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CRITICAL STUDY OF THE APPLICATION OF VOLD'S THEORY TO THE DETERMINATION OF REACTION ENTHALPIES FROM DTA TRACES

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ABSTRACT

Many authors have concluded that the decay of a DTA curve to the base line is described by Newton's cooling law beyond the point at which the reaction is complete and this means that the plot of the differential temperature against the time gives a straight line with a slope equal to the thermal conductivity of sample + crucible + thermocouple.

The present work shows that because of kinetic reasons, a linear plot of logarithm of the differential temperature versus time (or temperature) is obtained even if the reaction is still in progress. Hence, Vold's method cannot be used at all for determining reaction heats.

INTRODUCTION

It is very well known that provided that both thermal conductivity and heat capacity of sample crucible + content are equal, the basic equation for a DTA trace becomes

$$\frac{d\Delta T}{dt} = -\frac{K\Delta T}{m_s c_s} + \frac{\Delta H_o}{Mc_s}\frac{d\alpha}{dt} \qquad (1)$$

where ΔT is the difference between the temperature of the sample and the reference at the time t; K the thermal conductivity of the sample crucible + content ; m_s the sample weight; c_s the specific heat of the sample; M the molecular weight of the sample; ΔH_o the molar heat of reaction and $d\alpha/dt$ the rate of fractional transformation of the sample.

According to Vold's analysis, when the reaction is complete, $d\alpha/dt = 0$ and the integration of eqn.(1) leads to (ref.1)

$$\ln \Delta T = -\frac{K}{m_s c_s}\, t + \text{constant} \qquad (2)$$

If the DTA trace is recorded at a constant heating rate $\beta = (T-T_o)/t$ eqn.(2) becomes

$$\ln \Delta T = -\frac{K}{m_s c_s}\, T + \text{constant} \qquad (3)$$

Therefore, a plot of ln ΔT against time or temperature would lead to a straight line beyond the point at which the reaction is complete, the slope of which would yield the constant K provided the specific heat is known. Expressions similar in nature to eqn.(1) to (3) were also obtained from the theories developed by Boer-

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sma (ref.2) Otsubo and Yamaguchi (ref.3), Ozawa (ref.4), Baumgartner (ref.5),Bohon (ref.6) and Vertogradski (ref.7). According to these authors the temperature of the completion of the reaction can be determined by plotting the logarithm of the differential temperature against time. The point at which there is a deviation from a linear relationship is considered as the end point of the transformation. Moreover, Ozawa (ref.4) and Vertogradski (ref.7) consider that the exponential decay law expressed by eqn.(2) can be used for resolving overlappinig DTA peaks.

On the other hand, it has been pointed out (ref.8,9) that once that K has been determined from eqn.(2), the reaction heat ΔH_0 can be obtained by integration of eqn.(1) between the starting time of the reaction, t_0 and the time t at which the DTA trace has returned to the base line. Thus, we get

$$\Delta H_o = \frac{K\ M\ A}{m_s} \qquad (4)$$

A being the area enclosed by the DTA peak.

The scope of the present paper is to determine if the combination of eqn.(1) and (3) necessarily leads to proper values of the reaction heats.

EXPERIMENTAL

A very pure sample of mineral quartz from Spain has been used. Calcined Alumina Merck,a.r. has been used as reference material.

A DTA apparatus Stanton-Redcroft, model 673-4, has been used. Both sample and reference material were put into the respective platinum crucibles which were located in a ceramic block. The two thermocouples for measuring T were located at the bottom of the crucibles according to the DDK arrangement described by Satava and Veprek (ref.8). The DTA traces have been recorded under an atmosphere of air at a heating rate of 14 $K.min^{-1}$. The DTG of sample of magnesita described elsewhere (ref.9) has been recorded at a vacuum of 10^{-4} Torr and at a heating rate of 3,6 and 12 $K.min^{-1}$ using a CAHN electrobalance, model RG, equipped with a derivatograph, model Mark II.

RESULTS AND DISCUSSION

In order to analyse eqns.(2) and (3) the $\alpha \rightarrow \beta$ quartz polymorphic transformation of silica has been studied. The DTA of silica both, pure and diluted with alumina have been recorded in order to approach the heat capacities of both sample and reference, and are shown in fig.1 .

The plots of the logarithm of the values of ΔT taken from fig.1 against absolute temperature beginning at the top of the peak are shown in fig.2 . These results show that at the end of the DTA trace the points lie on a straight line as predicted by eqn.(2). The values of the constant K included in table 1 have been calculated from the slopes of these straight lines after taking into account the values of the specific heat of each sample at the temperature of the polymorphic transformation (573K) as calculated from data taken from ref.10. On the other hand, the values of ΔH_0 determined by means of eqn.(4), once that K is known, are also shown in table 1 .

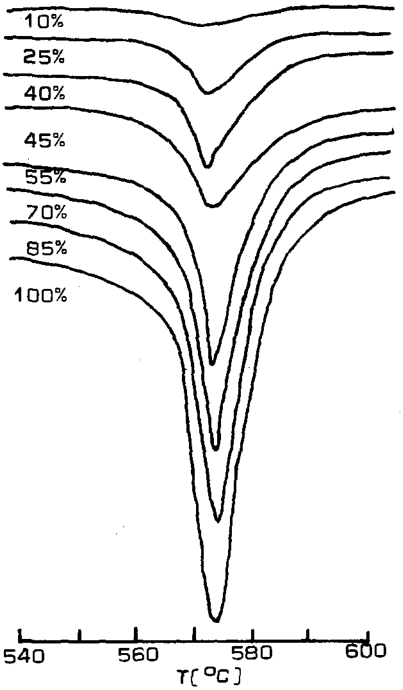

fig.1.- DTA of silica pure and diluted with alumina

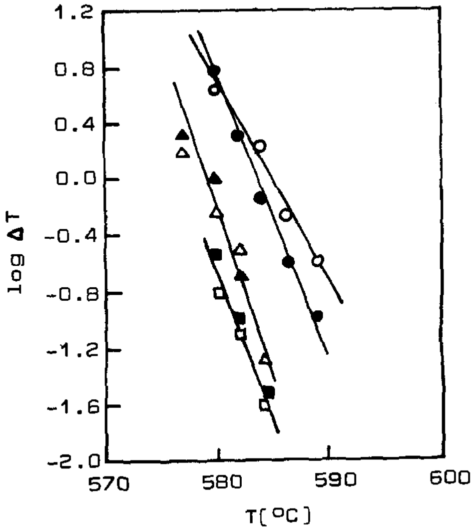

fig.2.- Plot of the values of log ΔT taken from fig.1 as a function of the temperature of the top of the peak.
● pure ; ○ 85% ; ▲ 70% ;
△ 55% ; ■ 45% ; □ 40% ;
⊡ 10% .

TABLE 1

K and ΔH_0 values of several SiO_2 samples

% SiO_2	K(cal/°Cmin)	ΔH_0(cal/g)
100	0.46	5.83
85	0.33	3.46
70	0.55	5.16
55	0.51	3.95
45	0.76	3.11
40	0.60	2.50
25	0.49	1.27
10	0.41	0.44

The above results indicate that the value of ΔH_0 determined from the Vold's theory for the $\alpha \rightarrow \beta$ quartz polymorphic transformation is strongly depending on the dilution of the sample. Taking into account that the difference between the heat capacities of the sample and the reference materials decreases upon increasing the dilution of the sample, it would become closer to the actual one, in proportion as the sample is more diluted. However, data in table 1 point out that regardless of the dilution of the sample the values calculated for ΔH_0 are in a strong disagreement with the theoretical value (2.60 cal/g) taken from ref.10 .

The results obtained in the present paper allow to conclude that Vold's method does not necessarily lead to proper values of the reaction heat and,hence,it cannot be used at all for determining this parameter.

The above statement would be understood by assuming that a exponential decay law like eqn.(3) is accomplished even if the reaction is not complete because of kinetic reasons.In order to check this argument the DTG of magnesite has been recorded by way of example in fig.3.Bearing in mind that according to the Borchardt and Daniel's theory(ref.11) ΔT is proportional to the reaction rate,the logarithm of the values of $d\alpha/dt$ taken from DTG curve in fig.3 as a function of the temperature is shown in fig.4. It is observed that a very good linear correlation has been obtained in spite that,in the case of a DTG trace,the reaction is not complete until the curve returns to the base line.

The results reported clearly show that a linear plot of log $d\alpha/dt$, and hence of log ΔT as a function of the time can be obtained beyond the peak of a DTA trace even if the reaction is still in progress. Therefore,the method outlined by Vold,Ozawa,etc,cannot be used for determining the thermal conductivity (or thermal diffusivity) of sample + crucible + thermocouple.

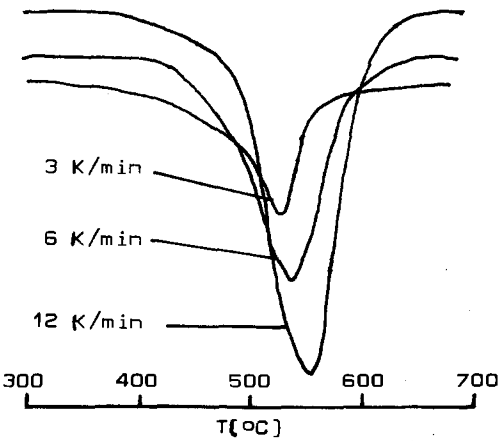

fig.3.- DTG curves of magnesite obtained in vacuum at heating rate of 3, 6 and 12 K/min.

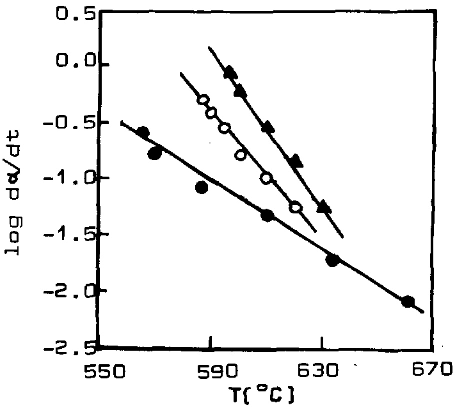

fig.4.- Plot of the values of log$d\alpha/dt$ taken from fig.3 as a function of the temperature of the top of the peak. ● 3 K/min ; ○ 6 K/min; ▲ 12 K/min .

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