Thermochimica Acta, 166 (1990) 251–265
Elsevier Science Publishers B.V., Amsterdam

COMBINING DSC AND TG DATA FOR MEASURING HEATS OF REACTION *

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ABSTRACT

The differential scanning calorimeter (DSC) has been used for numerous thermodynamic analyses and has many advantages over classical calorimetry. In spite of the advantages there are limitations in the accuracy that can be obtained. There are many variables which control this, but in order to obtain a more accurate measurement these variables and their effects must be addressed. This approach will focus on the error produced from the weight change in the sample during an experiment. The information produced from the thermogravimetric analyzer will be used to enhance the heat of reaction calculations from a DSC experiment. An approach to justifying the integrity of the enhanced calculations will be by comparing quasi-thermal runs on a DSC with theoretical values.

INTRODUCTION

The purpose of this research is to calculate the heat of reaction of material that undergoes decomposition during an experiment by including mass information in the calculation. The DSC does not have the capability to measure weight change on its own. Therefore, data information from thermogravimetry (TG) will be used. The best scenario would be to use simultaneous instrumentation such as a TG/DSC or a TG/DTA. However, these instruments are not always available in the laboratory. Therefore, a DSC and TG, which will require two experimental runs to calculate ΔH, will be used here.

The following is an outline of the approach used in this study. The materials used were first selected and the experimental conditions were defined. A comparative study was then carried out between a DSC quasi-thermal run and theoretical values in order to quantify the error in the heat of reaction calculation owing to a mass change during the course of a reaction. This comparison is important to establish the integrity of the enhanced calculations.

Some methods developed to enhance information retrieval in experiments, such as simultaneous, coupled, combined and complementary techniques,

* Presented at the 18th Annual NATAS Conference, San Diego, CA, U.S.A., 24–27 September 1989.

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provide quicker and more cost effective and/or complementary information than that obtained from a single experiment [1]. Differential thermal analysis (DTA) and TG have been used as combined techniques, since TG is utilized as a complementary technique to aid in the interpretation of DTA curve peaks. Generally, there has been little agreement between the two curves because of the different pyrolysis conditions. To alleviate this problem it is necessary to develop experimental conditions which are common in each analysis [2]. Consequently one of the objectives will be to have as little correlation interference as possible, so that the data file received from a TG experiment will provide accurate weight change information (via temperature or time parameters) in order to create a master data file having both TG and DSC information.

Differential scanning calorimetry is a thermal technique which alters the temperature of a sample and the reference sample at a controlled rate and records/monitors the net heat flow of the system. The following lists outline some advantages and some disadvantages of this technique over classical calorimetry [3].

Advantages

(1) Ease of the procedure and analysis of data.
(2) Speed of determination: with the scope of a wide range of temperature within minutes or hours.
(3) Small sample masses: can be liquids or solids.
(4) Ability to study many types of chemical reactions.
(5) Measurements can be made under high pressures, and subject to cooling processes.

Disadvantages

(1) Low accuracy in the range of 5–10%.
(2) Difficulty in determining the enthalpy change due to overlapping peaks.
(3) Errors in the peak area calculations from the change in the base line during a transition or reaction.
(4) Inability to determine a mass change directly during the course of the experiment.

Despite some shortcomings, design and engineering have improved the instrument so that more finite adjustments such as weight loss should be considered in the calculations. Therefore, enhancement of the DSC in turn to provide a more accurate heat of reaction through weight change calculation becomes of additional use. The information obtained then becomes important to the analysts who are interested in the exact energies which are produced or consumed in the sample.

Theory

The DTA measures the temperature difference between the sample and the reference material, $T_S - T_R$, whereas the DSC isothermally maintains T_S

and T_R by the use of individual heaters and measures the power difference to the heaters, which is used as the signal (dH/dt) [4].

The DSC is able to measure the heat flow difference from the sample and the reference. This heat flow, ΔH, can be expressed in numerical terms by measuring the area under the curve produced by the transition on a X–Y plot. The Y-axis usually represents net heat flow in or out of the sample in units of mV. The X-axis is represented as time or temperature. These components together can represent an area which is directly related to the total heat flow in the sample in units of J.

In order to reduce the error in the DSC, a close look at the equation used to calculate enthalpy change and the sources of error would be appropriate. The equation for determining the heat of reaction (or transition) from a DSC experiment is

$$\Delta H_{\text{convent}} m = KA \tag{1}$$

where ΔH is the heat of reaction (or transition), m is the mass of the sample at the start of the experiment, K is the calibration coefficient (instrument dependent), and A is the area under the peak. The calibration constant depends on the type of instrument employed and is independent of temperature when used with DSC [5]. The calibration is carried out with compounds having known heats of transition or heats of fusion [6]. The precision expected from this calibration is from 4–7 [7].

The mass m of the sample is used to give molar values of the enthalpy change or quantitative information about the sample. The same initial mass value is used whether there is a phase change or a thermal decomposition of the sample during an experiment. This produces some inconsistency in the results of the calculations. Calcium oxalate monohydrate (Fig. 1) has three basic transitions, and in every transition there is a decrease in the mass. At 149.6 °C calcium oxalate monohydrate loses water, at 458 °C it loses carbon monoxide and at 690.9 °C it loses carbon dioxide at 12.3%, 18.9% and 30.0% mass loss respectively. This gives us a classical example of weight loss error. This occurs because three decreases in mass can be observed in one experiment. The initial mass used to calculate $\Delta H_{\text{convent}}$ for each of the decompositions will be further away from the actual mass of the sample at that transition. This means that the experimental $\Delta H_{\text{convent}}$, which is the value observed, will produce a larger relative percent error because mass loss is not taken into consideration from previous and/or current decompositions. It must be borne in mind that the experimental $\Delta H_{\text{convent}}$ value is derived from the initial mass of the sample at the start of the experiment.

This weight change factor in the sample cannot be allowed for in the calibration constant because it is sample dependent. This gives rise to a means by which the weight change information can be incorporated into the DSC calculations. The summation equation below provides the dependent factor which is needed to compensate for any weight change sources of error

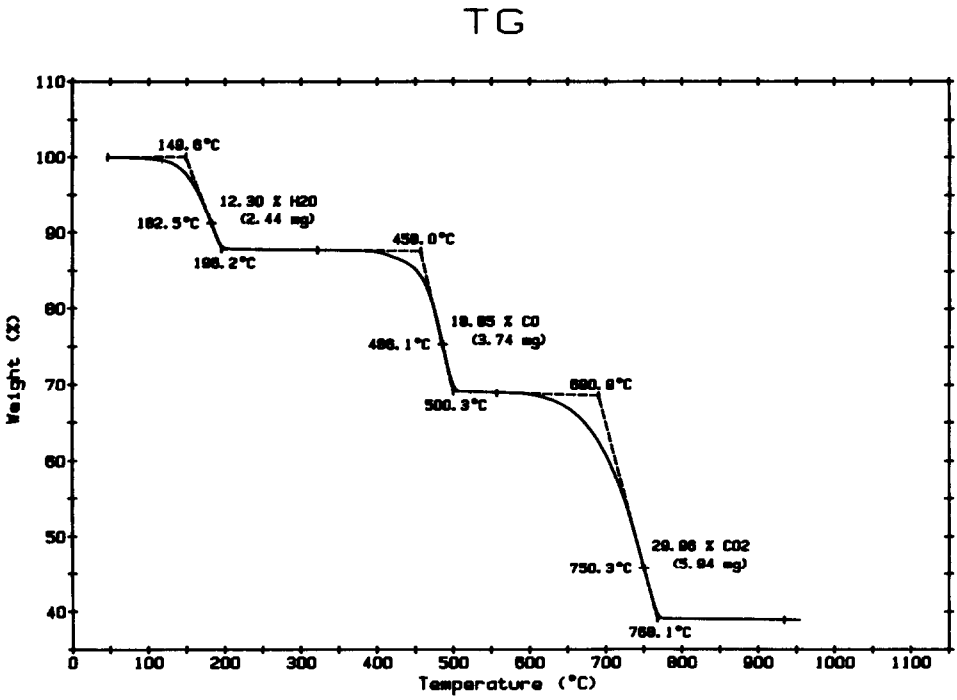

Fig. 1. TG curve for calcium oxalate monohydrate in nitrogen.

in the enthalpy change calculations

$$\Delta H_{\text{enhanced}} = \sum KA_T/nm_i \tag{2}$$

where K is the calibration constant, A_T is the area under the peak, n is the number of approximations, and m_i is the absolute weight of the sample at that approximation. In order for this equation to function in the calculation of the heat of reaction, weight change information about the sample under the same parameters is needed. TG has the capability to provide the percent weight change of a sample as a function of temperature. However, careful consideration needs to be given to provide an environment for the sample consistent to what exists in the DSC experiment. The parameters which can be controlled easily are programmed temperature rampings, initial sample weight, and sample reference conditions. Other parameters which are not as easily controlled, such as sample shape, difference in cell instrumental errors, and thermocouple placement, will have to be monitored and studied for their effects on the results.

Table 1 shows some characteristic effects (eqn. (2)) of samples which decompose, lose no net weight and samples which may gain weight during the experiment. When a sample decomposes during the experiment, the mass decreases. This decrease results in a higher heat of reaction value because of the input of a lower value for the mass of the sample from the approxima-

TABLE 1

Characteristics of the enhanced equations

Decomposition	$\Delta H_{enhanced} > \Delta H_{convent}$
Phase transitions	$\Delta H_{enhanced} = \Delta H_{convent}$
Reaction with gas	$\Delta H_{enhanced} < \Delta H_{convent}$

tions in the enhanced equation (eqn. (2)) compared with the initial mass used from the conventional equation (eqn. (1)). The complementary effect occurs when the mass of the sample increases during the course of the experiment. A lower heat of reaction value is obtained from the enhanced equation (eqn. (2)) compared with the results from the conventional equation (eqn. (1)). When there is no change in sample mass, there is no difference between the results from eqns. (1) and (2).

The problem of the effects of weight loss when calculating ΔH has been approached before, in a different manner [8–10]. In these studies coal was used as the sample and, to account for the mass loss, an improved base line was obtained after correlation for the difference in mass between the coal sample and the remaining char. This revised base line was then used to calculate heat flow from the decomposing coal sample. However, this method required that a blank experiment be done, and a run of the char be carried out in addition to the run of the actual coal sample. The need to use the TG data to correct the DSC data in calculating heat capacities and reaction enthalpies was emphasized. However, Agroskin et al. [11] appear to be the first to have taken into account volatile matter weight loss in calculating specific heats of coals. Values of ΔH can be expressed either in terms of the unit weight of the starting coal or in terms of the unit weight of coal left unreacted at a given temperature, as determined from the TG runs. The way in which ΔH is expressed is purely based upon what information is required. On the basis of theoretical considerations it is more appropriate to express the values of ΔH in terms of the amount of sample still remaining. However, in designing coal conversion plants, one is primarily interested in the values of ΔH for a given starting weight of coal.

Thermogravimetry can be useful for complementing DSC data in order to determine or classify the type of reaction taking place during the course of the experiment. Differential scanning calorimetry was used to determine the heat of pyrolysis of North Dakota coal, and experimental factors such as weight loss, emissivity and the effects of specific heat were measured and considered in the deduction of the heat of pyrolysis [12].

Homogeneous samples, such as CaC_2O_4, H_2O or $CaSO_4 \cdot 0.5H_2O$, having known heats of reaction can be used initially to provide the most ideal cases for validating the use of an equation to calculate heats of reaction (eqn. (2)). Subsequently, this method can be applied to heat of reaction analysis for heterogeneous samples.

Instrumentation and procedure

The instruments used were the Seiko TG/DTA 200, and the Du Pont PS/2 model 50Z TA2000 system, DSC 910, and TGA 951. The software used for developing the programs to perform the analysis was Borland's Turbo Pascal. The Du Pont TA2000 system operates using the company's own operating system. This means that, in order to apply any enhancement to the experimental data files, these files have to be passed through from their operating system to the MS-DOS partition of the PS/2 hardware. This capability is called User Programmability and is an option to the system package. It allows the user, if they wish, to pass the data, converted into the ASCII format, from one operating system to another so that it may be used in third party programs. This can be very useful if special work needs to be done on the data files created from a thermal analysis run.

In order to make an adjustment in the DSC calculations to take account of sample weight loss due to decomposition, there is a need to combine information from the TG data file. When two "sister" experimental data files are created from DSC and TG we can "splice" the data together and create a master data file which will be used in an enhanced weight correction program to generate the weight corrected molar $\Delta H_{\text{enhanced}}$.

An inherent problem that needs to be addressed here when interfacing these data files together is which parameter to use to combine the data files that are common to both. This can be either time or temperature. If time is used as the common link, then proper measures need to be taken to ensure that the timetables for both systems are synchronized with respect to the data. On the other hand, if temperature is used as the common link, then steps need to be taken to ensure that the temperature of the sample is measured constantly between the two systems. A problem here is thermocouple placement. The Du Pont TGA has the thermocouple placed close to the sample. However, the thermocouple in the Du Pont DSC 910 lies underneath the cell. Thus, if the temperature is used as the parameter to "splice" two data files together, then a skewing effect might occur, i.e. the temperature of the DSC and the TG might not coincide at the same points in the experiment. This skewing effect will vary depending on the heating rate of the experiment. Previous work by Elder on a Perkin–Elmer TGS-2 thermogravimetric system to determine a dynamic compensating factor for the TG instrument so that the sample and programmed temperatures agree within $\pm 2°C$ [13].

The instrument selected to provide the TG signal for the DSC was a TG/DTA, because the thermocouple is located underneath the sample and the sample could be placed in a sample pan instead of a sling as in the Du Pont TGA. The environments of the two systems matched more closely.

A Pascal program that we developed called DELTA calculates $\Delta H_{\text{enhanced}}$ from the input of the master data file created from combining DSC and TG

data files. The input data file of DELTA is in two parts: the header and the raw data. The header portion of the data file sets up the parameters for the program to work in and also other documentational notes. The key parameters of the header instruct the program as to what temperature range to operate in, how many approximations to make in the enhanced calculation by defining a number (2–100) for the series formula, and the initial weight of the sample. The program DELTA then calculates $\Delta H_{convent}$ and $\Delta H_{enhanced}$.

An additional Pascal program was developed to generate theoretical heat of reaction tables for a range of temperatures. This program was developed to reduce the number of time consuming manual calculations. The following heat capacity equation was used to calculate theoretical ΔH values

$$\Delta H = \int_{t1}^{t2} C_p \, dt \tag{3}$$

The input file for the program would contain the heat capacity coefficients, sample products, reactants and their corresponding ΔH values. To calculate ΔH at more than one temperature, an initial and limit temperature is entered along with the increment size. A program called ENTHTEMP will then take the input data and calculate the theoretical ΔH. The source code for ENTHTEMP can be seen in Table 2.

The parameters that were used for the thermal experiments are as follows. The mass of the sample was at least 10.0 mg or more in order to obtain at least three significant figures (unless the sample has a low density and 10.0 mg would fill the sample pan more than $\frac{1}{3}$ full. The heating rate was 10 °C min^{-1}. Nitrogen was used as the inert atmosphere at a flow rate of 100 ml min^{-1}.

Several quasi-isothermal conditions were imposed during the heating steps for calcium sulfate hemihydrate. Below is the significant set of conditions which will be discussed.

Temperature range (°C)	Heating rate (°C min^{-1})	Time at final temperature (min)
30.0– 80.0	10.0	15.00
80.0– 85.0	5.0	60.00
85.0–200.0	10.0	0.0

Various materials were selected; some had transitions with no decompositions; others had single and/or multiple decomposition peaks. The rule of thumb used in the selection of some of the materials was as follows. First, the reference data for calculating the theoretical value of ΔH needs to be available for at least one of the selected materials for comparison with the experimental value. Second, the peak from the experimental run needs to be a single peak with no bumps corresponding to changes in the sample. This will give optimum conditions for the comparisons. Third, there should be some samples which undergo a weight loss during the course of the experi-

ment. This is important because we want to show that when there is a decrease in the mass of the sample there is a corresponding increase in the percent relative error in the experimental heat of transition value.

TABLE 2

ENTHTEMP source code

```
program ENTHTEMP

{*********************************************************}
{                                                         }
{      Programmer: Roland Hoffman (P C Chemist)           }

{                     Version: 1.00                       }

{                  Last update: 8-21-89                   }
{                                                         }
{*********************************************************}

uses dos;
const
  T = 298.15;
var
 Compound : array[1..5] of string[12];
 A, B, C, H298, Hcpd, Mole : array[1..5] of real;
 Tstart, Tfinish, Ttemptr, n, Tstep : integer;
  delta_H, delta_H_J : real;
 MyFile : text;


procedure Read_Data_File;
var
  I : integer;
begin
  reset(MyFile);
  readln(MyFile,n);
  For I := 1 to n do
  begin
    readln(MyFile,Compound[I]);
    readln(MyFile,A[I],B[I],C[I]);
    readln(MyFile,H298[I], Mole[I]);
  end; {I loop}
  readln(MyFile,Tstart,Tfinish,Tstep);
end; {Read_Data_File}

{*********************************************}

procedure Calculate_H(Compd : integer; Temperature : real);
var
    a1, b1, c1 : real;
begin
  a1 := A[Compd] * (Temperature - T);
  b1 := B[Compd]/2 * (sqr(Temperature) - sqr(T));
  c1 := C[Compd] * (1/Temperature - 1/T);
  Hcpd[Compd] := H298[Compd] + (a1 + b1 - c1)/1000;
```

TABLE 2 (continued)

```
end; {Calculate_H}

{*********************************************}

procedure Print_Header;
begin
  writeln('  -- TEMP -- ');
  writeln('   C
K',compound[1]:12,compound[2]:12,'',compound[3]:12,
       '  /_\ H kcal/m',' /_\ H kJ/m  ');
end; {Print_Header}

{*********************************************}

procedure Print_Data;

begin
  writeln((Ttemptr - 273) : 6,Ttemptr : 6,Hcpd[1] : 12 :
2,Hcpd[2] : 12 : 2,Hcpd[3] : 12 : 2,
         delta_H : 12 : 2,delta_H_J : 12 : 2);
end; {Print_Data}

{*********************************************}

procedure Calculate_delta_H;
var
  Times, I, I1, Temp : integer;

begin
  Print_Header;
  Times := (Tfinish - Tstart) div Tstep;
  Ttemptr := Tstart - Tstep;
  for I := 1 to Times do
  begin
    Ttemptr := Ttemptr + Tstep;
    For I1 := 1 to n do
    begin
      Calculate_H(I1,Ttemptr);
    end; {I1 For loop}
    delta_H := Mole[1] * Hcpd[1] + Mole[2] * Hcpd[2] -
Mole[3] * Hcpd[3];
    delta_H_J := delta_H * 4.138;
    Print_Data;
  end; {I For loop}
end; {Calculate_delta_H}

{*****************************************}

procedure CheckParam;

begin  {CkeckParam}
    Assign(MyFile,paramstr(1));
    if paramcount <> 1
      then begin
```

TABLE 2 (continued)

```
            writeln('Usage : "This program uses a DataFile.
         Ex. Enthtemp datafile"');
            writeln('Version 1.00 written by P C Chemist');
            halt;
          end;
end; {CheckParam}
{*****************************************}

begin
  CheckParam;
  Read_Data_File;
  Calculate_delta_H;
end.
{*****************************************}
{*****************************************}
```

The materials used for the TG/DTA, TG and DSC experiments were reagent grade. The materials selected are given in Table 3. Calcium oxalate monohydrate and calcium sulfate hemihydrate are the only two samples discussed here.

RESULTS AND DISCUSSION

To establish the integrity of the enhanced calculations, a comparison was made between theoretical values obtained from the program output (given in Table 4) with the results from a DSC experiment on calcium sulfate

TABLE 3

List of materials used

Sample	Grade	Company	Form
Indium	Reagent	Seiko	Ingot
Tin	Reagent	Seiko	Ingot
Lead	Reagent	Alfa Products, Danvers, MA	Powder, 200 mesh
Tin	Reagent	Alfa Products, Danvers, MA	Powder, 200 mesh
Bismuth	Reagent	Fisher Scientific, Fair Lawn, NJ	Granular
$ZnCl_2$	Reagent	EM Science, Cherry Hill, NJ	Powder
LiBr	Reagent	MC&B Norwood, OH	Powder
$LiNO_3$	Reagent	T.J. Baker, Phillipsburg, NJ	Powder
Al_2Cl_6	Reagent	MC&B, Norwood, OH	Powder
$CaC_2O_4 \cdot H_2O$	Reagent	Seiko	Powder
$CaSO_4 \cdot 0.5H_2O$	Reagent	Aldrich Chem CO., Milwauke, WS	Powder

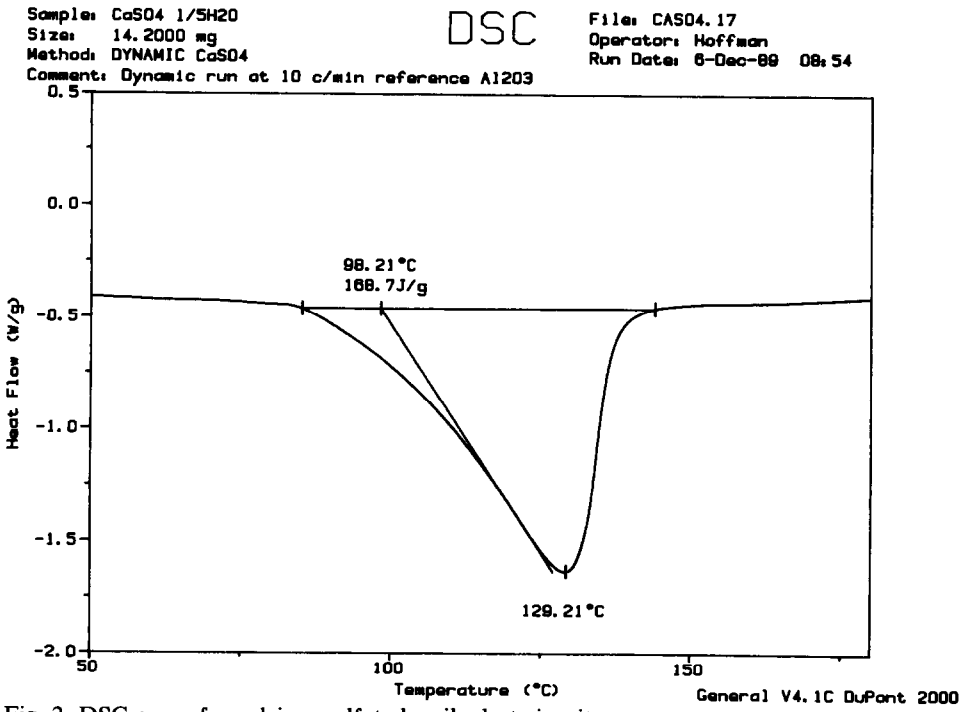

Fig. 2. DSC curve for calcium sulfate hemihydrate in nitrogen.

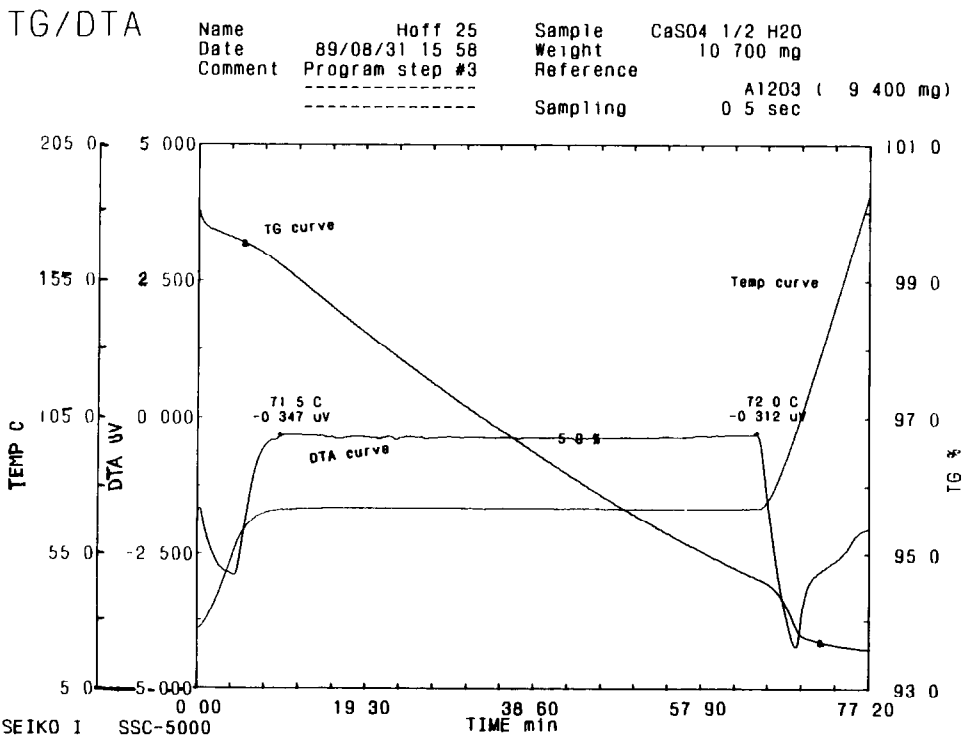

Fig. 3. Isothermal (70°C for 60 min) TG/DTA results for calcium sulfate hemihydrate in nitrogen.

TABLE 4

Theoretical calculations of the dehydration of calcium sulfate hemihydrate

Temperature		Heats of formation (kcal mol^{-1})			ΔH (kJ mol^{-1})	ΔH (kJ mol^{-1})
°C	K	$CaSO_4$	H_2O	$CaSO_4 \cdot 0.5H_2O$		
47	320	−341.87	−57.77	−375.75	4.99	20.63
52	325	−341.75	−57.73	−375.58	4.96	20.53
57	330	−341.63	−57.69	−375.41	4.94	20.43
62	335	−341.51	−57.65	−375.24	4.91	20.32
67	340	−341.38	−57.61	−375.08	4.89	20.22
72	345	−341.26	−57.57	−374.91	4.86	20.12
77	350	−341.13	−57.53	−374.74	4.84	20.02
82	355	−341.01	−57.49	−374.57	4.81	19.91
87	360	−340.88	−57.45	−374.39	4.79	19.81
92	365	−340.76	−57.41	−374.22	4.76	19.71
97	370	−340.63	−57.37	−374.05	4.74	19.61
102	375	−340.50	−57.33	−373.88	4.71	19.50
107	380	−340.37	−57.29	−373.70	4.69	19.40
112	385	−340.24	−57.25	−373.53	4.66	19.30
117	390	−340.11	−57.20	−373.35	4.64	19.20
122	395	−339.98	−57.16	−373.18	4.62	19.10
127	400	−339.85	−57.12	−373.00	4.59	19.00
132	405	−339.72	−57.08	−372.83	4.57	18.90
137	410	−339.59	−57.04	−372.65	4.54	18.79
142	415	−339.46	−57.00	−372.47	4.52	18.69
147	420	−339.32	−56.96	−372.29	4.49	18.59
152	425	−339.19	−56.92	−372.12	4.47	18.49
157	430	−339.05	−56.87	−371.94	4.44	18.39
162	435	−338.92	−56.83	−371.76	4.42	18.29
167	440	−338.78	−56.79	−371.58	4.40	18.19
172	445	−338.65	−56.75	−371.39	4.37	18.09

hemihydrate. Figure 2 shows a dynamic run on calcium sulfate hemihydrate at a heating rate of 10 °C min^{-1} and a $\Delta H_{convent}$ value of 168.7 J g^{-1}. The corresponding output (taken from Table 4) at T_{max} = 129 °C (from Fig. 2) is 19.00 kJ mol^{-1} or 131 J g^{-1}.

When enhanced calculations are applied to the dynamic experimental run (Fig. 2), $\Delta H_{enhanced}$ was found to be larger compared with $\Delta H_{convent}$. The resulting values of $\Delta H_{enhanced}$ and $\Delta H_{convent}$ from the output of DELTA was 176.1 J g^{-1} and 168.7 J g^{-1} respectively. This increase in the heat of dehydration on using the enhanced equation results from a loss of mass in the sample. Furthermore, the enhanced value increased in the opposite direction to the theoretical value at T_{max}. The differences in the results were mostly due to the nature of the theoretical conditions. In other words, the values produced by the theoretical dehydration calculations are considered to be those at a constant temperature. Therefore, a change in the experimen-

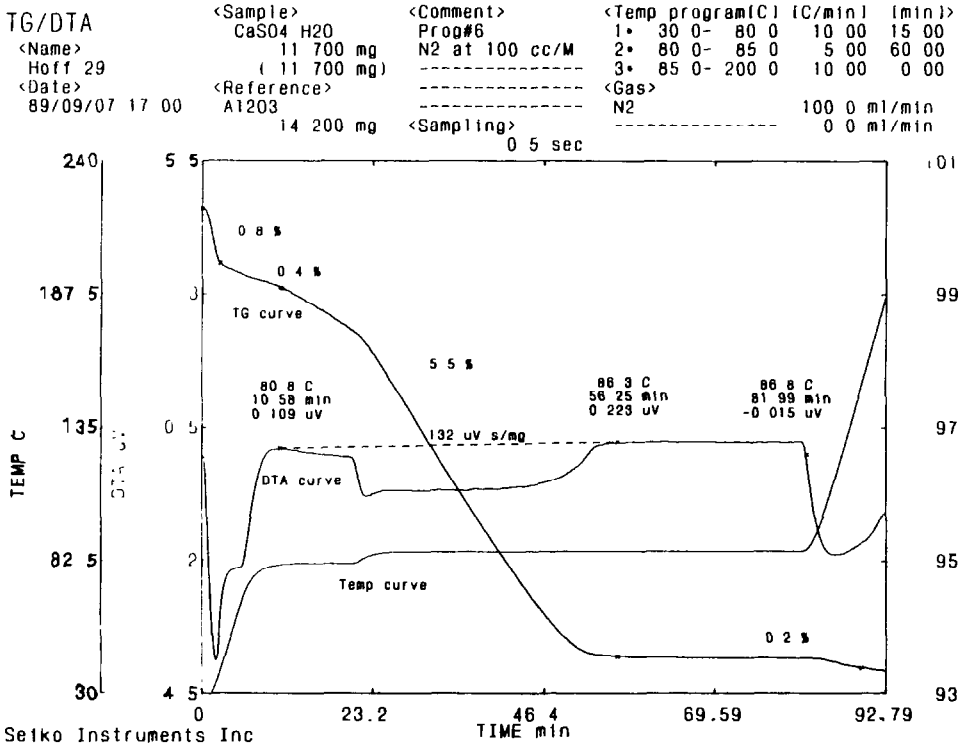

Fig. 4. A quasi-thermal TG/DTA curve for calcium sulfate hemihydrate.

tal conditions was necessary in order to reflect the isothermal heat of dehydration, which is the quantity considered in the theoretical calculations.

The change in the heat of hydration of calcium sulfate hemihydrate was studied under isothermal conditions. This was important in order to observe differences between the effect of a dynamic change in temperature (constant ramping rate) and a near static range (isothermal). A relative temperature was found at which the water of hydration starts to come off. The Seiko TG/DTA was used to monitor this process. Once this initial hydration temperature was known, the sample could be heated up to that temperature and then held isothermally for 30 min. This did not prove satisfactory because no net DTA curve was produced. One example is shown in Fig. 3. However, some results were obtained by bumping the temperature up 5–10 °C during the isothermal period. Figure 4 shows the results of a quasi-thermal run on a TG/DTA. The same conditions were then done on the Du Pont DSC. The results are shown in Fig. 5. Pure isothermal results were not obtained, but the relative trends can be seen by comparing a dynamic (constant heating rate) run with a near isothermal (quasi-thermal) run (Figs. 2 and 5).

When a comparison is made between $\Delta H_{\text{enhanced}}$, from the output of DELTA, under quasi-thermal conditions and ΔH_{theory}, from Table 4 at

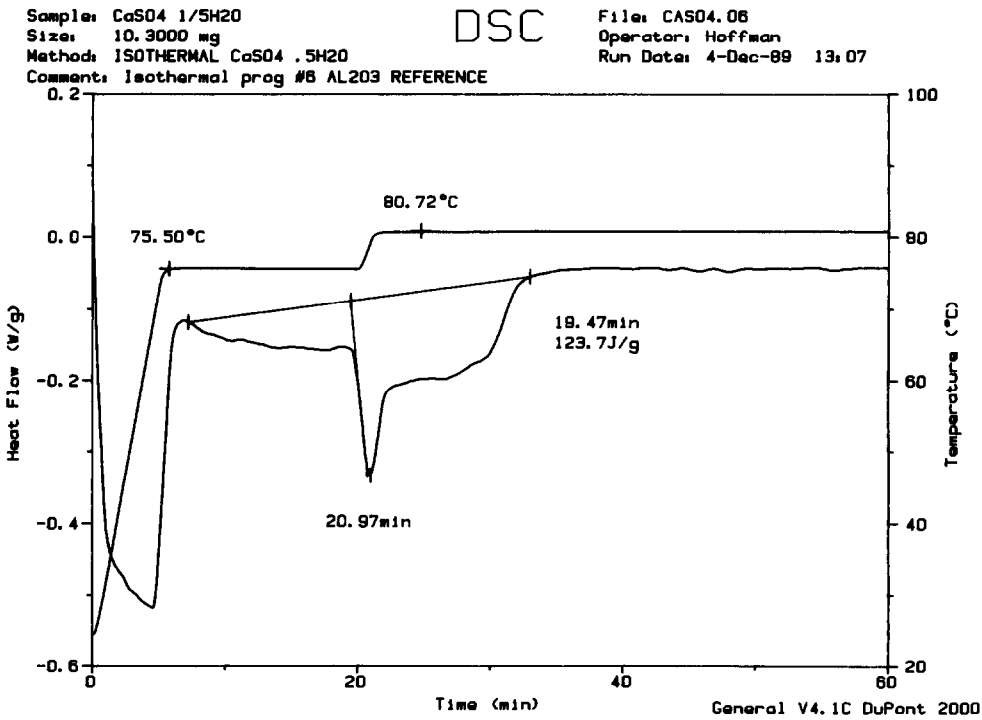

Fig. 5. A quasi-thermal DSC curve for calcium sulfate hemihydrate.

80 °C for calcium sulfate hemihydrate, the resulting values of $\Delta H_{enhanced}$ and ΔH_{theory} are 132.2 J g^{-1} and 137.3 J g^{-1}. It may be observed that $\Delta H_{enhanced}$ is 5.1 J g^{-1} units smaller than ΔH_{theory}. This partly results from the fact that not all of the mass loss due to dehydration was accounted for when observed under the same conditions in the TG/DTA curve, Fig. 4. A loss of 0.5 mol of water from calcium sulfate hemihydrate represents 6.2% of the total weight of the sample. The TG/DTA results only measured 5.5% of the dehydration from calcium sulfate hemihydrate. This would account for the lower $\Delta H_{enhanced}$ value compared with the theoretical value. It must also be borne in mind that the experimental conditions are quasi thermal, which means that the dehydration of water from the sample does not occur at the same temperature. Nevertheless, the enhanced equations do indeed approach the theoretical values closely and should be considered when the exact energies produced or consumed in the sample are of interest. A follow-up paper discussing the use of simultaneous instrumentation for determining the heat of dehydration and decomposition of various materials using the enhanced equation is in preparation.

CONCLUSION

When enhancement calculations are applied to quasithermal heats of dehydration the resulting values approach the theoretical values at the corresponding temperatures.

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