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CHANGE DETERMINATION OF TOTAL ENTHALPY AND ENTHALPIES OF TRANSFORMATIONS BY THE METHOD OF QUANTITATIVE DTA

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ABSTRACT

Employing computing technique for data collection and processing in quantitative DTA makes it possible to determine the enthalpies of transformations or reactions without necessity to define peak area by the interpolation of its basic line. The DTA curve is transformed into temperature dependance expressing the total change of heated material enthalpy and the change of enthalpy connected with followed transformation is determined by this dependance.

INTRODUCTION

Reading of measured DTA quantities in regular, short, time intervals makes conditions for the numerical processing of measurement results. If with the usual evaluating process of quantitative DTA results the enthalpy change of followed reaction (ΔH^{298}) is determined by defining the total area of relevant peak, then it is necessary, when integrating peak area, to determine the course of its basic line employing some of recommended methods. Contrary to this solution there appeares to be proper the determination of total enthalpy change in heated material following temperature dependance as well as reaction enthalpy change determination upon the course of this dependance.

In quantitative DTA, if employing a measuring head with separated sample holders for measured as well as standard materials, between which not heat exchange takes place, we start from heat balances in which there is independently considered the heat capacity of C_{pS} material sample ev. of C_{pR} standard as well as of C_{pSH} sample holder ev. C_{pRH} standard holder:

$$(C_{pSH} + C_{pS})\, dT_S - d\,\Delta H = K_S(T_0 - T_S)\, dt \qquad (1)$$

$$(C_{pRH} + C_{pR})\, d\, T_R = K_R(T_0 - T_R)\, dt \qquad (2)$$

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Basing on these heat balances, there is computed ΔQi heat quantity received when heating sample material in time interval (t_i, t_{i+1}) which corresponds with the total enthalpy change of sample material during heating in temperature interval (T_{Si}, T_{Si+1}) :

$$\Delta Q_i = \int_{T_{Ri}}^{T_{Ri+1}} (C_{pRH}+C_{pR})dT_R - \int_{T_{Si}}^{T_{Si+1}} C_{pSH}dT_S + \int_{t_i}^{t_{i+1}} K(T_R-T_S)dt \qquad (3)$$

By numerical integration following equation (3) - if temperature dependance K = f(T) determined upon calibration measurements is known - we obtain the temperature dependance of total enthalpy change in heated material.

MEASUREMENT METHOD

The measurements were carried out with the equipment for simultaneous thermal analysis made by Fa NETZSCH, mod. STA 429. The output analog signals (0-5 mV) were fed through the control unit (HP 3495A) to the digital voltmeter (HP 3455A). The measurement was controlled by the programmable calculator (HP 85F) which was also used for results processing. At first the course of basic line was determined where the measured as well as the referential sample were formed by same quantity of ignited Al_2O_3 weighed in Pt holders of identical mass. The T_R and $\Delta T = T_R-T_S$ values read in 5 s intervals, while heated up 10 $Kmin^{-1}$, were approximated by the method of Tschebysheff polynominals. The obtained dependance was used when correcting further measurement results.

RESULTS AND DISCUSSION

As example there are given the results obtained by heating $CaCO_3$. The total enthalpy change was computed from the results of thermogravimetric measurement and tabelled values (1). Till the start of $CaCO_3$ decomposition, heat is consumed for $CaCO_3$ heating only (fig.1). During reactive interval, from the start till the end of followed reaction, the total enthalpy change represents the sum of reaction enthalpy change $\Delta H^T_{CaCO_3}$ and heat consumption connected with the heating up of hitherto undecomposed $CaCO_3$ portion and formed reactive products (CaO,

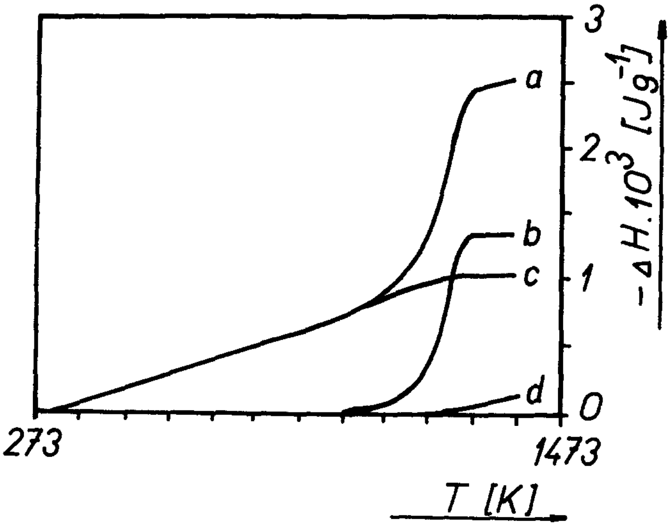

Fig.1 Enthalpy balance of $CaCO_3$ decomposition obtained by computation basing on TG measurement results (a-change of total enthalpy,b-change of enthalpy connected with $CaCO_3$ decomposition,c-heat consumption when heating $CaCO_3$,d-heat consumption when heating products of decomposition)

CO_2).After reaction has finished the products of reaction are heated on and inasmuch we do not take in consideration the liberation of CO_2 from heated sample, the enthalpy balance given in fig.2 represents the graphical illustration of Kirchhoff law. The determination of reaction enthalpy change $\Delta H^T_{CaCO_3}$ can be carried out by the extrapolation of temperature dependance on total enthalpy change before and after followed reaction. However the value of reaction enthalpy change will be determined best with temperature corresponding to the inflective point of temperature dependance in total enthalpy change. The described method of ΔH^T determination is correct in cases of reactions which are not connected with the change of sample mass. In the case of $CaCO_3$ decomposition, when we take into account the liberation of CO_2 from heated sample, the heat after the end of decomposition reaction is consumed only for CaO heating and $\Delta H^T_{CaCO_3}$ determination shows a small error. When evaluating the results of DTA

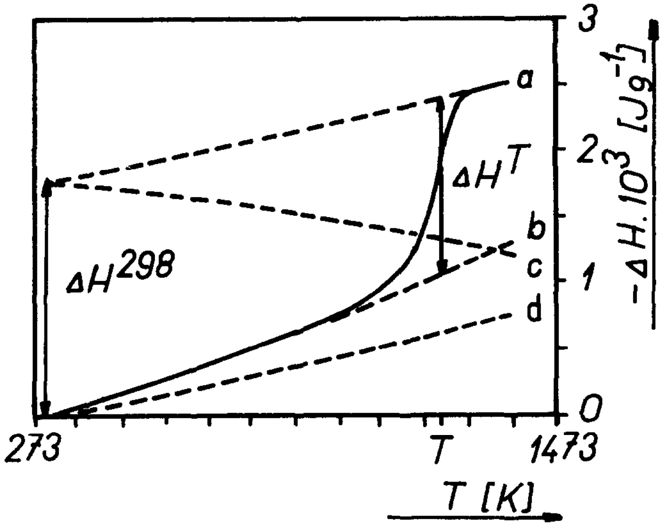

Fig.2 Graphical illustration of Kirchhoff law for $CaCO_3$ decomposition (a-change of total enthalpy,b-heat consumption when heating 1g $CaCO_3$,c-temperature dependance of reaction enthalpy,d-heat consumption when heating 0.56g CaO + 0.44g CO_2)

measurements there was observed only a very small difference between the temperature dependance course in total enthalpy change obtained by computation carried out on the basis of TG measurement results and of same temperature dependance obtained by numerical integration carried out by equation (3) after determining temperature dependance K=f(T).

CONCLUSION

The transformation of DTA curve into the temperature dependence of total enthalpy change while heating up material was in the first place carried out for the possibility to determine heat quantity needed in order to heat up the examined material up to requested temperature. The described method of evaluation results takes into account the temperature dependance of reaction enthalpy change and is proper especially for numerical processing of measurement results obtained if employing the above computing technique.