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THE DETERMINATION OF HEATING RATE CHANGES IN THERMAL ANALYSIS EQUIPMENT

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ABSTRACT

By recording the first derivative of the sample temperature, dT_s/dt, as a function of time or temperature, small changes or fluctuations in the furnace heating rate can be easily detected. This method is far more sensitive to heating rate changes than is the usual temperature–time plots. First derivative temperature curves are also given for the dehydration of $BaCl_2 \cdot 2H_2O$ and $CuSO_4 \cdot 5H_2O$.

INTRODUCTION

The precise determination of the heating rate of thermal analysis equipment is not an easy matter. The usual time–temperature curves are insensitive to small changes in the heating rate, especially at low rates of heating. They are useful, however, to detect gross changes in the heating rate or if the heating program is temporarily interrupted. Many commercial thermal analysis instruments have provision for plotting the time–temperature curve as well as the desired thermal analysis curve.

In differential thermal analysis (DTA) or differential scanning calorimetry (DSC), unsymmetric loading of the sample holders, e.g., large sample mass and empty reference container, permit small variations in the heating rate to be observed. This technique was first reported by Barrall and Rogers[1] who also studied the effect of unsymmetrical thermocouple location in a block-type sample holder. In the latter case, the thermocouples were displaced towards the side, top or bottom of the sample holder, causing the displaced thermocouple to heat up more quickly than the symmetrically located one and hence giving a displacement of the baseline. The displaced baseline curve indicated the heating rate fluctuations more than the curve obtained with symmetrically located thermocouples. Much larger fluctuations in the DTA curve were noted if a non-uniformly packed sample was also present. Wendlandt[2] has also described the use of an unbalanced DTA system to detect small changes in the heating rate program.

Fluctuations in the furnace heating rate can be easily detected in the Deltatherm calorimeter, as described by Dosch and Wendlandt[3]. The heat capacity of the sample,

C_p, is given by the equation:

$$C_p = \frac{k_1 P}{m}\left(\frac{dT}{dt}\right)$$

where P is the power, m the sample mass, dT/dt the heating rate, and k_1 a constant. For a constant dT/dt, the expression simplifies to:

$$C_p = \frac{k_3 P}{m}$$

Thus, the heat capacity is directly proportional to the power, P, assuming a constant heating rate. The power curve is thus sensitive to minute changes of dT/dt and can serve as a measure of its constancy.

A simple yet sensitive method for detecting heating rate fluctuations in thermal analysis is described here, which is based upon recording the first derivative of the sample, reference, or furnace temperature. Small changes in the heating rate program can be easily observed in the derivative curve, which is plotted as a function of time or temperature.

EXPERIMENTAL PART

The experimental arrangement, as shown in Fig. 1, was employed for the derivative temperature measurements. A laboratory constructed DTA furnace and sample holder[4] was used as the test system. The voltage output from thermocouple T_s, was differentiated with respect to time using a Harrop analog computer (Columbus, Ohio). This function was then recorded, along with the voltage output from thermocouple T_s, on a two-pen Linear Instruments potentiometric strip-chart

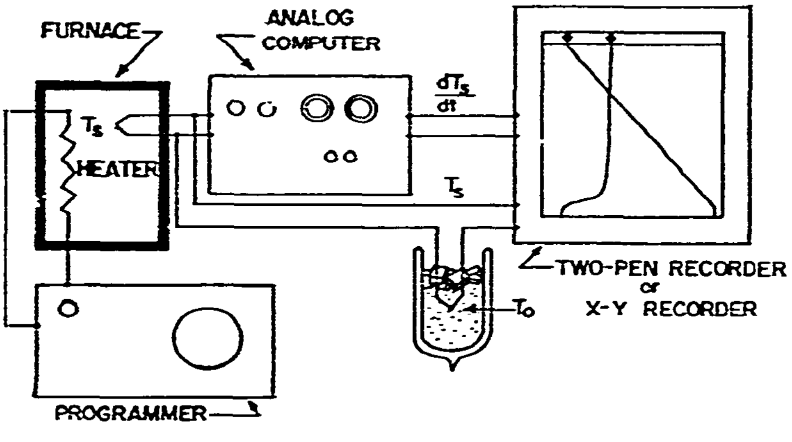

Fig. 1. Experimental arrangement for the determination of heating rate fluctuations of a DTA furnace and sample holder.

recorder (Irvine, Calif.). An ice–water mixture contained in a Dewar flask was used to maintain the reference thermocouple, T_0, at 0 °C. The heating rate of the furnace was controlled by a T & T Controls Programmer, Model No. TPC-2000 (Media, Pa.).

RESULTS AND DISCUSSION

The furnace temperature programmer for thermal analysis instrumentation should be capable of linear temperature control over a number of different temperature ranges. The heating rates should be constant and reproducible as fluctuations in the heating rate, as pointed out by Theall[5], will create spurious baseline shifts or even peaks in the DTA curve. In TG, small fluctuations in the heating rate are not as serious as they are in DTA but major changes can result in curve slope changes if time-base recorders are employed[6].

There are many different types of temperature programmes available, ranging from simple motor-driven variable voltage transformers to more sophisticated feedback, proportional-type programmers. In the case of the latter type, when the error signal between the command voltage and the output of the control signal differ by an amount more than the "dead-band" of the control amplifier, the error signal is amplified and a proportional amount of electrical power is applied to the heater. The heating rate fluctuations of this type of programmer are usually about ±5% or ±0.1 °C min^{-1}, whichever is greater. The accuracy of this type of programmer is controlled by the output of the control thermocouple and the internal power supply drift rate. Specifications on other programmers in commercial thermal analysis instruments vary from ±0.25 to ±1% linearity for any 100 °C temperature interval or slightly greater than this for the complete temperature range.

The temperature–time curves and the derivative of the temperature ($\mathrm{d}T_s/\mathrm{d}t$)–time curves are illustrated in Fig. 2. Three furnace heating rates are shown for each set of curves, namely, 5, 10 and 20 °C min^{-1}. Although the temperature–time curves appear to be straight lines (above 2 min), the derivative curves contain numerous fluctuations after an initial equilibration period. If there were no heating rate fluctuations, the derivative curves would appear as straight lines, thus, the curve irregularities are indicative of small changes in the heating rate. These changes are not observable on the temperature–time curves. The least heating rate changes are found with the slower heating rate, 5 °C min^{-1}, while the largest are at 20 °C min^{-1}.

Deliberate alterations of the furnace heating rate are shown in the two curves in Fig. 3. Using a nominal heating rate of 10 °C min^{-1}, heating rate changes were manually made at the points indicated on the temperature–time curves. Changes of −1 to −2 °C min^{-1} are observed as slight increases in the derivative curve while the +4 °C min^{-1} change appears as a decrease. As expected, there is a time lag between the heating rate change of the programmer and the response of the derivative curve. Also, the heating rate changes are not evident on the temperature–time curve except for the large +4 °C min^{-1} change. Thus, the derivative curve is a more sensitive indicator of the heating rate fluctuations.

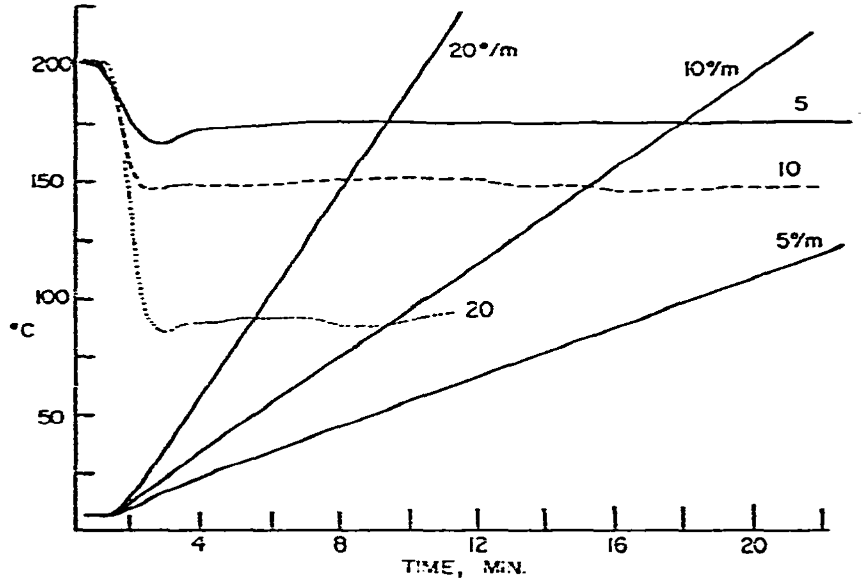

Fig. 2. Temperature–time and $\mathrm{d}T_s/\mathrm{d}t$ curve for DTA furnace and sample holder at heating rates of 5, 10 and 20°C min^{-1}.

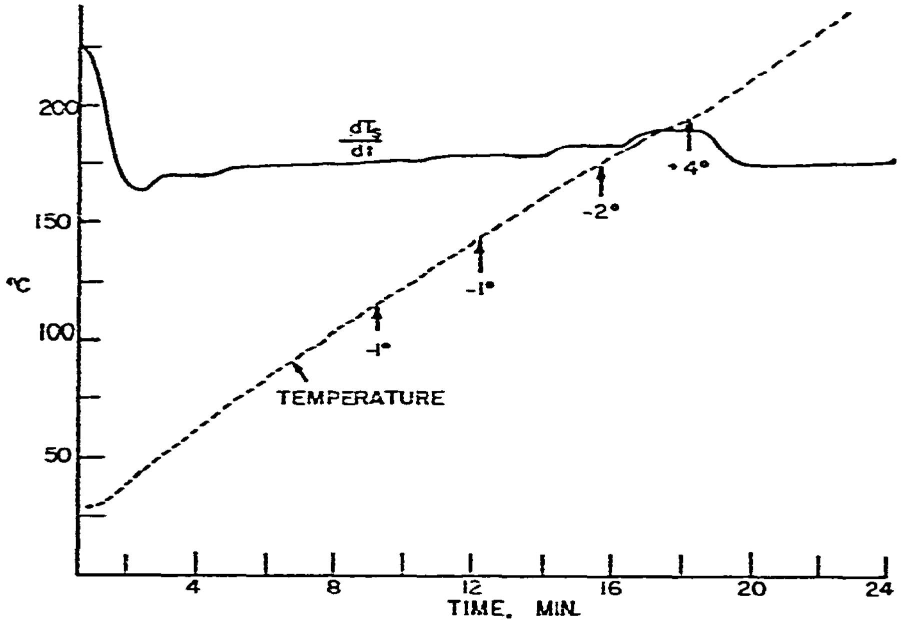

Fig. 3. Deliberate changes of heating rate and their effect on the temperature–time and derivative temperature curves (10°C min^{-1}).

Derivative temperature curves for the three heating rates, 5, 10 and 20 °C min^{-1}, plotted against the reference temperature are shown in Fig. 4. Small short-term random changes in the heating rate are evident in the 5 °C min^{-1} curve but there are longer-term events in the 20 °C min^{-1} curve. Also illustrated is the longer temperature equilibration time (i.e., higher temperatures) required for the faster heating rate; for 5 and 10 °C min^{-1}, it is about 50 °C while for 20 °C min^{-1} it is almost 100 °C.

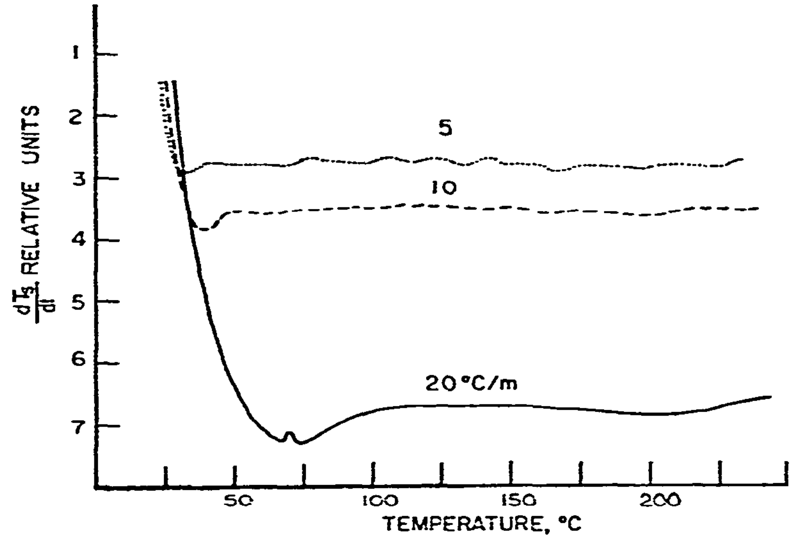

Fig. 4. Derivative temperature curves as a function of reference temperature.

The magnitude of the derivative curves is proportional to the furnace heating rate, as shown in Fig. 5. The derivative is not a linear function of the heating rate because it increases more rapidly at the higher heating rates (> 10 °C min^{-1}). This is

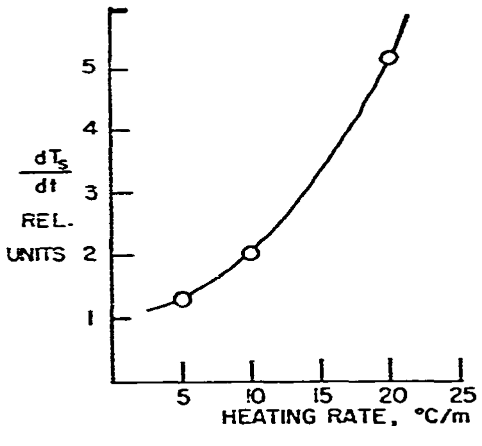

Fig. 5. The change of the derivative of temperature with heating rate.

not a serious limitation, however, because the heating rate fluctuations are the main concern here.

It was of interest to record the derivative temperature curve of a sample that undergoes a dehydration reaction in the temperature range of interest. Burgess[7] has suggested this method of recording as early as 1908 and it was recently mentioned by Blazek[8], the latter describing it as a derivative direct heating curve. Since this method uses only a single, rather than a double thermocouple system, it should simplify DTA instrument design. The data obtained by the derivative method are not equivalent, as will be seen, with the differential thermal analysis technique.

The dT_s/dt curves of two metal salt hydrates are shown in Fig. 6. For $BaCl_2 \cdot 2H_2O$, the derivative curve shows the usual equilibration change followed by curve changes due to the deaquation of the 2- to the 1-hydrate followed by the deaquation of the latter to anhydrous $BaCl_2$. For the first transition, the derivative curve indicates the beginning of the deaquation reaction starting at about 100 °C and has maximum and minimum peak temperatures of 125 and 135 °C, respectively. Unfortunately, the last transition was incomplete due to the maximum temperature limit of the recorder (250 °C).

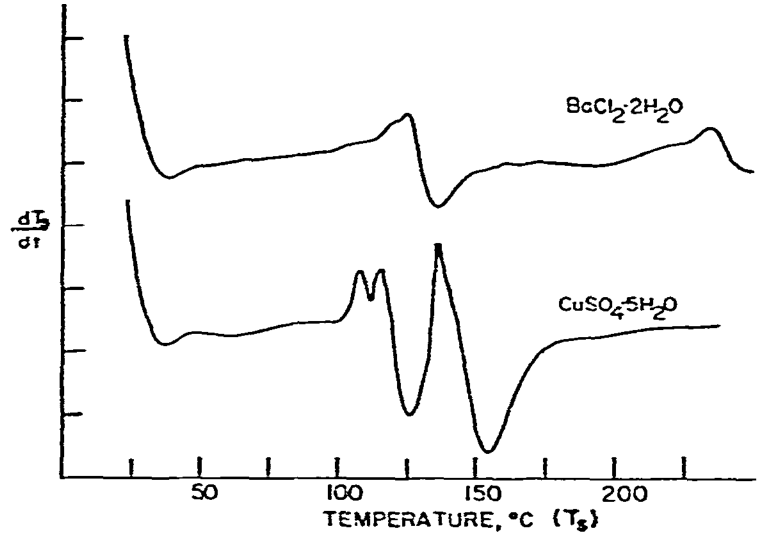

Fig. 6. Derivative temperature curves of $BaCl_2 \cdot 2H_2O$ and $CuSO_4 \cdot 5H_2O$ (heating rate of 10 °C min^{-1}).

For $CuSO_4 \cdot 5H_2O$, more maxima and minima curve peaks are indicated due to the greater complexity of the deaquation reactions. Peak maxima temperatures of 107, 115 and 135 °C, respectively, were observed as well as peak minima temperatures of 112, 125 and 155 °C, respectively. All of the curve peaks were caused by the deaquation transition of $5 \rightarrow 1$ hydrate, which involves a number of intermediate steps[9] such as the formation of a liquid water phase and the resultant saturated solution of the salt.

In both of the compounds studied, it is evident that the deaquation reactions cause a drastic perturbation of the sample heating rate. A single thermocouple DTA system is possible using this approach but the interpretation of the resultant derivative temperature curve is more difficult. Curve peak area integration is impossible thus preventing the use of these curves for quantitative studies. However, for qualitative purposes, small thermal transitions are easily detectable as would be changes in the baseline due to second order transitions, e.g., glass transitions in polymers.

ACKNOWLEDGMENT

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