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A SYSTEMATIC ERROR IN QUANTITATIVE DIFFERENTIAL THERMAL ANALYSIS

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ABSTRACT

The accuracy obtainable by differential thermal analysis is limited by a systematic error which is due to the apparent heat transfer coefficient and the apparent heat capacity of the sample and the sample holder. These thermal parameters must be evaluated in any method aimed at quantitative analysis. It is suggested that in many cases, the logarithm of the peak area furnishes an approximate measure of these parameters. The ratio of the logarithms of the areas obtained with the calibration substance and the sample substance, furnishes a possible correction factor for the empirical calibration constant.

INTRODUCTION

In the common procedure of quantitative differential thermal analysis, the calibration of the instrument is carried out with a substance whose heat of reaction is known. The heat of reaction (Q) of the sample is then related to the area under the peak by

$$Q = \psi \int_{t_i}^{t_f} \theta \, dt \tag{1}$$

where ψ is the empirical proportionality constant found with the calibration substance, and θ is a linear function of the e.m.f. generated by the differential thermocouples in response to the differential temperature. The limits of integration, t_i and t_f, are the initial and final time of the detectable differential temperature. The latter are generally taken to be equivalent to the limits of the thermogram peak[1]. Over the years, numerous experiments have shown Eqn. (1) to be, at best, only approximately true. Careful investigations proved that there are many factors which cannot be accommodated by a simple proportionality constant, among these are changes in the specific heat, the density, and thermal conductivity of the sample during the reaction. For these and other known causes, the accuracy achievable to date by the methods of DTA[2] is not better than 5%. It may be unrealistic to expect a much higher accuracy. However, any attempt directed toward finding a quantitative or improved semiquantitative method ought to shed light on the nature of the problems involved, and possibly pave the way to new approaches and techniques.

In attempting to isolate and correct a systematic error in DTA, the present investigation is confined to measurements of heats of fusion. No consideration is given to such complicating factors as variation of the atmosphere during the reaction, the time lags associated with rate-controlled reactions or the effect on the peak area of different types of sample holders. All experiments were carried out with sample holders consisting of individual (*i.e.* mutually isolated) cups. In order to obviate the need to consider the effects of heat radiation, the same material was used as "calibrating substance" and as "sample".

DISCUSSION

Previous work

The attempts made over the years to find a technique or method of quantitative differential thermal analysis may be divided into two groups: Those that are based on the identification and evaluation of the various processes and physical variables of DTA, and those that deal with their combined effects. Thus, Deeg[3] whose work belongs in the former group identified 16 variables, Dilaktorskii and Arkhangelskaja[4] listed 25. Among these are the tendency of the sample to swell or shrink, its thermal conductivity and heat capacity, its particle size, the size of the thermocouple junctions, and the sample holder geometry. The approach characteristic of the second group implies that the several variables are part of a system whose physical characteristics change continuously and cannot be evaluated separately. The area under the peak is considered a function of all the variables combined. Thus, Boersma[5], suggesting the use of separate crucibles or cups for the sample and the inert reference substance, and the placement of the thermocouples outside but in contact with the sample cups, used heat transfer equations to derive relatively simple expressions which incorporate and generalize the effects of several variables. The effect of the thermocouples on the size of the peak area was investigated by de Jong[6]. He found that for cylindrical sample holders, maximum sensitivity can be achieved if the ratio of the thermocouple wire radius to that of the sample is 0.2. The underlying assumption in these papers, and those quoted below, is that it is nearly impossible to evaluate the numerous variables and that it is therefore desirable to treat the sample, the sample holder assembly, and the thermocouples, as a single unit whose response to changes in temperature can be characterized by mathematical expressions. This is also the approach taken here.

The area under the thermogram peak

The literature abounds in apparently conflicting examples regarding the validity of empirical calibration procedures involving the use of substances of known heats of reaction. Barshad[7] working with kaolinite (a clay mineral) and $CaSO_4 \cdot 2H_2O$ presented data showing that the peak area is proportional to the concentration of the sample, provided that the sample is sufficiently diluted so that its thermal conductivity is similar to that of the calibrating substance. Work by de Bruijn and van der Marel[8] illustrates that the linear relationship implied by the use of an empirical calibration constant is only approximately correct. Their data (Fig. 1) show a systematic deviation of the observed areas from those computed with the calibration constant. In most cases, the peak areas observed tend to be larger than expected, the differences becoming more pronounced and therefore more easily detected for larger areas. Sabatier[9] carried out experiments with various amounts of kaolinite. His data show a similar trend to that observed by de Bruijn and van der Marel. Wittels[10,11] reported

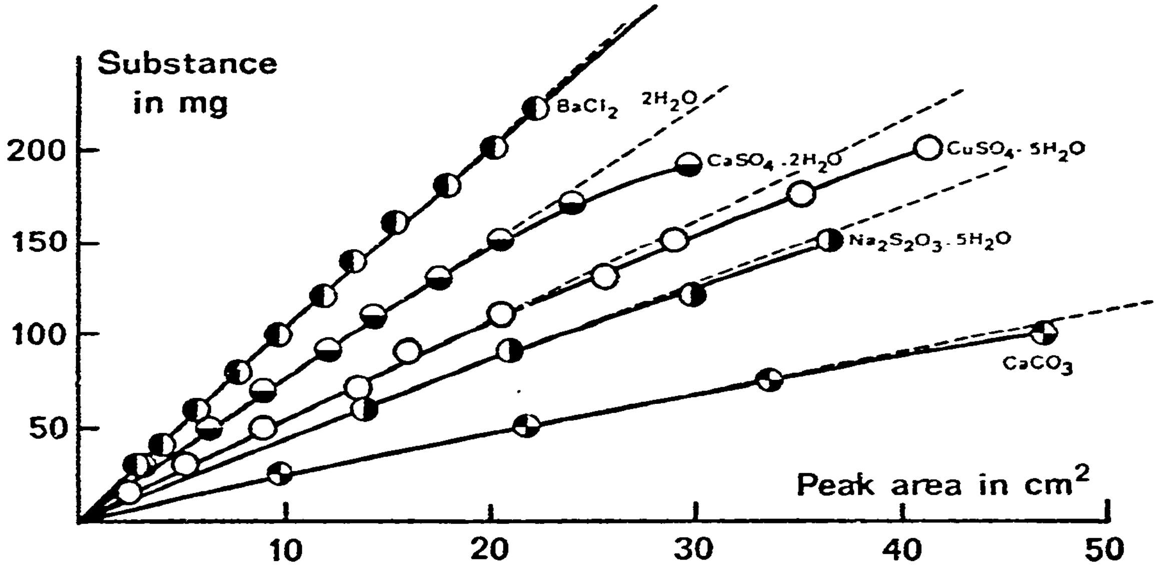

Fig. 1. Peak areas *vs.* weights of reactants. The calibration lines are dashed. Redrawn after de Bruijn and van der Marel[8].

that if the heating rate is kept constant, the plot of area *vs.* heat is linear only if the sample is relatively small. An attempt to define the nature of the proportionality constant ψ, and by implication its non-linearity, led Sturm[12] to an equation that included the apparent thermal conductivity and the apparent heat capacity of the total sample. He points out that the total sample includes an undefined portion of the thermocouple wires, which, under conditions of DTA, perform the double role of temperature transducer and heat sink. A somewhat similar expression was recently derived by Ozawa, Isozaki, and Negishi[13]. The non-linearity of ψ was first implied by Vold[14] who pointed out that the high temperature end of most thermograms, representing the post-reaction portion, plots as a straight line on semi-log paper. From the slope of that line, the thermal characteristics for the total sample may be found. Bohon[15] illustrated the soundness of this approach in his work with explosives. The rapid thermal reactions yield sharp asymmetric exothermic peaks in which the post-reaction part of the curve can easily be identified. The latter is used to plot the log θ *vs.* time, or temperature for linear heating rates, where θ is the differential temperature (Eqn. 1). Bohon shows that in these reactions, the heat liberated equals the product of the sample's apparent heat capacity, apparent heat transfer coefficient and ψ.

Strella[16] developed an expression for the heat front advancing through a cylindrical sample holder, in which the term containing the thermal parameters appears in the exponent. Dosh[17] reports results of experiments with different sample cups, carried out at room temperature, which demonstrate that under static conditions the sample holders approach thermal equilibrium in a manner analogous to that of a single capacitance system.

It should be pointed out that the references quoted here suggest directly or by implication that the thermal parameters (*i.e.* the apparent heat capacity and the apparent heat transfer coefficient of the total sample) are significant factors in quantitative DTA. Further, in mathematical expressions relating the quantity of heat to the area under the thermogram peak, the thermal parameters occur either in the exponent or in an expression which can be transformed into an exponential form.

The proposed correction factor

The discussion of the systematic error and its proposed correction factor is facilitated by the schematic presentation in Fig. 2. Here, the response of a DTA

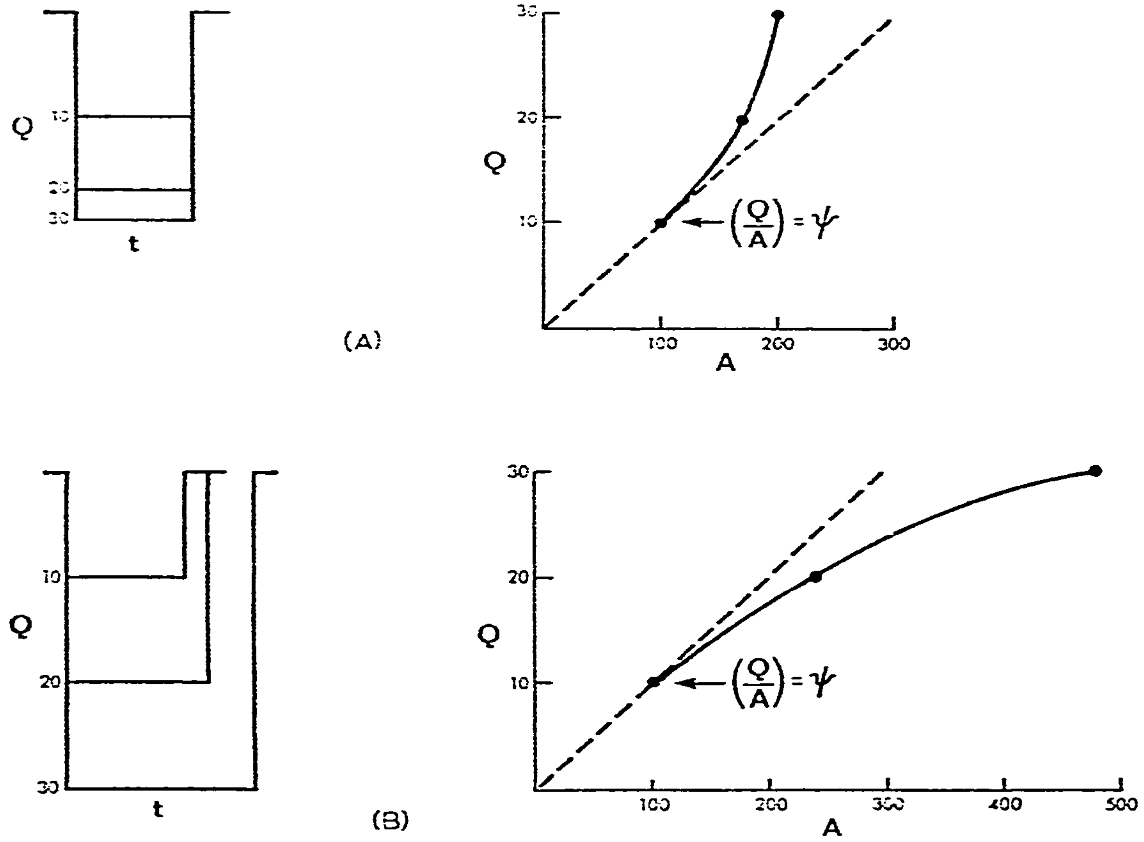

Fig. 2. Schematic presentation of the hypothetical peak areas for three quantities of heat and the corresponding points on the area vs. heat curves. (A) The expected results if the heat capacity only were operative. (B) The expected results if the heat transfer coefficient only were operative.

system to three quantities of heat is averaged so that the area under the peak is in the form of an easily visualized step function. In Fig. 2 (A) only the heat capacity is operative. The amount of heat transferred per unit time should increase with the thermal potential. The expected area *vs.* heat graph is shown to the right. The slope of the linear calibration curve is determined by the first Q/A ratio. The computed values of the heats of reaction will tend to be smaller than the true values. In Fig. 2 (B) the expected response of a system in which only the heat transfer coefficient is operative is shown. Here, the amount of heat transferred per unit time would be constant; therefore the time required to dissipate heat would vary with its quantity. The area *vs.* heat graph shows the systematic error to be positive, that is, the computed quantities of heat will be successively larger for the larger areas. In actual cases, the systematic error is due to both thermal parameters of course, and, depending on which of the two is more prominent, may be characterized by positive or negative deviations from the linear calibration curve (Figs. 1, 3, and 4).

The area under the peak is therefore a function of the instantaneous differential temperature due to the heat generated or absorbed by the sample and the rate of recovery, that is, the rate of approach to the dynamic quasi-equilibrium existing between the instantaneous temperatures of the sample and the furnace (or the reference substance). The latter may be thought of as a quasi-steady state heat reservoir. Therefore, the size of the area is a function not only of the heat to be measured, but also of the rate at which the heat is transferred into or out of the sample. Keeping in mind the dependence of the rate of heat dissipation on the instantaneous differential temperature, and the fact that in most equations developed for quantitative DTA the thermal parameters occur in exponential form, we may argue phenomenologically that an approximation relating the area under the peak to the heat of the reaction and the thermal parameters may take the following form,

$$\mathrm{f}(\theta)\,\mathrm{e}^{-(\mathrm{T.P.})t} \approx \Delta \text{ peak area} \tag{2}$$

where $\mathrm{f}(\theta)$ is a linear function of the differential temperature due to the reaction. This quantity is dissipated as the sample and the sample holder tend to return to the quasi-steady state, *i.e.* to the almost constant differential temperature between the sample and the furnace. The symbol (T.P.) stands for the thermal parameters, that is, the apparent heat transfer coefficient and the apparent heat capacity. The right-hand side is a non-defined portion of the peak area. From Approximation (2) we may argue that the logarithm of the area varies directly with the thermal parameters. Thus

$$-(\mathrm{T.P.})t \approx \ln \frac{\Delta \text{ peak area}}{\mathrm{f}(\theta)} \tag{3}$$

It must be emphasized that Approximations (2) and (3) have not been derived but are suggested by the nature of the area *vs.* heat curves. Rough curve-fitting suggests a function involving the logarithm of the area. Also, in a number of equations that have been derived for quantitative DTA, the thermal parameters appear either in the exponent or in an equivalent expression. Further, in equations describing transient voltages in electrical analogs, that is, in single capacitance systems, the terms containing the conductance and capacitance also appear in the exponent. In view of the above, the following is suggested.

$$\ln(A_c+1)\frac{Q_c}{A_c} \approx \ln(A_s+1)\frac{Q_s}{A_s} \tag{4}$$

where the subscripts refer to the calibration substance and the sample. Changing to common logarithms, we write

$$\frac{\log(A_c+1)}{\log(A_s+1)}A_s\Psi \approx Q \tag{5}$$

where $\psi = Q_c/A_c$, the empirically determined proportionality constant (Eqn. 1), and Q is the sample's heat of reaction.

The ratio of the logarithms of the appropriate areas in the suggested correction factor for ψ. The correction factor was tested in a number of DTA runs, discussed below. It was also used on data gleaned from the literature.

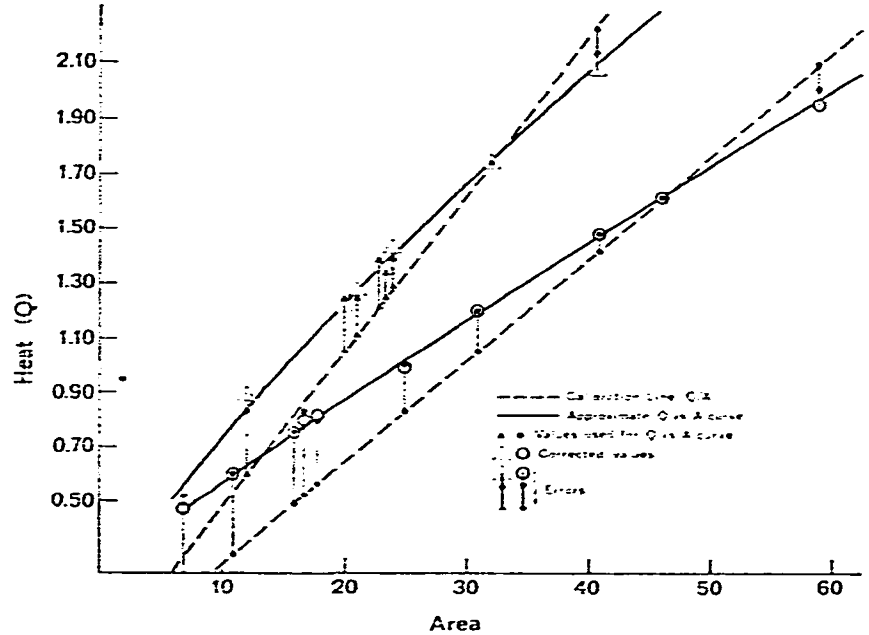

Fig. 3. The area *vs.* heat curves for the data in Table I.

The application of the correction factor

Table I is a summation of the results of two sets of experimental runs. A standard, commercial instrument was used in these experiments. The sample holders consisted of separate crucibles, supported on ceramic tubes. The thermocouples were external and in contact with the sample holders. The experiments were carried out during two periods and under slightly different conditions. The latter accounts for the different proportionality constants ψ used for each set of runs. The purpose of the experiments was to test the effectiveness of the correction factor. For that reason, the individual runs were designed to result in large, systematic errors. This was achieved by using a variety of size distributions and by varying the techniques of packing the sample holders. Although no undue precautions were taken with weighing and preparing the samples, it must be emphasized that the large errors in columns 6 and 7 were the desired and expected results. The effectiveness of the correction factor can be assessed by comparing the values in columns 6 and 8 and also in columns 7 and 9. The data of Table I are plotted in Fig. 3, where the general trends can be more easily visualized. It should be noted that in these experiments, designed to increase the systematic error, the nature of the area *vs.* heat curve is identical to those obtained by other workers who, it must be assumed, took pains with careful sample preparations. The data summarized in Table II and Fig. 4 were obtained by Wittels[11], who used tremolite, a silicate of Ca and Mg in amounts varying from 20 to 130 mg. His data were used here to test the correction factor on a series of runs whose area *vs.* heat

TABLE I

THE APPLICATION OF THE CORRECTION FACTOR TO DATA WITH LARGE SYSTEMATIC ERRORS

Sample[a]	Size[b]	Weight[c]	Area[d]	Q_{theor}	$Q(A)$[f]	Error[g]	$Q(A, CF)$[h]	Error[g]
1 Na	170	31.0	22.9	1.39	1.25	−10.0	1.37	−1.4
2 Na	St.	31.0	24.1	1.39	1.31	−5.8	1.44	+3.6
3 Na	170	39.0	31.9	1.74	$\psi = 0.54$ for samples 1–8			
4 Na	St.	28.0	20.0	1.25	1.09	−12.8	1.25	0.0
5 K	170	29.8	12.1	0.83	0.66	−20.5	0.90	+8.5
6 Na	170	48.0	40.5	2.14	2.20	+2.8	2.06	−3.7
7 Na	St.	28.0	20.8	1.25	1.13	−9.6	1.27	+1.6
8 Na	St.	29.9	22.7	1.34	1.24	−7.5	1.35	+0.8
9 Na	170	45.0	59.4	2.01	2.08	+3.5	1.95	−2.5
10 K	270	21.8	11.0	0.61	0.39	−3.6	0.61	0.0
11 Na	270	26.8	31.0	1.20	1.09	−9.0	1.20	0.0
12 Na	270	18.0	17.9	0.81	0.63	−22.3	0.83	+2.5
13 Na	270	36.0	46.0	1.61	$\psi = 0.35$ for samples 9–18			
14 K	270	37.7	25.0	1.05	0.88	−16.0	1.04	−1.0
15 Na	170	17.0	15.8	0.76	0.55	−22.7	0.76	0.0
16 K	St.	18.6	7.0	0.52	0.25	−52.0	0.48	−7.7
17 Na	St.	33.0	40.8	1.48	1.43	−3.4	1.48	0.0
18 K	270	30.2	17.0	0.84	0.60	−28.6	0.80	−5.0

[a] Na = $NaNO_3$, K = KNO_3; both were diluted in calcined Al_2O_3. [b] Particle size: 170 = retained on mesh 170 (particles > 0.088 mm); 270 = retained on mesh 270 (0.088 mm > particles > 0.053 mm); St. = particle size distribution unknown (stock). [c] Weight of reactant (mg). [d] Weight of cut-out of the area under the thermogram peak (mg). [e] Heat of fusion (cal). [f] Heat computed by use of empirical proportionality constants; samples 3 and 13 (cal). [g] Percentage errors for values in adjacent columns. [h] Heat computed with the aid of the correction factor (cal).

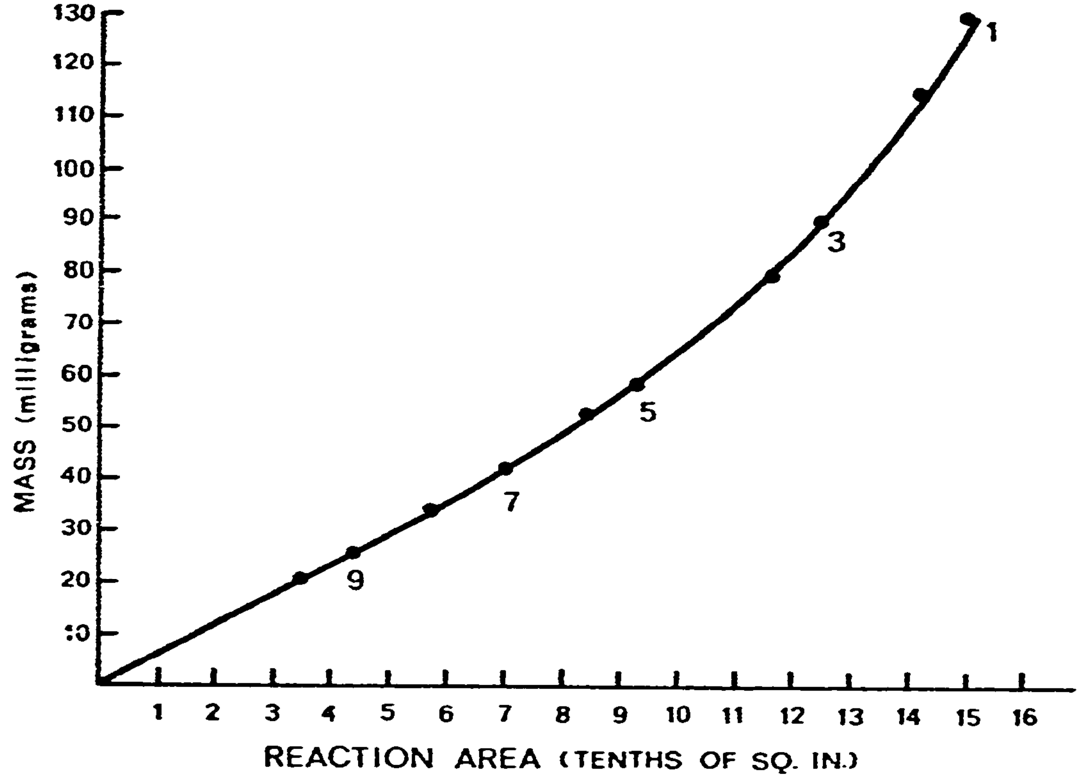

Fig. 4. The area *vs.* weight of reactant curve for the data in Table II. Redrawn after Wittels[11].

TABLE II

THE APPLICATION OF THE CORRECTION FACTOR TO DATA OBTAINED BY WITTELS[11]

Sample	Weight[a]	Area[b]	$Q(A)$[c]	Error[d]	$Q(A, \text{CF})$[e]	Error[d]
1	130	1.50	93.3	−28.4	129.7	−0.2
2	115	1.42	88.3	−23.2	118.3	+2.9
3	90	1.25	77.8	−13.5	95.6	+6.2
4	80	1.16	72.2	−9.7	84.2	+5.2
5	58	0.93	$\psi = 58/0.93 = 0.62(10^{-2})$			
6	52	0.84	52.2	0.0	48.5	−6.7
7	42	0.70	43.5	+3.6	35.4	−15.7
8	34	0.57	35.5	+4.5	24.2	−28.6
9	25	0.44	27.4	+9.6	15.1	−39.6
10	20	0.35	21.8	+9.0	9.9	−50.0

[a] Weights of tremolite samples (mg). [b] Areas under the thermogram peaks (in.^{2}). [c] Heats of reaction taken to be proportional in value to the weight of the reactant (column 2). [d] Percentage errors of values in adjacent columns. [e] Heats of reaction computed with the aid of the correction factor [Approximation (6)].

curve resembles that in Fig. 2(A). It is significant that the areas observed are in agreement with those computed with the proportionality constant for samples up to 60 mg. For larger samples, the computed areas are larger than those observed; that is, the area *vs.* heat curve deviates from the calibration line progressively toward smaller areas. The correction factor applied to Wittels' data was

$$\frac{\log (A_s+1)}{\log (A_c+1)} A_s \Psi \approx Q \tag{6}$$

Here, the logarithm of the area of the sample appears in the numerator and that of the calibration substance in the denominator. The median value (Table II, sample No. 5) was arbitrarily chosen to serve as the "calibration substance", that is, $\psi = Q_5/A_5$. For samples smaller than 60 mg, the application of the correction factor gave erroneous results.

CONCLUSION

It is suggested that a systematic error exists in DTA, and that it is probably due to the tendency of each element of the total sample, that is, the sample substance and an undefined portion of the sample holder assemblage, to return to the quasi-steady state in a manner approximately analogous to that of a single capacitance system. Further, for simple reactions, the rate of approach appears to depend on the apparent heat transfer coefficient and the apparent heat capacity of the total sample. Based on the general trend of many area *vs.* heat curves, on the electrical analog of a single capacitance system, as well as on the fact that in most expressions developed for quantitative DTA the thermal parameters appear in the exponent, lead to the suggested correction factor for the systematic error. It must be emphasized that the correction factor as presented here is not universal and may be used only in those cases where the general trend of the area *vs.* heat curve is known, and where the reaction does not involve heat transfer by gases or other complicating mechanisms of heat exchange. The correction factor was introduced mainly to test the contention that low accuracy in DTA may be largely due to a systematic error and that the error depends on the size of the area under the peak.

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