SOME ASPECTS OF MINERAL CALORIMETRY

MARK WITTELS,* *Massachusetts Institute of Technology,*
Cambridge, Massachusetts

ABSTRACT

An empirical expression was established relating the thermographic response and heating rate of a differential thermal analyzer. As a result, accurate calorimetric measurements are made at heating rates between 10° C and 30° C per minute.

Samples of large mass are to be avoided when measuring small heat changes by differential thermal analysis. A simple experiment gave a relation between sample mass and thermographic response which indicated that precise calorimetric measurements are made by first determining the optimum mass of the sample to be tested.

INTRODUCTION

The recent improvements of differential thermal apparatus[1] have led to the development of refined heat-measuring techniques. As a result many mineralogic transformations can be detected and energies of transformation accurately measured. A calibration of one of these instruments for micro-calorimetric purposes was described in a recent issue of this journal.[2] In the discussion of that calibration two important features were emphasized: (1) the use of high heating rates, and (2) the testing of samples of small mass.

Subsequent investigation of the thermal characteristics of the apparatus indicated that a more precise relationship exists between the thermographic response and the two features above. An empirical expression was established relating heating rate and thermographic response. In addition, the effect of sample mass on thermographic response was experimentally determined. The conclusions reached in the earlier investigation are upheld by the analysis described below.

RELATION BETWEEN HEATING RATE AND THERMOGRAPHIC RESPONSE

Three additional calibrations of the apparatus were made at heating rates slower than 30° C per minute by the same method described in the earlier investigation. The results of the calibration for the four heating rates are graphically shown in Fig. 1. A cursory examination of this plot reveals that some regular relation exists between the rate of heating
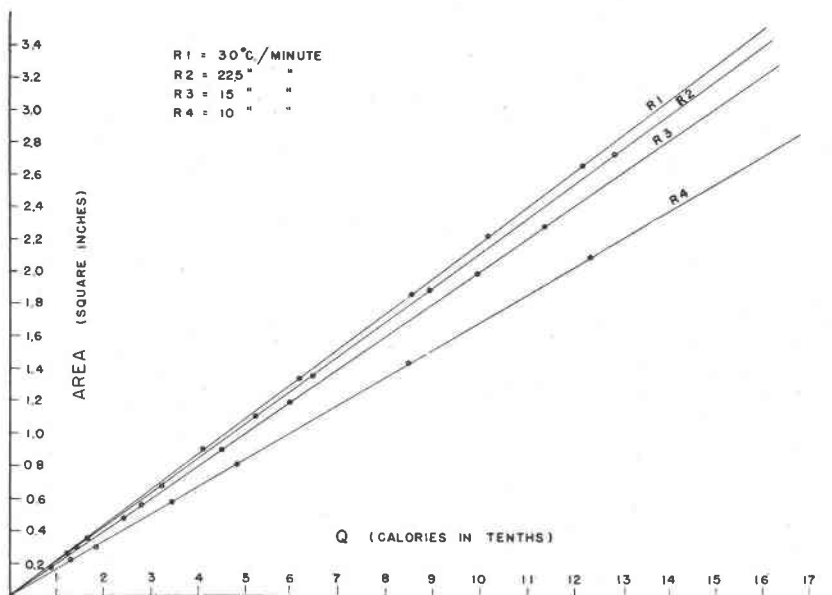
FIG. 1. Thermographic response for four rates of heating.

and the corresponding thermographic responses for a given energy change.

In order to obtain a clearer picture of this relation the following terms are first defined.

From Fig. 1,

A = Area

Q = Calories

$\theta = \tan^{-1}\left(\dfrac{A}{Q}\right)$ measured in degrees and tenths on scale of Fig. 1.

R = Rate of heating

$$Q = \frac{A}{\tan\theta} \tag{1}$$

The use of units in the above terms are prohibitive in the derivations following, obviously, because the numerical values are strictly relative, e.g. square inches versus calories in Fig. 1.

The graphical representation of R and θ in Fig. 1 indicates that some form of exponential relation exists between these two functions. A plot of R versus θ (Fig. 2) as compared to the plot of e^x against x verifies this

observation. The values for R and θ are tabulated below.

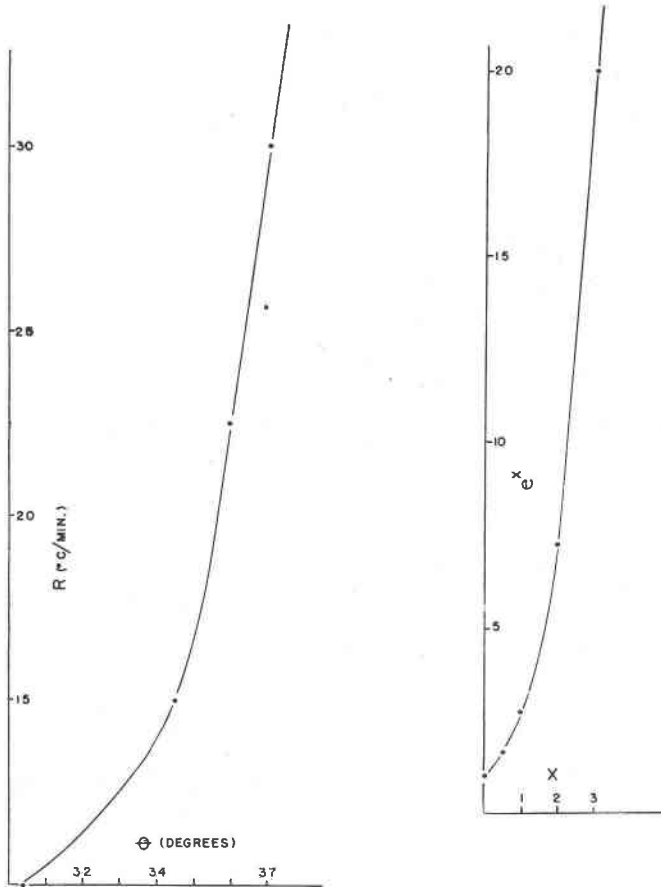| R	θ
10	30.17
15	34.50
22.5	36.00
30	36.92

Fig. 2. Relation between R and θ.

We shall now proceed to find the relation between R and θ so that some function of R can replace θ in equation (1). The solution of this problem is carried out as follows:

$$R = e^{\theta/k} \tag{2}$$

and

$$k \cdot ln\ R = \theta \qquad (3)$$

Substituting the above values of R and θ in equation (3) and solving for k we find the values shown below.

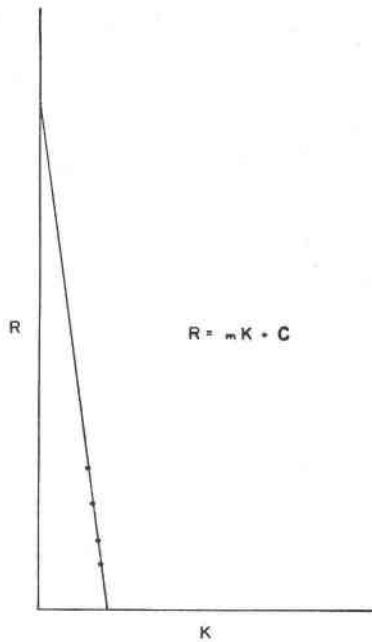| R	θ	k
10	30.17	13.13
15	34.50	12.78
22.5	36.00	11.58
30	36.92	10.82

FIG. 3. Relation between R and K.

It is seen that k is a variable having an inverse relation with respect to R, and so another substitution must be made for k in order to find a more general term that can be substituted for θ in equation (2). Continuing the empirical derivation, a plot of R versus k (Fig. 3) shows the general form

$$y = mx + c$$

where R and k are y and x, respectively, or

$$R = mk + c$$

and,

$$k = \frac{R - c}{m}.$$ (4)

Substituting for k in equation (2) we have,

$$R = e^{m\theta/R-c}$$

$$ln\ R = \frac{m\theta}{R - c}$$

and,

$$\theta = \frac{ln\ R\ (R - c)}{m}$$ (5)

where, $m = 8.10$ and $c = 117.50$.

We now have an expression for θ in terms of R and the constants m and c. A final substitution in equation (1) gives

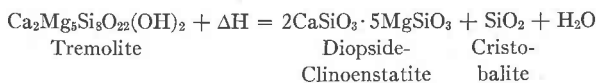$$Q = \frac{A}{\tan\left(\dfrac{ln\ R\ (R - c)}{m}\right)}.$$ (6)

Equation (6) is the expression for calorimetric determinations with the apparatus used in this investigation. Since the derivation of the equation is empirical it is necessary to restrict its validity to the heating rates 10° C to 30° C per minute.

An examination of Fig. 1 indicates that the heating rate of 30° C per minute closely approaches the maximum linear heating rate for the best thermographic response with this apparatus. It is also clear that the thermographic response falls off rapidly at heating rates below 15° C per minute. This is an interesting characteristic in view of the fact that most investigators use a heating rate of about 12° C. per minute.

RELATION BETWEEN MASS OF SAMPLE AND THERMOGRAPHIC RESPONSE

During an investigation of the thermal properties of some amphibole minerals it became desirable to determine the optimum mass of the sample to be tested in the analyzer. The optimum mass is defined here as the minimum mass that can be employed without diminishing the accuracy of the calorimetric measurements.

Preliminary tests indicated that for the reaction[3]

$$Ca_2Mg_5Si_8O_{22}(OH)_2 + \Delta H = 2CaSiO_3 \cdot 5MgSiO_3 + SiO_2 + H_2O$$
Tremolite   Diopside-   Cristo-
                                    Clinoenstatite   balite

ΔH is of the order of magnitude of 5 k.cal. per mole tremolite. Since the

[3] Posnjak, E., and Bowen, N. L., The role of water in tremolite: *Am. Jour. Sci.*, **22**, 203–214 (1931).

thermographic response for this reaction is in the range of 1 square inch per 100 milligrams it appeared likely that smaller samples might be thermally analyzed with no loss in the accuracy of the calorimetric measurements. A series of differential thermal analyses were then run on a random specimen of tremolite, the amounts ranging between 20 and 130 milligrams. These tests were made at a heating rate of 30° C per minute. The resulting thermographic curves describing the reaction are shown in Fig. 4 and the compiled data in Table 1. A graphic representa-
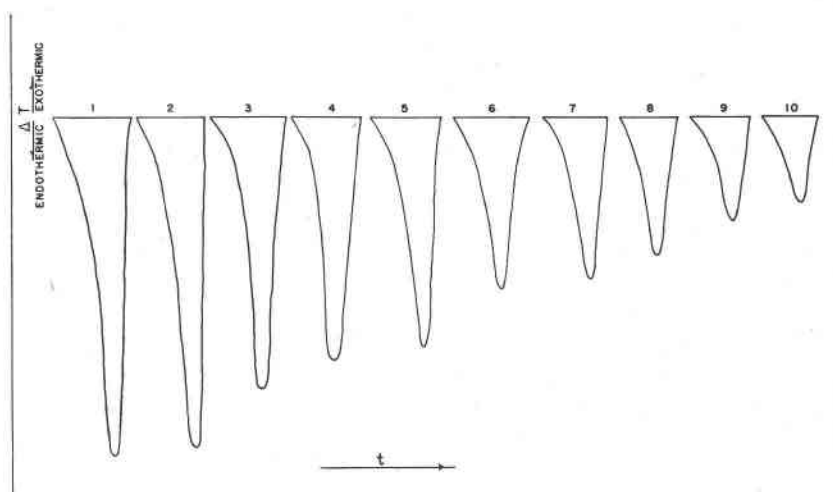

FIG. 4. Thermographic curves.

TABLE 1

Reactive Specimen (Tremolite)		Thermographic Response
Sample Number	Weight in Milligrams	Area in Square In.
1	130	1.50
2	115	1.42
3	90	1.25
4	80	1.16
5	58	0.93
6	52	0.84
7	42	0.70
8	34	0.57
9	25	0.44
10	20	0.35

tion of the data shows the relation between mass of sample and thermographic response in Fig. 5.

The plot is clearly defined and displays a marked departure from linearity when the mass exceeds approximately 60 milligrams. This loss in thermographic response is directly due to thermal gradients in the sample that become noticeably effective in samples weighing more than 60 milligrams. It should be emphasized that this relation is valid only under the conditions described here, and that other analyzers and other reactive substances might give an entirely different relation.
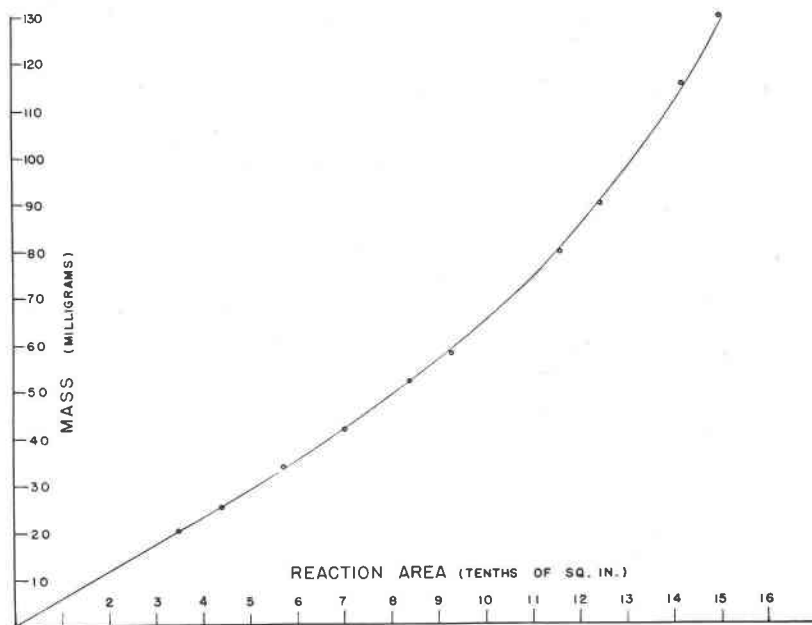

FIG. 5. Relation between mass of sample and thermographic response.

DISCUSSION

The value of Equation (6) becomes apparent when one realizes that many chemical and physical transformations are more easily detected, and more accurately measured by differential thermal analyses at different heating rates. The chemical and physical characteristics of the particular reaction to be studied will govern the heating rate that is best suited for the investigation. Apparatus that is once calibrated can be used to make accurate calorimetric measurements without restricting the analysis to some undesirable heating rate.

The decrease in thermographic response as a result of thermal gradients

in the sample reveals the importance of a proper choice in the mass of sample to be tested. The optimum mass of sample is determined by the thermal characteristics of both the reactive sample and the analyzer apparatus. As a result they must be examined together before any accurate calorimetric measurements can be made.

Increased sensitivity of thermographic response is one of the most-sought improvements in differential thermal analysis equipment. The results of this investigation indicate that further reduction of the mass of the furnace housing would increase the sensitivity in two ways, (1) allow a wider range of heating rates to be used, and (2) permit larger samples to be tested without decreasing the accuracy of the thermographic response. Where heats of reaction are very small, say less than 0.2 cal. per gram, the second improvement would be especially useful.