	Incomplete
2	1:3	1181	3.30	2.3150	0.29000	876.569	265.392	Incomplete
3	1:4	1177	4.10	2.8146	0.34000	876.474	337.680	Incomplete
4	1:5	1159	4.50	3.2562	0.38370	876.059	419.458	Incomplete
5	1:6	1149	5.10	3.9400	0.64130	875.826	755.190	Incomplete
6	1:7	1153	5.32	4.0429	0.62000	875.919	795.429	Incomplete
7	1:7.5	1156	5.60	4.2386	0.65000	875.989	869.618	Nearly complete
8	1:8	1157	5.70	4.2777	0.63000	876.012	875.500	Complete
9	1:8	1157	5.70	4.2800	0.63230	876.012	878.697	Complete
10	1:8	1157	5.65	4.2457	0.63000	876.012	875.500	Complete

Quantity of the sample taken for each set of experiment =  $0.15 \times 10^{-4}$  kg.

4. Kinetics

Kinetics studies of aluminothermic reduction of  $MnO_2$  and  $Fe_2O_3$  has been carried out with a thermit mixture  $MnO_2:Al=1:5$  and  $Fe_2O_3:Al=1:8$  on molar basis. These ratios have been selected on the basis of good matching of theoretical and experimental heat values as shown in Tables 1 and 2.

Under rising temperature conditions the rate of reaction ( $d\alpha/dt$ ) where  $\alpha$  is degree of reaction depends on time and temperature, Maccullum and Tanner<sup>10</sup> accordingly suggested:

$$\text{If } \alpha = f(T, t) \dots\dots\dots(4)$$

$$\text{then } (d\alpha/dt) = (\delta\alpha/\delta t)_T + (\delta\alpha/\delta T)_t (\delta T/\delta t) \dots\dots\dots(5)$$

There have been much controversy<sup>11,12</sup> regarding this equation. It has been pointed out that  $(\delta\alpha/\delta T)_t$  must be zero for  $\alpha$  cannot change instantaneously. Various authors have subsequently given arguments<sup>11-13</sup> to counter Eq. (5). It is now accepted that the reaction rate is given by the slope of the  $\alpha$  vs.  $t$  plot. Actually Eq. (4) is true for state function where  $\alpha$  is a path function.

It is possible to analyse non-isothermal kinetic data by combining three equations.

1) The differential form of the kinetic equation:

$$d\alpha/dt = k \cdot f(\alpha) \dots\dots\dots(6)$$

Where,  $\alpha$ : degree of reaction,  
 $t$ : time (min),  
 $k$ : rate constant ( $\text{min}^{-1}$ ), and  
 $f(\alpha)$ : a function of  $\alpha$  whose appropriate form depends on the reaction mechanism.

2) The second equation is the so called Arrhenius expression describing the variation of rate constant with temperature  $T$

$$k = A \cdot \exp(-E/RT) \dots\dots\dots(7)$$

Where  $A$  is a pre-exponential constant,  $R$  is the universal gas constant, and  $E$  is the activation energy.

3) The third equation describing the variation temperature rise, the temperature at time  $t$  is given by

$$T = T_0 + \beta t$$

i.e  $(dT/dt) = \beta \dots\dots\dots(8)$

Where  $T_0$  is the initial temperature and  $\beta$  is the constant which describes the linear heating rate.

The basic kinetic equation for non-isothermal kinetic data is thus obtained by combining Eqs. (6), (7) and (8).

$$d\alpha/f(\alpha) = A/\beta \cdot \exp(-E/RT) \cdot dT \dots\dots\dots(9)$$

Equation (9) cannot be integrated analytically. Review of some of the methods of approximate solution of the integral reported in the literature have been given by several workers. Coats and Redfern<sup>15</sup> have suggested that for constant rate of heating

$$\frac{g(\alpha)}{T^2} = \left[ \frac{AR}{\beta E} \left\{ 1 - \frac{2RT}{E} \right\} \right] \cdot \exp\left(\frac{-E}{RT}\right) \dots\dots(10)$$

Hence the plot of  $\ln[g(\alpha)/T^2]$  against  $1/T$  gives a straight line with slope  $-E/R$  from which  $E$  is obtained. Whereas,

intercept gives  $\ln[(AR/\beta E)\{1 - (2RT/E)\}]$ . The term inside the bracket  $\{1 - (2RT/E)\}$  is nearly equal to 1, because the value of  $2RT/E$  could be negligible compared to 1. Hence  $A$  is calculated from  $\ln(AR/\beta E)$ .

Figure 3 shows the procedure for delineation for DTA peak area, due to reduction only. Assuming the beginning and the end of the theoretical DTA peak thus obtained to represent the initiation and completion of the reduction, we calculated the degree of reduction at any given temperature on the basis of area fraction. Figures 4 and 5 show  $\alpha-T$  plots for different heating rates for  $MnO_2-Al$  and  $Fe_2O_3-Al$  systems respectively at 1:5 and 1:8 molar ratios. Plots so generated for these two systems are 'S' type as is typical of non-isothermal plots. The results show that  $\alpha-T$  plots shifts to the right with decreasing heating rates, which may be attributed to the fact that when heating rate is higher the system achieves higher temperature sooner. Therefore, in a given time there is more reaction. Since there is no *a priori* knowl-

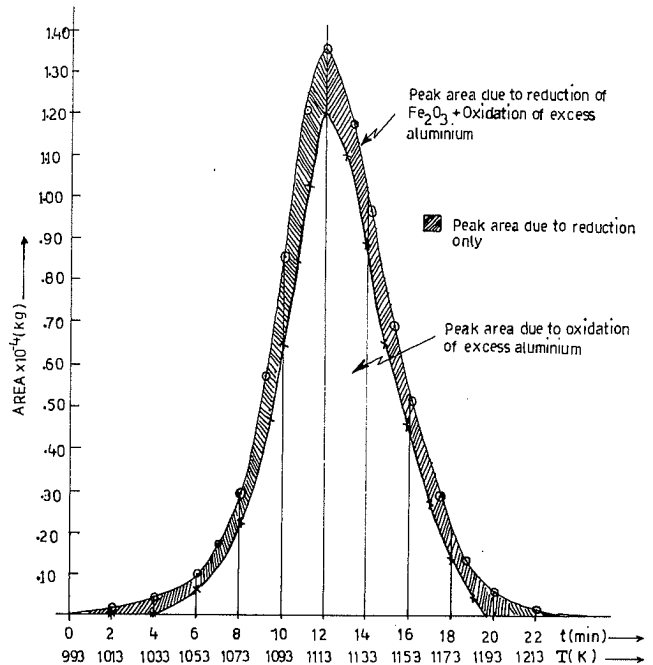


Fig. 3. Determination of DTA peak area due to aluminothermic reduction of  $Fe_2O_3$  only.

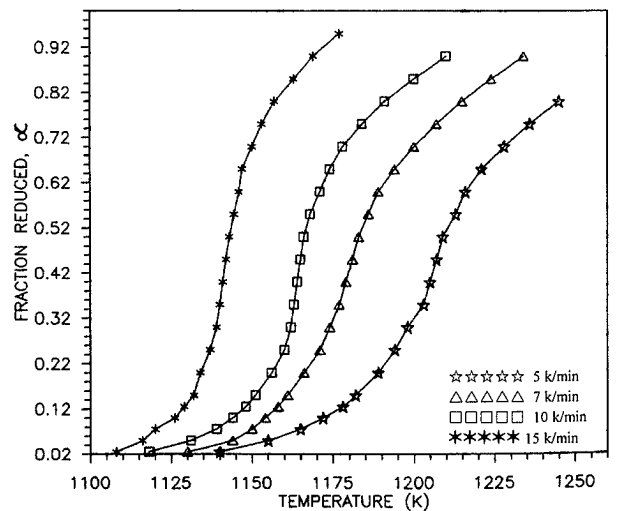


Fig. 4.  $\alpha-T$  plots for aluminothermic reduction  $MnO_2$ .

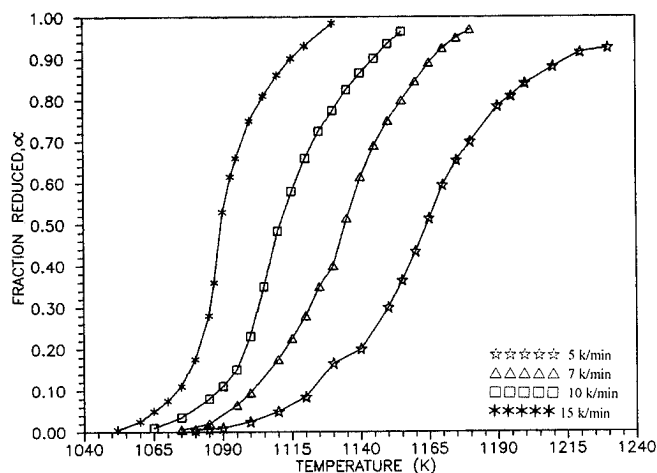


Fig. 5.  $\alpha$ - $T$  plots for aluminothermic reduction of  $Fe_2O_3$ .

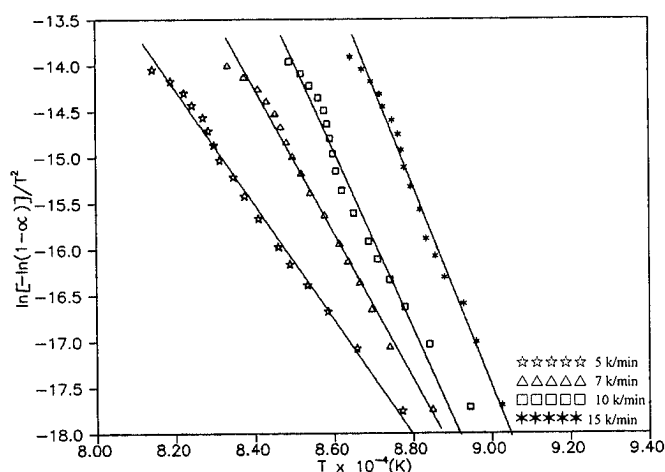


Fig. 6. Coats and Redfern plots for aluminothermic reduction of  $MnO_2$ .

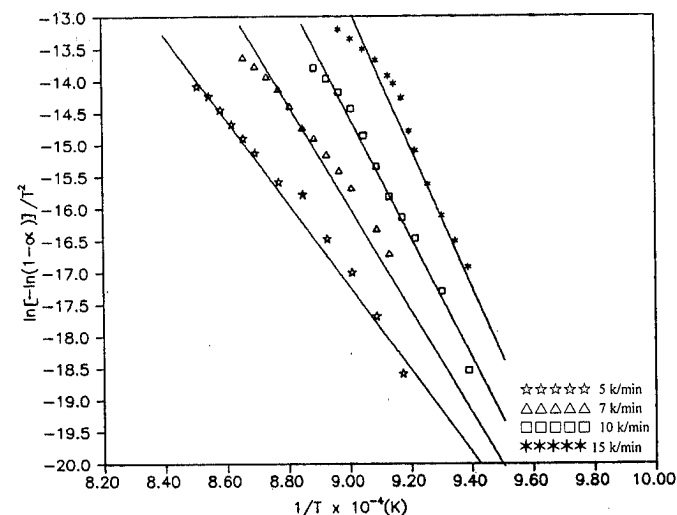


Fig. 7. Coats and Redfern plots for aluminothermic reduction of  $Fe_2O_3$ .

edge about the kinetic model, nine possible mechanistic models proposed by Sharp *et al.*<sup>14)</sup> have been considered. These pertain to rate controlled by phase boundary reaction, diffusion process and nucleation and growth reaction. A correlation coefficient analysis indicates that the best fit is obtained in case of both the systems with

Table 3. Activation energy and pre-exponential factors of aluminothermic reduction of  $Fe_2O_3$  (for  $Fe_2O_3$ -Al at 1:8 molar ratio).

Heating rate (K/min)	Method	Activation energy $E$ (kJ/mol)	Pre-exponential factor $\log A$
5	Coats & Redfern	-546.0	23.59
7		-675.3	30.44
10		-791.1	36.71
15		-917.0	43.59
5	Dixit & Ray	-553.8	30.72
7		-670.2	36.29
10		-704.3	38.59
15		-990.6	53.24

Table 4. Activation energy and pre-exponential factors of aluminothermic reduction of  $MnO_2$  (for  $MnO_2$ -Al at 1:5 molar ratio).

Heating rate (K/min)	Method	Activation energy $E$ (kJ/mol)	Pre-exponential factor $\log A$
5	Coats & Redfern	-518.3	21.20
7		-658.8	28.35
10		-805.3	35.54
15		-909.9	41.23
5	Dixit & Ray	-506.5	27.01
7		-552.3	29.59
10		-717.9	37.67
15		-994.2	51.28

first order equation having highest correlation coefficient values. Data shown in Figs. 4 and 5 have been analysed using different methods such as Coats & Redfern and Dixit & Ray. Figures 6 and 7 show Coats & Redfern<sup>15)</sup> plots for the data shown in Figs. 4 and 5. The plots are found to be linear.  $E$  and  $A$  values thus found are mentioned in Tables 3 and 4. Same data were analysed using Dixit and Ray<sup>16)</sup> (Figs. 8 and 9). It has been found that in both the methods  $E$  values increases with increasing heating rate. The values obtained in both the cases are close to each other within the reasonable range.

#### 4.1. Kinetic Compensation Effect (K.C.E)

In a homogeneous reaction, the evaluation of the kinetic parameters ( $E$  and  $A$ ) should be important because they were considered to be indicative of the reaction mechanism. However, in the heterogeneous reactions taking place in the solid state, (as in the present investigation) both these parameters lose their relevance because the concept of "order of reaction" and "concentration" are not applicable.<sup>17-19)</sup> In case of rising temperature  $E$  and  $A$  values, which generally do not agree with isothermal values, have no well defined meaning.<sup>10,20,21,22)</sup> Thus  $E$  and  $A$  may be treated as derived parameters. It is also evident from the literature that the value of  $E$  depends on various experimental factors such as sample mass, particle size and its distribution, rate of heating, impurities in the sample, gaseous atmosphere in and around the sample, Packing density *etc.* Thus the

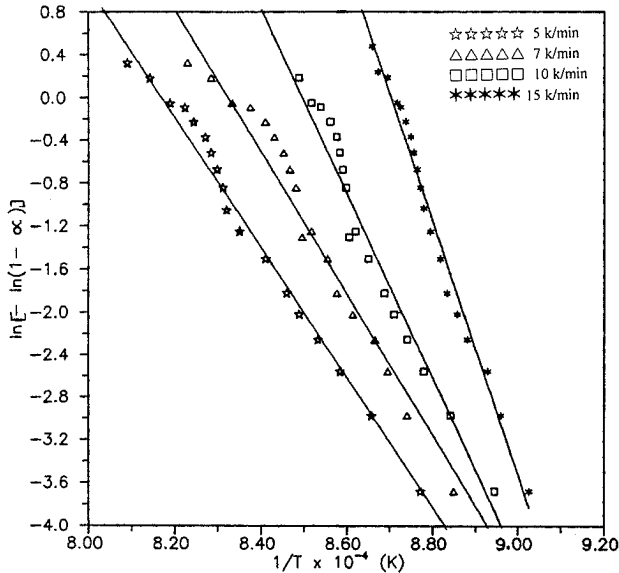


Fig. 8. Dixit and Ray plots for aluminothermic reduction of MnO<sub>2</sub>.

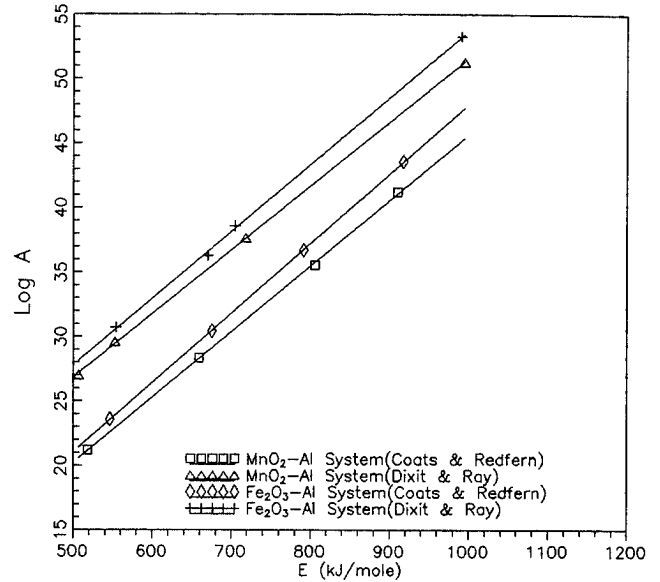


Fig. 10. Kinetic compensation plots for aluminothermic reduction of MnO<sub>2</sub> and Fe<sub>2</sub>O<sub>3</sub>.

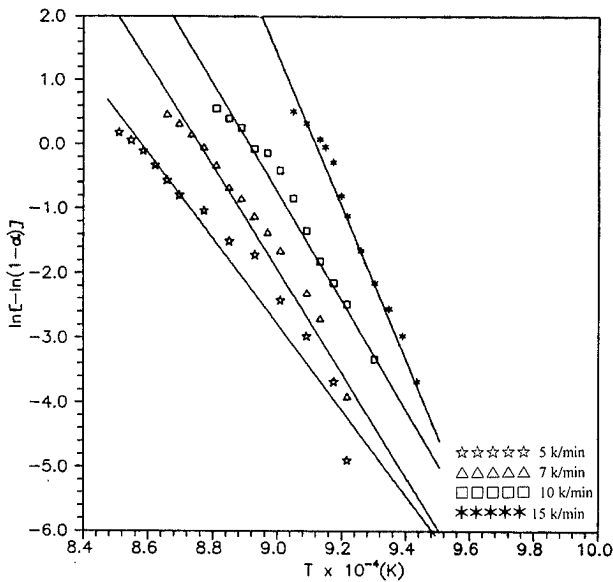


Fig. 9. Dixit and Ray plots for aluminothermic reduction of Fe<sub>2</sub>O<sub>3</sub>.

practical application of the experimentally determined Arrhenius parameters have been realised. It has been observed that for a set of related reactions or for a reaction under varying experimental conditions, there exists a linear relationship between  $E$  and  $A$ . This relationship is known as kinetic compensation effect (K.C.E). Which may be stated as follows: for any change in experimental activation energy ( $E$ ) arising from experimental artifacts, a corresponding change in preexponential factor ( $A$ ) also occurs, which can be mathematically expressed as<sup>23,24)</sup>

$$\log A = a + bE \dots\dots\dots(12)$$

Where  $a$  and  $b$  are characteristic of the system. A detailed mathematical treatment of the problem is available elsewhere.<sup>25)</sup> In the case of aluminothermic reduction of MnO<sub>2</sub> and Fe<sub>2</sub>O<sub>3</sub> kinetic compensation effect law was found to be valid as shown in Fig. 10, and is expressed as

- 1) MnO<sub>2</sub>-Al system
  - a) For Coats and Redfern  
 $\log A = -5.19814 + 5.08599 \times 10^{-2} \times E$
  - b) For Dixit and Ray  
 $\log A = 2.10155 + 4.94949 \times 10^{-2} \times E$
- 2) Fe<sub>2</sub>O<sub>3</sub>-Al system
  - a) For Coats and Redfern  
 $\log A = -5.90906 + 5.39236 \times 10^{-2} \times E$
  - b) For Dixit and Ray  
 $\log A = 1.90385 + 5.18070 \times 10^{-2} \times E$

**5. Conclusions**

- (1) Prediction of reduction kinetics only in a aluminothermic reduction system is impossible unless one deduct the DTA data for oxidation of aluminium from the total DTA data which is generated due to the oxidation of excess aluminium and reduction of metal oxide (MnO<sub>2</sub> and Fe<sub>2</sub>O<sub>3</sub> were the metal oxide for the present case).
- (2) Using derivative differential thermal analysis (DDTA) technique kinetic parameters for aluminothermic reduction of MnO<sub>2</sub> and Fe<sub>2</sub>O<sub>3</sub> can be obtained. In this approach reaction rate values are obtained in terms of rate of changes in DTA peak areas.
- (3) Heat values for both systems can be successfully estimated using DTA peak area provided the unit is calibrated properly *i.e.* reliable calibration constant is available. Heat values thus obtained are very much helpful in selecting a thermite mixture for better recovery of metal(s) and also for kinetic studies.
- (4) Activation energy values obtained from Coats and Redfern and Dixit and Ray for the system MnO<sub>2</sub> and Fe<sub>2</sub>O<sub>3</sub> are comparable.
- (5) As in both the cases kinetic compensation effect (K.C.E.) is applicable with the data which indicates that the reactions are isokinetic within the experimental domain.
- (6) Reduction of both MnO<sub>2</sub> and Fe<sub>2</sub>O<sub>3</sub> are found to be chemically controlled and are followed by  $g(\alpha)=$

$-\ln(1-\alpha)$ .

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