

DETERMINATION OF HEATS OF ALUMINOTHERMIC REDOX REACTION OF V_2O_5 AND MnO_2

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Abstract

Differential thermal analysis has been used for quantitative determination of heats of aluminothermic redox reaction of MnO_2 and V_2O_5 over a wide range of temperatures. Heat of reaction V_2O_5 -Al and MnO_2 -Al systems have been determined using the calibration plot established. The experimentally determined values compare well with those predicted from thermodynamic data available in the literature. It has been found that V_2O_5 -Al system involves a higher heat of reaction in comparison to the MnO_2 -Al system.

Keywords: DTA-TG, thermodynamic data, V_2O_5 -Al and MnO_2 -Al systems

Introduction

Knowledge of heat of reaction of metallothermic reduction reaction is essential for the ferroalloy industry. Carbon is the most economical and extensively used reducing agent for the extraction of ferroalloys. However, high affinity of carbon for many metals Co, V, Ti, Cr, Fe, Mn etc. results in the formation of their carbides. Secondly carbon cannot reduce many metal oxides at usual operating temperatures. These problems however can be overcome by using aluminium as a reductant.

Since aluminium is a costly reducer, in the aluminothermic process, it is important to know the optimum aluminium requirement from the point of view of maximum recovery of the alloy. The recovery of vanadium and manganese in the aluminothermic reduction of V_2O_5 and MnO_2 is particularly dependent on the aluminium present in the charge.

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Though differential thermal analysis technique has been previously used for quantitative heat measurement [1–11], it has been seldom used for calorimetric measurements in metallurgical systems.

The DTA method is beset with several problems associated with delineation of peak area and calibration of the apparatus. These problems have been resolved and discussed in our previous publication [1, 2]. In DTA the peak area is related to the amount of heat change occurring during a reaction. This led to many attempts for using DTA for quantitative heat measurements.

A knowledge of the heat evolved or absorbed in a reaction is useful for proper heat balancing. Heat measurement is of fundamental importance to determine a suitable stoichiometric ratio of the mixture of the oxides and aluminium and, thus control of heat economy. In ideal cases, the heat generated in a metallothermic reduction should be sufficient to raise at least one of the reaction products to liquid stage, thus allowing a liquid/liquid or liquid/solid separation.

In the present investigation the heat of reaction of aluminothermic redox reaction of two systems, namely V_2O_5 -Al and MnO_2 -Al, have been determined experimentally and the same have been compared with theoretically calculated values.

Experimental

Differential thermal analyser has been used as a heat flux calorimeter. Experimental details are given in our previous communication [10]. For a low thermal conductivity separating medium, the DTA peak area is directly proportional to the heat of reaction and the properties of the reactive sample do not influence the peak area. Mathematically the DTA peak area (A) is given by the equation

$$A = k \cdot \Delta H \quad (1)$$

where k is an instrument constant obtainable through calibration. The details of the calibration procedure have been discussed elsewhere [13].

V_2O_5 and MnO_2 (purity > 99.5%) powders used, were obtained from Emerk, Germany. Aluminium powder (99.9% pure) was supplied by Loba Chemie, Bombay. A Shimadzu DT-30 simultaneous thermal analyser was used to collect TG and DTA data.

DTA is not an adiabatic system and heat dissipation characteristics cannot be predicted from theory. It is therefore not possible to predict the ultimate temperature attainable by aluminothermic reaction of any given oxide-aluminium mixture. In fact it has been found that the redox reaction is incomplete in the case of stoichiometric mixture. Excess aluminium is required not only for initiation and completion of reaction but also to act as a diluent to control the final

reaction temperature within safe limits. Suitable composition has to be selected on the basis of preliminary trial runs. It has been found that no reaction took place for aluminothermic mixture in argon atmosphere. All experiments were, therefore, carried out in static air environment only. It appears that the aluminothermic reaction is triggered in the DTA set up by the heat initially made available by oxidation of excess aluminium which requires oxygen in gaseous environment.

To ascertain the formation of intermetallic product, X-ray diffraction study was carried out using a JEOL, 8PX X-ray diffractometer.

Measurement of peak area

DTA peak area in all the cases was obtained by cutting and weighing the reaction area of the chart paper using the well accepted tangent intercept method recommended by Cunningham and Wilburn [14]. Further experimental details are available elsewhere [10].

Results and discussion

It has been mentioned previously that oxide-aluminium mixture used for the study contains certain excess of aluminium as it is required for completion of the reaction. Where the reaction is complete the stoichiometric amount of alu-

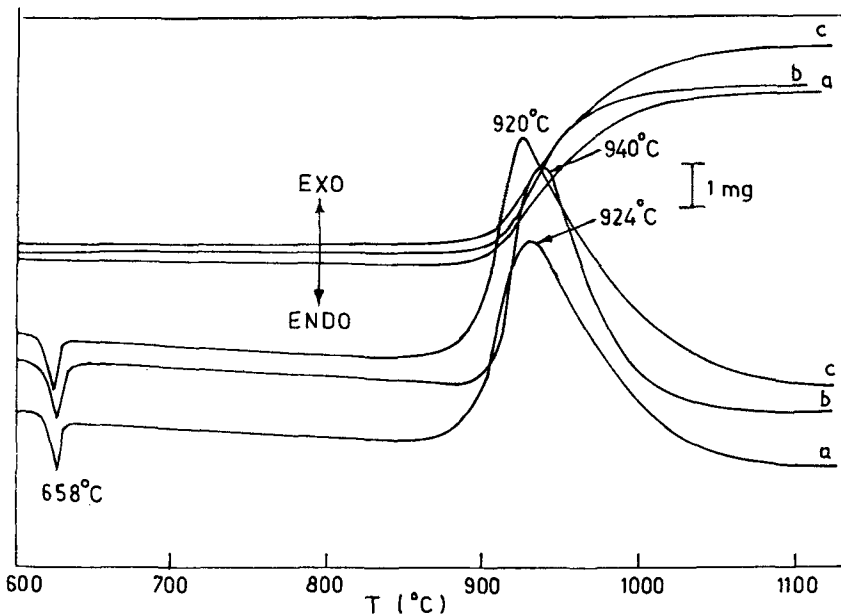


Fig. 1 DTA and TG curves of MnO₂/Al for various molar ratios (a) 1:3 (b) 1:4 (c) 1:5 sample mass = 15 mg; heating rate = 10 · min⁻¹; reference material = α -Al₂O₃

minium is oxidised by oxygen made available by the oxide. A major part of the excess aluminium is oxidised by atmospheric oxygen and some unoxidised aluminium dissolves the metal to form intermetallic compounds. A large number of simultaneous DTA-TG runs were carried out on powder mixture of V_2O_5 and Al and MnO_2 -Al with different molar ratios. In each case single well defined DTA peak indicates a single stage reduction. Figure 1 shows the DTA-TG plots for mixture with three different MnO_2 /Al molar ratios, and Fig. 2 shows simultaneous DTA-TG plots for three different V_2O_5 /Al molar ratios. It is seen that as the molar ratio of the reaction mixture changes, the DTA peak area also changes accordingly. The mass gain in no case represents complete oxidation of excess aluminium. In every case the exothermic DTA peak represents the total heat effect due to the following contributing factors.

- Heat of aluminothermic redox reaction (exothermic, no mass gain).
- Heat of oxidation of some excess aluminium (exothermic with mass gain).
- Dissolution of metal produced in excess aluminium and formation of intermetallic compounds (exothermic, no mass gain).

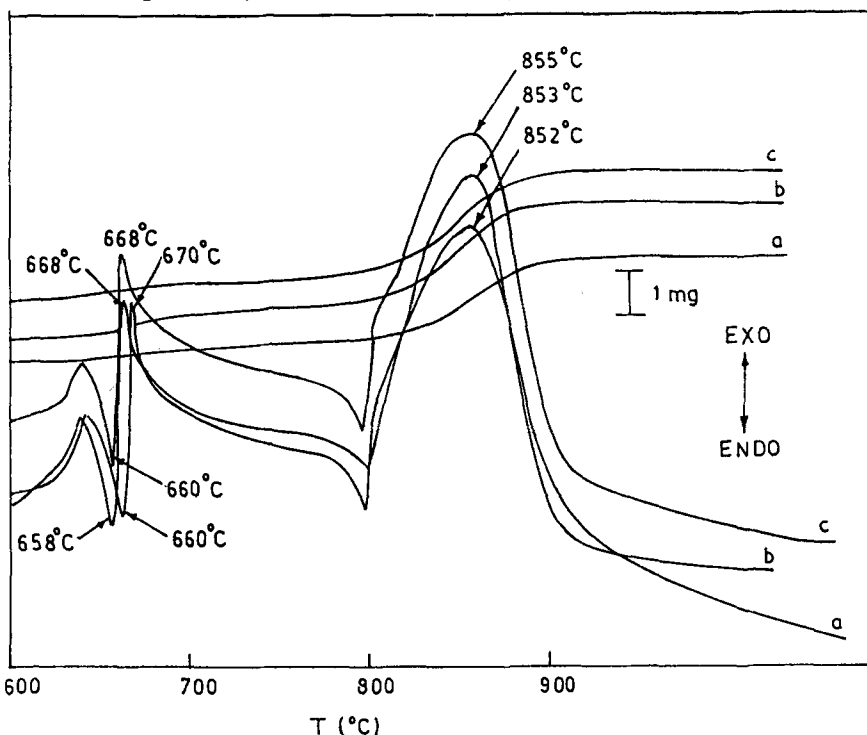


Fig. 2 DTA and TG curves of V_2O_5 /Al for various molar ratios (a) 1:3, (b) 1:3.5, (c) 1:4, sample mass = 15 mg; heating rate = $10 \text{ deg} \cdot \text{min}^{-1}$; reference material = $\alpha\text{-Al}_2\text{O}_3$

Table 1 Heats of aluminothermic reduction of MnO₂

Exp. No.	MnO ₂ :Al molar ratio	DTA peak temperature / K	Mass gain / mg	Peak area due to reduction /		Total exp. peak area / mg	Heat of reaction / kJ/[MnO ₂]		Remarks
				mass gain / mg	reduction / mg		theoretical	experimental	
1	1:2	1205	4.0	234.2	66.0	300.0	501.82	349.24	Incomplete
2	1:3	1197	4.1	240.2	31.0	271.7	501.60	198.00	Incomplete
3	1:3	1193	5.1	301.2	71.3	372.5	503.30	444.26	Incomplete
4	1:4	1213	3.8	217.3	46.2	263.5	499.64	343.65	Incomplete
5	1:5	1187	5.8	344.8	61.0	405.8	502.82	498.74	Complete
6	1:5	1183	5.8	346.7	61.3	408.0	503.23	497.20	Complete
7	1:5	1183	5.8	346.7	61.3	408.0	503.23	497.20	Complete
8	1:5	1183	5.8	346.7	61.3	408.0	503.23	497.20	Complete

Quantity of the sample taken for each set of experiment = 15 mg

Table 2 Heats of aluminothermic reduction of V_2O_5

Exp. No.	V_2O_5 :Al molar ratio	DTA peak temperature / K	Mass gain / mg	Peak area due to reduction /		Total exp. peak area / mg	Heat of reaction / $\text{kJ}/[V_2O_5]$		Remarks
				mass gain / mg	reduction / mg		theoretical	experimental	
1	1:3	1125	2.5	161.29	96.7	258.0	1035.7	869.00	Incomplete
2	1:3.5	1126	3.2	205.90	104.0	309.9	1035.4	985.39	Incomplete
3	1:4	1118	4.2	275.28	103.7	379.0	1037.6	1012.29	Complete
4	1:4	1118	3.9	255.62	104.3	359.9	1037.6	1018.18	Complete
5	1:4	1116	4.0	263.54	105.3	368.8	1038.2	1022.29	Complete
6	1:5	1099	6.3	423.98	103.5	527.5	1042.8	1076.99	Excess

Quantity of the sample taken for each set of experiment = 15 mg

Table 1 summarises the data for Fig. 1. In this case reaction is complete with 1:5 molar ratio where as Table 2 summarises the data for Fig. 2, where reaction is complete with 1:4 molar. A single exothermic peak represents the summation of heat effects due to the reduction of metal oxide and oxidation of excess aluminium. Melting of aluminium shows up as a distinct pre-reaction endothermic dip and hence heat of melting of aluminium does not come into picture during heat calculations.

Thermodynamic data used in calculation are taken from the literature [14].

Standard heat of formation

$$\Delta^{\circ}H_f(\text{Al}_2\text{O}_3) = -1680 \text{ kJ}\cdot\text{mol}^{-1}, \text{ at } 298 \text{ K}$$

$$\Delta^{\circ}H_f(\text{MnO}_2) = -517.86 \text{ kJ}\cdot\text{mol}^{-1}, \text{ at } 298 \text{ K}$$

$$\Delta^{\circ}H_f(\text{V}_2\text{O}_5) = -1563.66 \text{ kJ}\cdot\text{mol}^{-1}, \text{ at } 298 \text{ K}$$

Heat capacity

$$C_p(\text{Al}_2\text{O}_3) = 1070.016 + 17.85 \cdot 10^{-3} \cdot T - 28.644 \cdot 10^{-5} \cdot T^2 \quad \text{J}\cdot\text{g}^{-1}\cdot\text{deg}^{-1} \\ (298-1800 \text{ K})$$

$$C_p(\text{Mn})_{\alpha} = 21.672 + 16.002 \cdot 10^{-3} \cdot T \quad \text{J}\cdot\text{g}^{-1}\cdot\text{deg}^{-1} \quad (298-1000 \text{ K})$$

$$L_t = 2.016 \text{ kJ/gfw}$$

$$C_p(\text{Mn})_{\beta} = 34.986 + 2.772 \cdot 10^{-3} \cdot T \quad \text{J}\cdot\text{g}^{-1}\cdot\text{deg}^{-1} \quad (1000-1374 \text{ K})$$

$$C_p(\text{V}) = 22.68 + 8.4 \cdot 10^{-3} \cdot T \quad \text{J}\cdot\text{g}^{-1}\cdot\text{deg}^{-1} \quad (298-1900^{\circ}\text{K})$$

Heat calculation

a) For MnO_2 -Al system (1:5 molar)

In 15 mg of the reaction mixture MnO_2 present = $6.762 \cdot 10^{-5}$ moles. The heat of reaction of aluminothermic reduction of $6.762 \cdot 10^{-5}$ moles of MnO_2 leading to the final reaction temperature T_f (1187 K)

ΔH_R at 298 K + Heat required to heat Mn to final reaction temperature T_f + Heat required to heat Al_2O_3 to

$$T_f = -0.0407162 + 2.128409 \cdot 10^{-3} + 4.4726219 \cdot 10^{-3} = -0.0341151 \text{ kJ.}$$

The equivalent peak area for the above heat of reaction of

$$-0.0341151 \text{ kJ} = 62.0 \text{ mg of the chart paper.}$$

b) For V_2O_5 -Al system (1:4 molar)

In 15 mg of the reaction mixture V_2O_5 present = $5.175636 \cdot 10^{-5}$. The heat of reaction of aluminothermic reduction of $5.1756 \cdot 10^{-5}$ moles of V_2O_5 leading to

the final reaction temperature T_f (1118 K) = ΔH_R at 298°K + Heat required to heat V to final reaction temperature T_f + Heat required to heat Al_2O_3 to

$$T_f = -0.0639884 + 2.429889 \cdot 10^{-3} + 7.8554172 \cdot 10^{-3} = -0.053703 \text{ kJ}$$

The equivalent peak area for the above heat of reaction of
 $-0.053703 \text{ kJ} = 106.33 \text{ mg}$ of the chart paper.

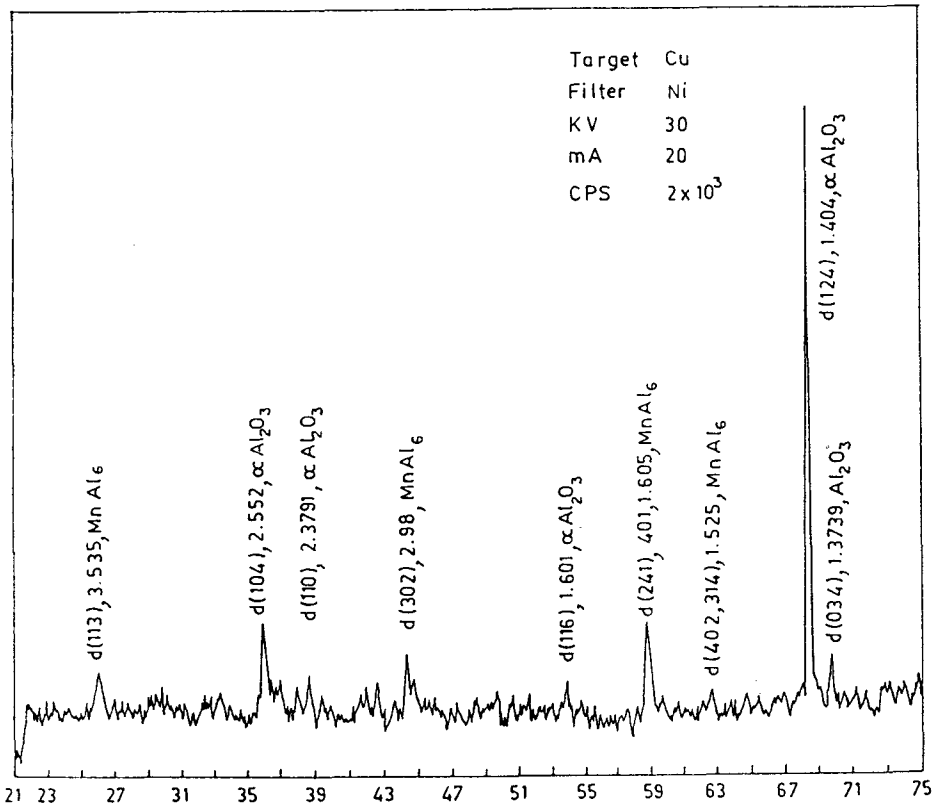
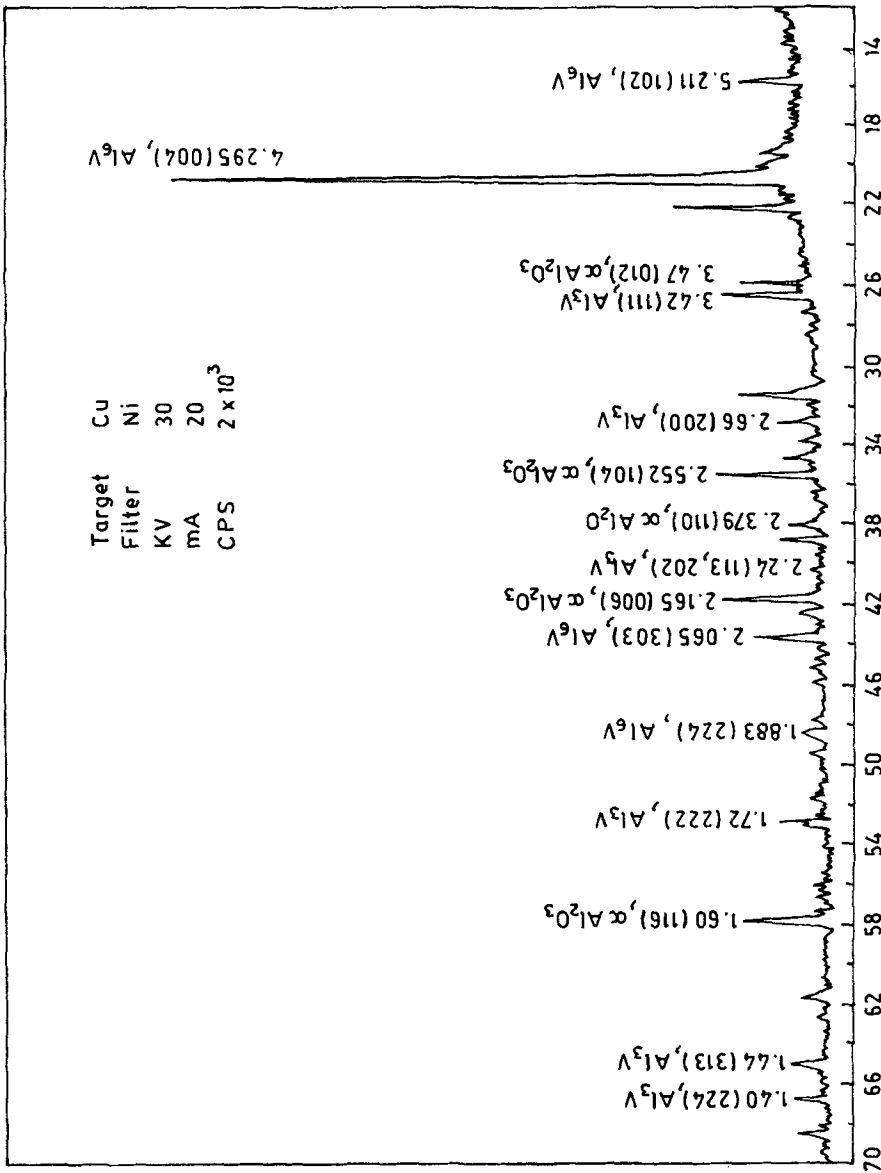


Fig. 3 XRD pattern of products of aluminothermic reduction of MnO_2 (molar ratio - 1:5)

Figures 3 and 4 show the X-ray diffraction pattern of the product which indicates the formation of intermetallic compounds. Heats of formation of intermetallic compounds are very small [15] in comparison to the heat of reaction of aluminothermic reduction and, therefore, can be neglected during heat calculation. The actual mass gain obtained from TG plot which corresponds to oxidation of aluminium by air has been used to calculate the corresponding heat value and this has been deducted from actual heat measured. The difference gives heat due to aluminothermic reduction.

Fig. 4 XRD pattern of products of aluminothermic reduction of V₂O₅ (molar ratio = 1:4)

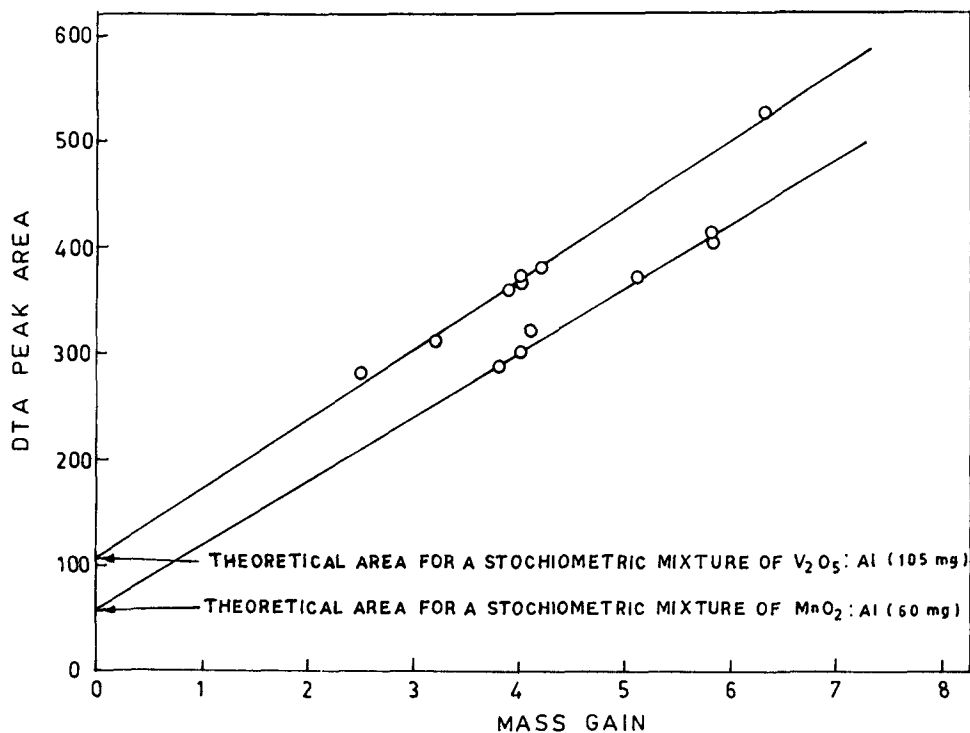


Fig. 5 Plot of peak area vs. mass gain

Figure 5 shows the plots of the peak area data shown in Tables 1 and 2 against mass gain in TG runs. Interpolation of the data to zero mass gain describes a reaction corresponding to a stoichiometric mixture in a hypothetical situation with no oxidation of excess aluminium. The value of peak area obtained by interpolation match satisfactorily with those predicted by theory for V_2O_5/Al 1:4 molar and MnO_2/Al 1:5 molar, respectively. Here uncertainties arising from factors (b) and (c) are eliminated and data indicate completion of reduction in the presence of excess aluminium.

Conclusion

It has been shown that a differential thermal analyser can be used as a quantitative heat flux calorimeter at higher temperature. Heat of aluminothermic redox reaction of MnO_2 and V_2O_5 can be successfully estimated using DTA peak areas. However, conversion of peak area into heat requires a constant which is obtained from calibration of the instrument. The experimentally obtained heat values at 1:5 molar for MnO_2-Al as well as 1:4 molar for V_2O_5-Al system are

each within three percent of those obtained theoretically on the basis of available thermodynamic data.

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Zusammenfassung — Mittels DTA wurden in einem weiten Temperaturbereich die Reaktionswärmern der aluminothermischen Redoxreaktionen von MnO_2 und V_2O_5 quantitativ bestimmt. Die Reaktionswärme der Systeme V_2O_5-Al und MnO_2-Al wurden unter Zuhilfenahme der ermittelten Kalibrationskurve bestimmt. Die experimentell bestimmten Werte stimmen gut mit den anhand von thermodynamischen Literaturangaben geschätzten Werten überein. Man fand, daß das System V_2O_5-Al im Vergleich zu dem System MnO_2-Al eine höhere Reaktionswärme aufweist.