THERMOANALYTICAL INVESTIGATION OF THE ALUMINOTHERMIC REDUCTION OF IRON(III) OXIDE

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Differential thermal analysis technique has been applied to determine the heat of reduction of iron oxide by aluminium. It has been observed that the DTA curve can be used for quantitative determination of heats of reactions at high temperature ranges where differential scanning calorimetry is not applicable. The experimental results obtained agree closely with the theoretical value of the heat of reaction.

Chemical reactions, in general, are accompanied by either absorption or evolution of heat. A knowledge of the heat evolved or absorbed in a reaction is useful for a proper heat balance and thus control of heat economy of the reaction process. In general, the aim of heat measurement in extractive metallurgy is to obtain the equilibrium constant for the reaction under consideration. By this measurement it is possible to characterize equilibria encountered in metallurgical processes by a small number of parameters using Vant Hoff's equation [1].

Several metals and alloys are produced from their compounds such as oxides, sulphides, halides by using reactive metals as reductants. The chemical reaction is of the following type

$$M_xO_y + \frac{x \cdot y}{z} R = \frac{y}{z} \cdot R_xO_z + x \cdot M \tag{1}$$
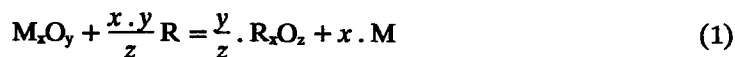
where, M_xO_y is the oxide of metal M, R is the metal reductant, and z the

valency of the reductant. These reactions are exothermic in nature. In ideal cases, the heat generated in a chemical reaction should be sufficient to raise at least one of the products of reaction to liquid stage, thus allowing a liquid/liquid or liquid/solid separation to occur. Measurement of the heat of reaction is of fundamental importance in these processes in order to design a suitable stoichiometry of the mixture of the compound and the reductant metal. The measurement of the heat obtained may also give some idea about the kinetics of the reaction in metallothermic reduction.

Heats of reaction can be quantitatively determined among several techniques by differential scanning calorimetry (DSC).

In DSC the difference between the heat change exhibited by the reference material and that by the sample can be measured in two ways

1. power compensated DSC, and

2. heat flux DSC

In power compensated DSC, additional energy is supplied to either the reference material or the sample to establish a zero difference in heat exchange by the two specimens with the surroundings maintained at the same temperature. Here the rate of energy addition is measured as a function of temperature.

Heat flux DSC involves the measurement of a temperature difference ΔT developed between the reference material and the sample as a function of temperature. In heat flux DSC, the difference in heat exchange of the specimens with the surroundings remains undisturbed. Thus this is carried out using an ordinary DTA arrangement.

Differential scanning calorimetry (DSC) is a sensitive tool for detecting and quantifying heat effects in samples, especially at low and moderate temperature ranges up to about $700°$. In DSC, since the level of the base line is proportional to the heat capacity of the sample, specific heat can also be measured by comparing the level of the base line with that of a standard substance with known specific heat.

The base line may change due to many factors, such as

a) wrong alignment of the crucibles,

b) moisture removal and packing of starting material,

c) lack of thermal match (Dissimilarities of thermal characteristics between the reference material and the sample).

The ordinate of the DSC curve is represented by the equation

$$\mathrm{d}q / \mathrm{d}t = K . \beta . \mathrm{d}H / \mathrm{d}T \qquad (2)$$

where, K is the calibration constant, H is the heat content of the sample and β is the rate of heating and dH/dT is equivalent to heat capacity at constant pressure, c_p respectively. A knowledge of the calibration constant K will therefore help in measurement of heat capacity at constant pressure and hence specific heat, from difference in values of dq/dt in the presence and absence of the sample in the sample pan of the calorimeter. Although power compensated DSC appears to be a versatile technique, its application is limited to temperatures below about 700°. Due to its complex design characteristics, it is difficult to match heat losses of the sample holder and reference holder at high temperatures, thereby rendering power compensated DSC impracticable. However, differential thermal analysis (DTA) may be used for such purposes at high temperatures provided reliable calibration plots are available. It is shown later in this paper that in heat flux DSC (i.e. DTA), the calibration constant, changes with temperature. Therefore the apparatus needs to be recalibrated in different temperature ranges.

Application of DTA as heat flux DSC

In differential thermal analysis the temperature difference is recorded between a substance and a reference material when they are subjected to identical thermal effects in an environment heated or cooled at a controlled rate. The temperature of the reference substance, which is thermally inactive, increases even when an endothermic reaction or phase change occurs in the sample, because heat supplied from outside is consumed by the reaction or phase change in the sample. When the reaction is completed, the sample temperature is appreciably different from the ambient temperature. Therefore it increases rapidly to catch up, and then having done so, it begins to increase uniformly again. Thus, the plot of temperature difference, ΔT, with respect to the standard vs. temperature (T) or time (t) will produce a deflection from the base line and subsequent return to the base line in the form of an endothermic peak. Conversely, if the sample undergoes an exothermic reaction, the heat generated causes an increase in the temperature of the sample compared to that of the reference resulting in exothermic peak. Hence in general, each substance yields a DTA curve whose shape, size and position can serve as a means of qualitative identification of the substance. The technique can also be used for quantitative evaluation of the amount of substance present by making use of the fact that the heat of reac-

tion reflected in the DTA peak area is proportional to the amount of the reacting substance. Although the peak height has been occasionally used in quantitative analysis of DTA curves [2] the peak area is preferred as a satisfactory criterion for quantitative DTA.

The accuracy of measurement of areas of peaks, however, is limited by several factors, such as overlapping of peaks, chemical reactions, the accuracy of area delineation and measurement, the intimacy of mixing of reactants, the extent and nature of dilution, gas evolution, the magnitude of the thermal effect concerned, the difference in thermal conductivity, particle sizes, bulk density, degree of crystallinity of reactants, etc. Therefore, DTA measurement must be done under strictly controlled experimental conditions and procedures. Aluminothermic reduction of iron oxide has important application is joining rail roads in situ and used for production of Ferro-alloys. The authors were the first to make an attempt to measure the heat of an aluminothermic reaction.

Theory of DTA curves

When a substance undergoes any physical or chemical change accompanied by appreciable thermal effects in a thermal analyser then a DTA curve is obtained. This may show a series of peaks in the plot of temperature difference, ΔT, vs. temperature change. The latter is linear in commercial thermal analysers. Here sample temperature is continuously compared against the temperature of the thermally inert reference material.

The area under the DTA curve, [3] when the temperature difference ΔT, is plotted against time, is given by equation

$$\text{Area} = \int_{t_1}^{t_2} \Delta T \, . \, dt \tag{3}$$

where, t_1 & t_2 represent, respectively the time at the beginning and end of the peak. The peak area depends on the thermal properties of the substance as well as those of the apparatus. With the configuration of isolated cups, shown is Fig. 1a there is no rapid transfer of heat from the reference to the sample. When the cups are not isolated, as in Fig. 1b, but rather situated in a highly conductive block, then there appears a diminution of peak height due to free heat exchange between the sample and the reference material. However, the highly conductive nature of the block, permits the approach of
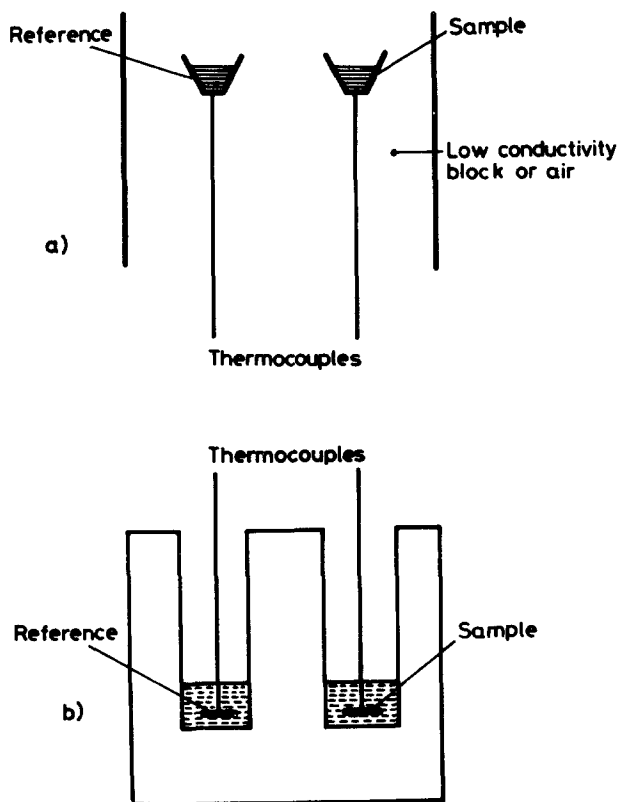
Fig. 1 Cell recommended for quantitative (a) and for qualitative DTA (b)

the thermal equilibrium quickly after the completion of the reaction, so that subsequent reactions may be observed as separate peaks.

Theoretical expressions for peak area

Differential thermal analysis can be used both as a qualitative and quantitative tool, for which different mathematical analysis methods have been developed by different workers [4-6]. The main aim of all such analyses is to describe the DTA peak in terms of the transfer or absorption of heat by the test sample as it undergoes a physical or chemical change. A review of several mathematical models is available elsewhere [4-6].

In order to obtain the peak area free from the effect of the rate of heating, it is necessary to record the differential thermocouple signal against time (t) and not temperature.

For a cylindrical sample placed in a holder of infinite thermal conductivity where the thermocouple is placed at the centre of the sample, (Fig. 1b), the area under the DTA peak is obtained from the expression

$$\text{Area, } A = \frac{G.M.\Delta H}{K_s} \tag{4}$$

Where,

G is a constant

M = mass of the sample, g

ΔH = enthalpy change of the reaction per g of the active substance.

K_s = thermal conductivity of the sample.

This expression is independent of the rate of heating. The presence of the term K_s makes the cell non-quantitative, because peak area changes from one sample to another or even for the same sample due to the variation of thermal conductivity.

If the holders are isolated by low thermal conductivity medium, e.g. air, (Fig. 1a), and the thermocouple is located outside, then the peak area is given by the following expression

$$\text{Area, } A = \frac{M.\Delta H}{2 K_m} \tag{5}$$

Where, K_m is the thermal conductivity of the separating medium of small thermal conductivity. From equation (5) it is inferred that for a sample of fixed volume and shape, the peak area is inversely proportional to the conductivity of the holder and independent of the sample conductivity and rate of heating. Thus the peak area of the reaction curve is directly proportional to the heat of reaction and the properties of the reactive sample do not influence the peak area. Mathematically

$$\text{Area, } A = k \Delta H \tag{6}$$

Where, k is a constant obtained from calibration and ΔH is the enthalpy change of the reaction. As the above expression does not contain any term related to the physical properties of the sample, it is important to ensure

that identical crucibles are employed in the experiments such that the sample diameter will remain constant throughout the experiment. There are, however, evidences to suggest that the thermal properties of the sample do have an effect. It is therefore advisable to calibrate the apparatus for various temperature ranges using materials of similar thermal properties (i.e. the enthalpy change should be of the same order).
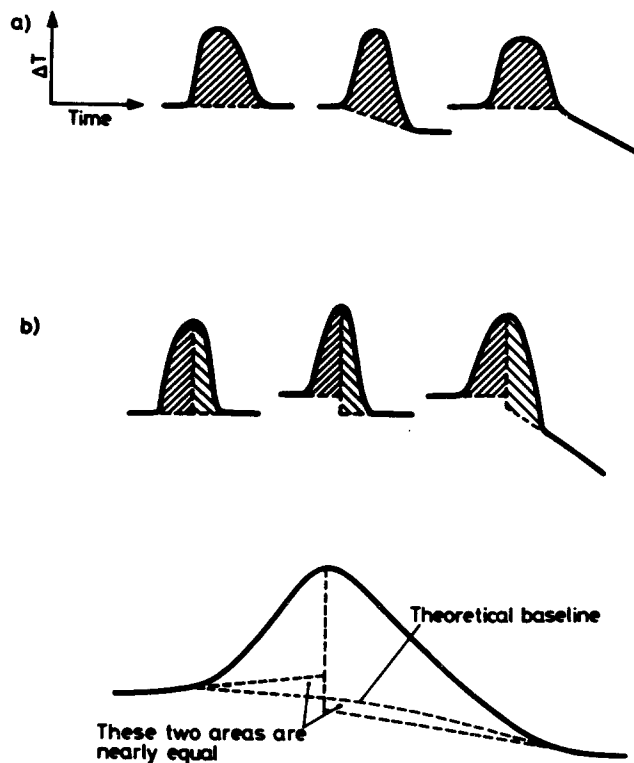

Fig. 2 Traditional method of delineating peak area, (a) suggested method of delineating peak area, (b) the traditional construction and 'Wilburn' construction for delineation of DTA peak area

Determination of peak area

In order to measure the area under a DTA peak correctly, so that it can be correlated to the true heat effect, different types of graphical base line
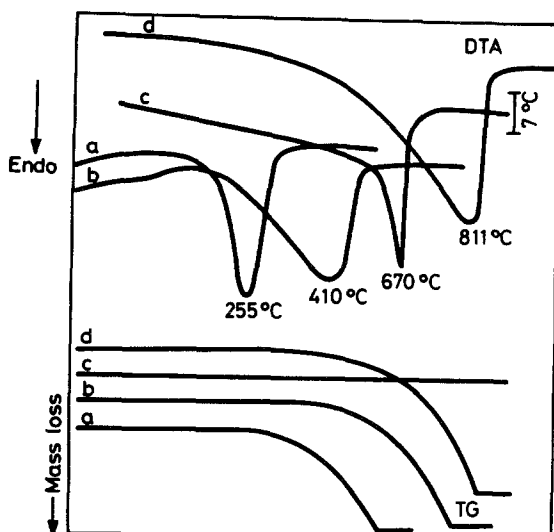
Fig. 3 DTA and TG plots for decomposition and melting of compounds. Heating rate 10 deg/min. a) $ZnCO_3$; b) $CdCO_3$; c) V_2O_5; d) $CaCO_3$

construction have been suggested by different workers [6-12]. Cunningham and Wilburn [6] suggested a method (Fig. 2b), to avoid the difficulties that arise from Garn's [7] method of construction. This method closely approximates the theoretical base line, and gives an area very close to the area bounded by the theoretical base line. This method has been checked to be valid by Ray [3]. In the present paper DTA peak areas have been obtained by cutting out and weighing the reaction area of the chart paper. The area was defined by the method of Cunningham and Wilburn [6].

Experimental

The chemical compounds used in this investigation were all of reagent grade. Aluminium powder, zinc carbonate, cadmium carbonate and calcium carbonate were supplied by Loba-Cheme, Bombay; vanadium pentoxide by Emark, Germany and iron(III) oxide (Fe_2O_3) was supplied by Howards of Ilford Ltd. London, respectively. A simultaneous TG, DTA, Thermal Analyser (model Shimadzu DT-30) was used for this investigation. Alumina cups were used both for the sample and the reference material supplied by Shimadzu Corporation, Japan.

By theoretical calculations the ratio of Fe_2O_3/Al needed was found to be 1:2.29 so as to yield a final post reaction temperature of 1401°, provided the reaction is adiabatic and Fe_2O_3 gets reduced completely. Some runs were also carried out for ratios of Fe_2O_3/Al 1:3.17 and 1:1.67 to yield theoretical post reaction temperature of 1200° and 1543°, respectively. However, most of the runs were carried out at a 1:2.29 ratio to obtain TG and DTA plots.

The accuracy of the sensitivity scale was also checked by measuring peak areas at different values of sensitivities provided in the apparatus. It was found that when the DTA sensitivity was doubled, the peak area was also doubled. This check was necessary because during actual experiments different scales of sensitivity may have to be used.

Results and discussion

The simultaneous plots of DTA and corresponding TG for cadmium carbonate, zinc carbonate, calcium carbonate and vanadium pentoxide are shown in Fig. 3. Each of the endothermic peaks describe a melting (c) or decomposition (a, b, d) process as indicated. According to equation (6) the apparatus constant k is given by $K=\dfrac{A}{\Delta H}$

A plot of k versus T is shown in Fig. 4. It is found that the calibration constant k varies with T linearly. ΔH can be estimated quantitatively with some degree of accuracy if the calibration constant is selected appropriately according to the reaction temperature range.
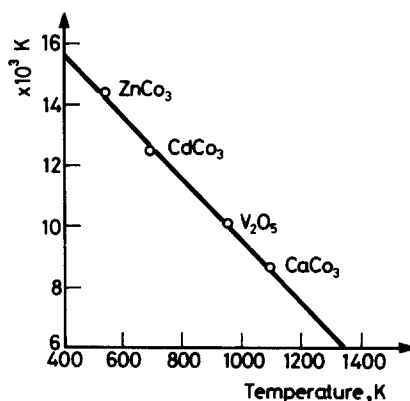

Fig. 4 Plot of K vs. T, K

Table 1 Comparison of theoretical and experimental peak areas and heat values for 15 mg sample

Experiment No.	Fe$_2$O$_3$:Al ratio	Experimental peak area, mg	Mass gain, mg	Theoretical peak area, mg	Experimental heat value, kcal	Theoretical heat value, kcal
1	1:2.29	235.00	3.25	226.130	0.0313	0.0302
2	1:2.29	258.00	4.00	270.130	0.0344	0.0360
3	1:2.29	180.50	2.30	177.114	0.0232	0.0227
4	1:2.29	189.93	2.45	186.376	0.0248	0.0243
5	1:2.29	230.50	3.00	219.919	0.0296	0.0283
6	1:2.29	213.00	2.70	201.510	0.0274	0.0259
7	1:2.29	188.00	2.50	189.344	0.0242	0.0243
8	1:2.29	189.00	2.50	177.916	0.0246	0.0231
9	1:2.29	253.09	3.35	247.783	0.0329	0.0322
10	1:2.29	269.50	3.70	262.725	0.0346	0.0338
11	1:2.29	181.80	2.40	182.905	0.0234	0.0235
12	1:2.29	253.49	3.35	236.720	0.0334	0.0312
13	1:3.17	176.00	2.50	172.000	0.0226	0.0221
14	1:1.67	420.00	5.90	422.000	0.0532	0.0535

A large number of DTA runs were carried out on the mixture of powder iron(III) oxide and aluminium with aluminium in excess of stoichiometry as described earlier. Table 1 summarises the peak areas and weight changes obtained in different runs. The theoretical peak area is shown in the Table. It should be noted that although, in every case, there is a single DTA peak, it represents the total heat effect due to the following contributing factors:

a) Heat of aluminothermic redox reaction (exothermic, no weight change)

b) Heat of oxidation of some of the excess aluminium (exothermic with weight gain)

c) Dissolution of iron produced in excess aluminium and formation of inter-metallic compounds (exothermic)
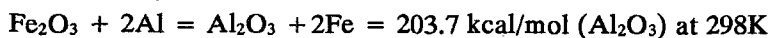
Although these are separate heat effects, they appear as one combined peak. A separate endothermic peak is found due to the melting of aluminium at lower temperatures around 660°. Therefore the peak area may be analysed for individual heat effects. The heat of melting of aluminium is not included because it shows up as a distinct pre-reaction endothermic peak. There may be some additional complications, namely, the aluminothermic reduction and the oxidation of excess of aluminium may be incomplete, the dissolution of iron in aluminium which also may tend to reduce the oxidation of excess aluminium. Thermodynamic data used in the calculation as taken from the literature [1] are listed below.

Standard heat of formation

ΔH_f^o (Al$_2$O$_3$) = 400 kcal/mol at 298K

ΔH_f^o (Fe$_2$O$_3$) = 196.3 kcal/mol at 298K

Heat of reaction ΔH_R for

Fe$_2$O$_3$ + 2Al = Al$_2$O$_3$ + 2Fe = 203.7 kcal/mol (Al$_2$O$_3$) at 298K

Heat capacity cal/g.deg at constant pressure:

C_p (Fe) = 4.18 + 5.92x10^{-3}T (298-1033K)

C_p (Fe) = 9.0 (1033-1181K)

C_p (Fe) = 1.84 + 4.66x10^{-3}T (1181-1674K)

C_p (Al$_2$O$_3$) = 25.48 + 4.25x10^{-3}T

-6.82x10$^5T^{-2}$ (298-1800K)

The heat of reaction (for aluminothermic reduction leading to the final reaction temperature, T_f), = ΔH_R at 298K + heat required to heat Fe to T_f + heat required to heat Al$_2$O$_3$ to T_f = 0.0142806 - 6.18182 x 10^{-4}- 1.69194 x 10^{-3} = 0.01197 kcal. The equivalent peak area for the above heat of reaction = 87.98. The latent heat of aluminium it not taken into account because is has a separate pre-reaction peak.
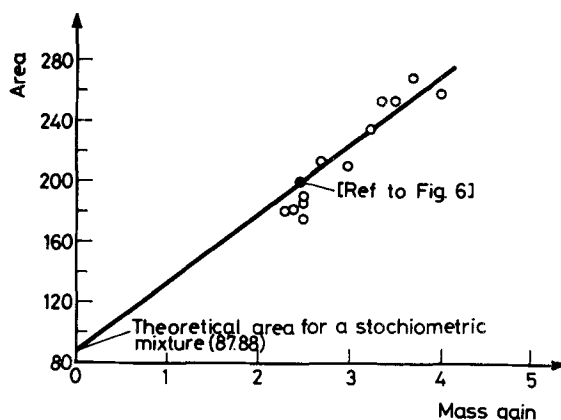

Fig. 5 Plot of peak area *vs.* weight gain

It is easily shown that compared to ΔH_R at 298K, the heats required for heating iron and alumina from 298K to 1181K (T_f) are negligible. Figure 5 shows the plot of the peak area data shown in Table 1 against weight gain in TG runs. Interpolation of the data shown in Fig. 5 to zero weight gain however, describes a reaction corresponding to a stoichiometric mixture in a hypothetical situation with no oxidation of excess aluminium. It is interest-

ing to note that the value of peak area obtained by interpolation, 87.88 mg matches excellently with the theoretical value of 87.98 mg.

This interpolation effectively eliminates uncertainties arising from factors (b) and (c) and the possibility of incomplete reduction in the presence of excess aluminium.

The scatter of data shown in Fig. 5 may be attributed to the following factors:

a) Different degrees of segregation of aluminium and iron(III) oxide particles in the starting mixture.

b) Unequal extent of reduction reaction due to local variation in the samples.

c) Different degrees of dissolution of iron is excess aluminium de to, among other factors, (a) and (b). The scatter, however, can be reduced by strict control in the mixing, sampling and experimental procedure. For example, one special run was carried out taking extreme precaution in sampling, the DTA and TG plots of which are shown is Fig. 6. The peak area and weight gain data fall exactly on the average line shown in Fig. 5.
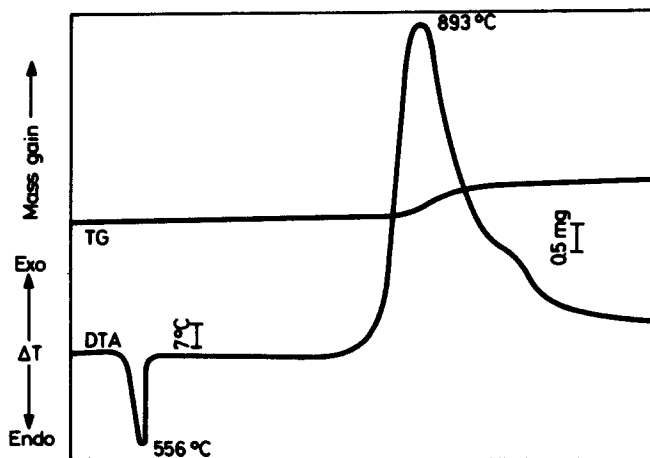

Fig. 6 Special run taking extreme precaution in sampling, β = 10 deg/min

Some special experiments were carried out to study the role of excess aluminium and distribution of aluminium particles. There was no reduction reaction when aluminium particles were laid out as alternate layers on iron(III) oxide layers. There was also no reaction when a reaction mixture

with excess aluminium was mixed inside the sample holder itself. Presumably the aluminothermic reduction takes place only when aluminium particles are uniformly distributed throughout the mass and which after melting, trickle through the mass slowly ensuring good contact with iron(III) oxide particles. When mixing is not proper aluminium particles form a segregated layer. These particles are then likely to sinter and melt as a stream which may sink to the bottom of the crucible rapidly without any reaction. It has been observed that molten aluminium does not oxidize completely or readily below 1000° in the sample holder. It is also observed that the reduction reaction of iron(III) oxide with aluminium does not take place in inert atmosphere. Oxidizing conditions e.g. presence of oxygen are necessary to initiate the reaction.
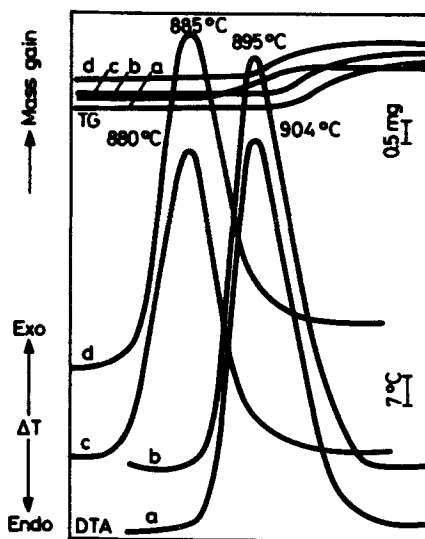

Fig. 7 DTA and TG plots, for two different Fe₂O₃/Al ratios, a) and b) Fe₂O₃:Al = 1:2.29 c) and d) Fe₂O₃:Al = 1:3.17

Figure 7 shows DTA peaks, two each for two different Fe_2O_3/Al ratios. It is seen that even though the ratio is changed, the peak area is not changed accordingly. Secondly, the weight gain in no case represents complete oxidation of excess aluminium.

From the simultaneous DTA-TG curves, it is possible to calculate the amount of excess aluminium oxidized by air, neglecting the heat of dissolu-

tion of iron in excess of molten aluminium. This assumption is justified because of the fact that, the contact time available for the dissolution is very small. The total heat effect may thus be due to the reduction of iron(III) oxide by aluminium and oxidation of excess aluminium by oxygen in the ambient air. Since the weight gain from the TG yields the idea of aluminium oxides and the peak may be considered as a heat effect due to these two reactions. Assuming this, the calculations were carried on for the theoretical peak area which was found to agree closely with the experimental value as shown in Table 1.

Conclusions

It is shown that differential thermal analysis plots may be used for quantitative determination of heats of reactions at high temperatures where differential scanning calorimetry is not applicable. However, conversion of peak areas into heats requires use of an apparatus constant which must be obtained from calibration. For this purpose endothermic peaks of decomposition and fusion of chemical compounds in similar temperature ranges may be employed.

It is observed that the apparatus constant decreases with increasing temperature. A DTA setup has been applied for calorimetric studies on the aluminothermic reduction reaction. Results on the reduction of Fe_2O_3 are presented and analysed to discuss the uncertainties that may arise. The DTA technique may be used for measurement of heats of aluminothermic reduction of ores and minerals for which no thermodynamic data are available.

References

1 O. Kubaschewski, E. LL. Evans and C. B. Alcock, Metallurgical Thermochemistry, Pergamon Press, London, 1967, Vol. 1.
2 B. EL. Jazairi, Thermochim. Acta, 21 (1977) 381.
3 H. S. Ray and F. W. Wilburn, Application of Differential Thermal Analysis in Extractive Metallurgy, Trans., IIM 35 (1982), 537.
4 R. Malling, F. W. Wilburn andd R. M. Mcintosh, Anal. Chem., 41 (1969) 1275.
5 R. C. Mackenzie, Differential Thermal Analysis Theory. Ed. A. D. Cunningham & F. W. Wilburn, Academic Press, London, 1970, Vol. 1.
6 F. W. Wilburn, J. R. Hesford and J. R. Flower, Anal. Chem., 40 (1968) 777.
7 P. D. Garn, Thermoanalytical Methods of Investigation, Academic Press, London, 1965.
8 R. H. Nortorn, J. Am. Ceram. Soc., 22 (1939) 54-63: C. A. 33:2298.
9 L. H. Berkelhamer, U. S. Mines, Rept. Invest., 3763 (1944) 18.
10 L. A. Dean, Soil Sci. 63 (1947) 95-105.

11 L. G. Berg, Compt. Rend. Acad. Sci. U.S.S.R. 49 (1945) 648-51: (in English) C. A. 40:5629.
12 M. Witteis, Am. Mineralogist, 36 (1951) 760-7.

Zusammenfassung — Unter Anwendung von DTA wurde die Bestimmung der Reaktionswärme der Reduktion von Eisenoxid mit Aluminium durchgeführt. Es konnte festgestellt werden, daß DTA zur quantitativen Bestimmung von Reaktionswärmen bei hohen Temperaturen geeignet ist, bei denen DSC nicht mehr angewendet werden kann. Die ermittelten experimentellen Ergebnisse stimmen gut mit dem theoretischen Wert für die Reaktionswärme überein.