

THE DELTATHERM DYNAMIC ADIABATIC CALORIMETER: SOME APPLICATIONS

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ABSTRACT

The Deltatherm dynamic adiabatic calorimeter is described. The operation and calibration of the instrument are discussed and its application to the determination of the C_p of several metals and the ΔH of several dehydration reactions. The accuracy and precision of the calorimeter are about $\pm 1\%$.

INTRODUCTION AND THEORY

Although it is a convenient technique to use, quantitative differential thermal analysis (QDTA) has a number of disadvantages when compared to dynamic calorimetry^{1,2}. The usual relationship used in QDTA is

$$m\Delta H = KA$$

where m is the mass of the sample, ΔH is the heat of reaction of the system, A is the area of the curve peak, and K is the calibration constant³. The determination of K is the main source of error since it varies with the thermal conductivity of the system and hence the temperature. Small errors in the evaluation of K introduce much larger errors in the ΔH values obtained. In general, heats of fusion, heats of reaction, and other thermochemical measurements, can be determined by QDTA with a precision and accuracy of about ± 5 to $\pm 10\%$.

To obtain a higher order of precision and accuracy, say $\pm 1\%$, some type of a dynamic calorimeter must be employed for the measurements. A number of these instruments have been described, perhaps the most sophisticated is the differential scanning calorimeter (DSC) described by Watson *et al.*⁴ and O'Neill⁵. Other calorimeters have been discussed by Speros and Woodhouse⁶, Thomasson and Cunningham⁷, Sherwin⁸, Solomons and Cummings⁹, and more recently by Hill and Slessor¹⁰. The Hill and Slessor calorimeter is a rather interesting one in that heating and temperature control is done by means of focused radiation from projection lamps. There are several excellent reviews on dynamic calorimetry. The general area of microcalorimetry is reviewed by Calvet and Prat¹¹ while the entire area of calorimetry, including applications and instrumentation, is discussed by Wilhoit¹².

The Deltatherm adiabatic calorimeter

The Deltatherm calorimeter has previously been described by Dosch¹³. The calorimeter is a constant heating-rate type in which the sample chamber is heated at a constant rate, any departure from which is detected and applied to it as a correction factor. The temperature difference between the sample chamber and its adiabatic enclosure is detected by a differential thermocouple whose output is used to automatically vary the power applied to the sample, thereby maintaining adiabatic conditions.

The specific heat of a substance, C_p , is defined as

$$C_p = \frac{q}{m(T_2 - T_1)} \quad (1)$$

where q is the amount of heat required to raise the temperature of mass m from T_1 to T_2 . Substituting the electrical equivalent for heat,

$$q = k_1 Pt \quad (2)$$

into Eqn. (1) and rewriting in differential form,

$$C_p = \frac{k_1 P}{m} \left(\frac{dt}{dY} \right) \quad (3)$$

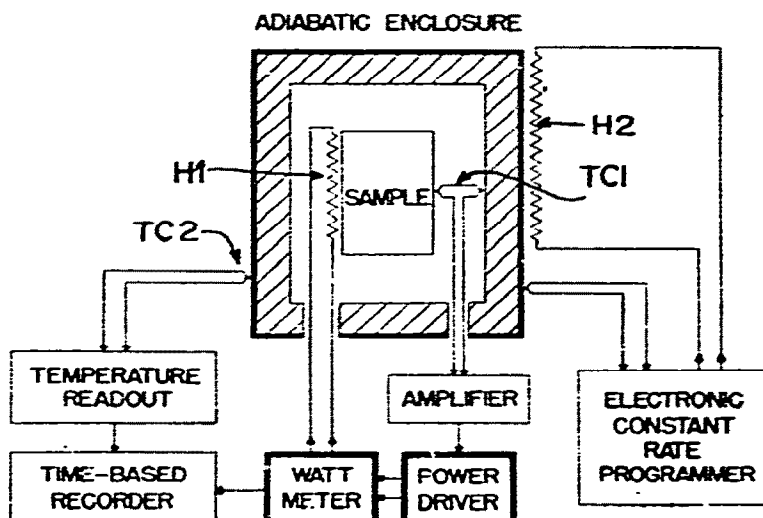
where P is the power, t is the time, and k_1 a constant. Rewriting Eqn. (3) for a constant heating rate, dT/dt , the specific heat becomes

$$C_p = \frac{k_3 P}{m} \quad (4)$$

Hence, the specific heat of a substance is directly proportional to the electrical power input to the calorimeter since k_3 and m are constant for a given system. With proper calibration, k_3 can be evaluated so that the C_p of a substance can be calculated for any temperature. The advantage of the constant heating-rate mode the conventional constant input power type of system is that the power curve gives the variation of C_p directly with temperature without first computing the reciprocal of the heating rate. Also, the former type of system provides data having a kinetics significance due to the constancy of the heating rate.

EXPERIMENTAL*The calorimeter*

A block diagram of the calorimeter is shown in Fig. 1. The temperature difference between the sample and the adiabatic enclosure is detected by the differential thermocouple TCl. The voltage output of TCl is amplified by a chopper stabilized d. c. amplifier whose output controls a solid-state power driver which supplies up to 4 watts of power to the heater, H1. The differential temperature is also recorded on one channel of the multi-channel recorder to indicate the extent with which adiabatic



AUTOMATIC ADIABATIC CALORIMETER SYSTEM

Fig. 1. Block diagram of the Deltatherm calorimeter system.

conditions are being maintained in the adiabatic enclosure. In general, adiabatic conditions are maintained to within $\pm 0.05^\circ$ after dynamic conditions are established in the calorimeter (above $50\text{--}75^\circ\text{C}$). The power input to the sample chamber is measured by a Hall effect multiplier watt-meter and is continuously recorded on another channel of the recorder. The main furnace heater, H2, is controlled by the electronic constant rate programmer; heating rates from 2 to 20°C per min are available. The temperature of the calorimeter is detected by thermocouple TC2 and is recorded on the chart 50°C intervals.

A cross-section of the calorimeter assembly is shown in greater detail in Fig. 2. The calorimeter is mounted upon a cast ceramic pillar which can be inserted into the standard Deltatherm furnace. The adiabatic enclosure consists of a massive copper block (A) enclosed by the copper covers (B), (C), and (D). Surface temperature uniformity in the inner chamber is about 0.1°C at a heating rate of $10^\circ/\text{min}$ and proportionately less at slower heating rates. The sample chamber (F) and its cover (F) are made of silver and are thermally isolated from the block by the ceramic pillar (K). The sample container heater (G) consists of an Inconel sheathed Nichrome wire resistance element wound in the form of a helix on the inside of the sample chamber. The temperature of the sample container and block are detected by Inconel sheathed Chromel-Alumel thermocouples (J) and (L), respectively. These two thermocouples are connected together in a differential mode for temperature detection. The sample (H) consists of either a machined ingot of a solid substance, a packed powder, or a container for powdered or liquid samples.

Sample preparation

The sample may consist of a solid, powdered or liquid material. For machinable

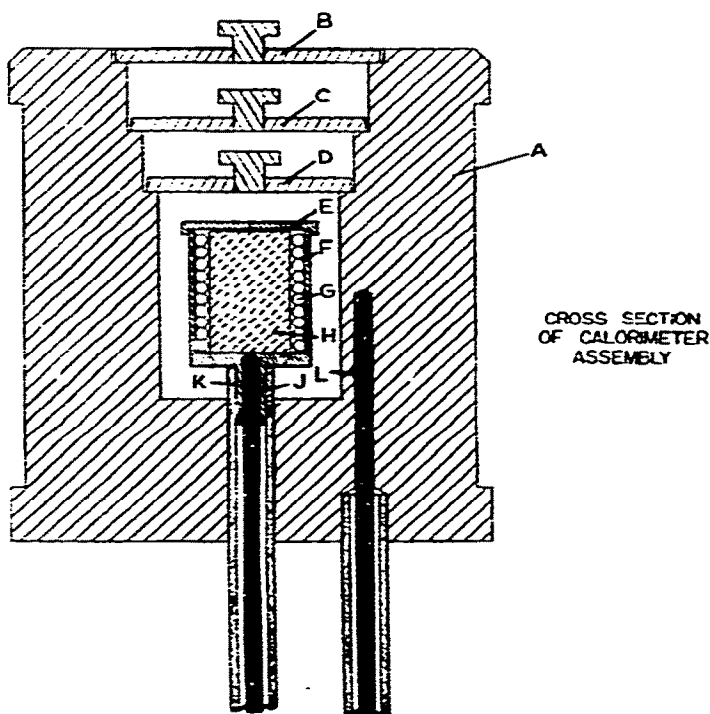


Fig. 2. Cross-section of calorimeter. (A) Copper block; (B), (C), and (D), copper covers; (E) sample chamber cover; (F) sample chamber; (G) heater; (H) sample; (J) thermocouple; (K) ceramic support; (L) thermocouple.

solids, a cylinder having the maximum dimensions of 0.35 in (in diameter) by 0.55 in (in length), may be employed. Non-corrosive and non-fusible (in the temperature range to be investigated) powdered substances may be placed directly into the sample chamber. For corrosive or fusible solids and/or liquids, a stainless steel sample capsule may be used. The inside dimensions of the stainless steel capsules are 0.285 in (in diameter) by 0.520 in (in length) and have a volume of 0.6 ml. The sample is weighed out into the capsule and enclosed by means of a press-fit cover.

Calibration of calorimeter

The C_p calibration procedure consists of the determination of the ordinate of the chart paper in terms of calories per inch. The calibration constant, k_3 [Eqn. (4)] is thus

$$k_3 = \frac{\Delta P}{mC_p} \quad (5)$$

The procedure consists of first obtaining a "power curve", at the operating conditions to be employed for the C_p determinations, of the calorimeter and empty sample capsule. The standard C_p reference substance is usually a machined ingot of metal.

From the difference between the power curves for the standard substance and the empty calorimeter, the ΔP may be obtained and hence, k_3 . Using α -nickel, the calibration constants, at different power settings, are given in Table I. The agreement between the individual k_3 values was $\pm 2\%$ of each other.

TABLE I
CALIBRATION OF CALORIMETER WITH α -NICKEL^a

Temperature (°C)	ΔP (in)	C_p (Ni) (cal/g/°C)	Heat absorbed (cal)	k_3 (cal/in)
<i>Power = 25%</i>				
100	2.24	0.114	0.815	0.364
200	2.46	0.125	0.894	0.363
300	2.76	0.138	0.987	0.360
400	2.51	0.123 ^a	0.880	0.350
500	2.47	0.126 ^a	0.901	0.365
				k_3 (average) = 0.360 cal/in
<i>Power = 50%</i>				
100	4.76	0.114	0.815	0.171
200	4.97	0.125	0.894	0.180
300	5.26	0.138	0.987	0.188
400	4.69	0.123 ^b	0.880	0.188
500	4.61	0.126 ^b	0.901	0.195
				k_3 (average) = 0.184 cal/in

^a $m = 7.151$ g; Ni(α), $C_p = 4.06 + 7.04 \times 10^{-3} T$ and Ni(β), $C_p = 6.00 + 1.80 \times 10^{-3} T^2$; $\Delta T = 2.5X$; heating rate, 5°/min. ^b β -Nickel.

The calorimeter was also calibrated for ΔH measurements by use of a substance having a known heat of fusion, ΔH_f . The standard substance used was pure tin with a ΔH_f of 1720 cal/g atom or 14.5 cal/g¹⁴. The procedure consisted of first obtaining the power curve for the calorimeter plus empty capsule, at the operating conditions to be employed for the various investigations. A known amount of tin is then sealed into the capsule and a power curve obtained as above. The fusion peak in the second curve is integrated by means of a planimeter and its area determined. The calibration constant, K_H , is calculated from

$$K_H = \frac{m \Delta H_f}{A} = \text{cal/in}^2 \quad (6)$$

where m is the mass of the sample, in g; ΔH_f is the heat of fusion of the sample, in cal/g; and A is the peak area in in². The results of this calibration procedure are given in Table II while the power curve is given in Fig. 3.

Heats of fusion and reaction studies

The procedure was identical to that used for the calibration studies. Compounds studied included lead, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, and $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$. Samples of pure copper and aluminum were used for the C_p determinations.

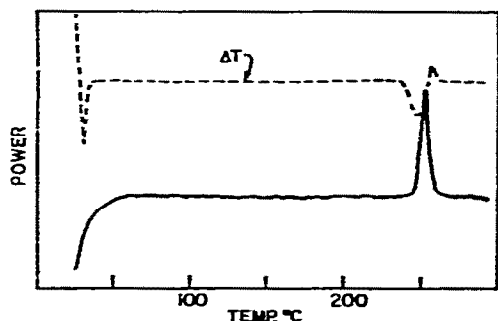


Fig. 3. Calorimeter power curve for tin; heating rate, 5°/min.

TABLE II

K_H CALIBRATION DATA USING TIN AS THE STANDARD

Heating rate (°/min)	Area (in ²)	Heat absorbed (cal)	K_H (cal/in ²)
10	2.848	23.46	8.241
10	2.800	23.47	8.382
10	2.912	23.47	8.060
10	2.688	23.47	8.731
5	2.752	23.47	8.760
5	2.752	23.47	9.051
5	2.864	23.47	8.700
2.5	2.688	23.47	8.917

RESULTS AND DISCUSSION

C_p Determinations

A typical calorimeter C_p power curve is shown in Fig. 4. Three curves are shown in the figure: (a) the power curve for the empty calorimeter plus sample container; (b) the power curve for the calorimeter containing the sample; and (c) the ΔT curve. The ΔP in Eqn. (5) is obtained by measuring the distance between the two power curves.

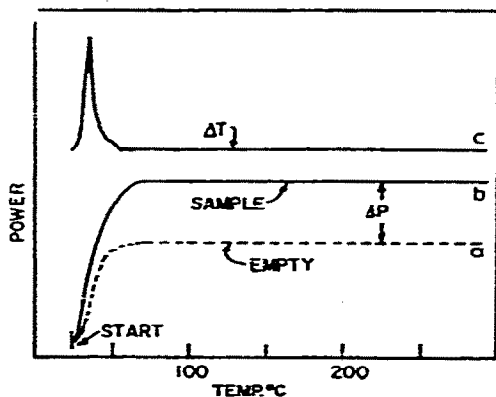


Fig. 4. A typical calorimeter C_p power curve.

The specific heats of copper and aluminum, at various temperatures, are given in Table III. The C_p values for copper are in good agreement with the calculated values¹⁴, especially at the higher temperatures. The values found for aluminum were 4 to 16% lower than the calculated values with the errors becoming smaller at the higher temperatures. The reason for this large difference is not known.

TABLE III

 C_p DETERMINATIONS (HEATING RATE OF 5°/MIN)

Temperature (°C)	C_p , copper (cal/g/°C)		C_p , aluminum (cal/g/°C)	
	found	calc. ^a	found	calc. ^b
100	0.104 ^c	0.094	0.188	0.224
200	0.107	0.095	0.253	0.235
300	0.106	0.099	0.261	0.246
400	0.102	0.101	0.265	0.257
500	0.102	0.103	0.278	0.268

^aCalc. from $C_p = 5.41 + 1.50 \times 10^{-3} Y$. ^bCalc. from $C_p = 4.94 + 2.96 \times 10^{-3} Y$. ^c C_p data in cal/g/°C.

ΔH Determinations

The ΔH for the dehydration of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ was obtained by use of Eqn. (6). The calorimeter power curve for the dehydration reaction is shown in Fig. 5.

Copper sulfate 5-hydrate dehydrates by the following reactions:

- $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}(\text{c}) \rightarrow \text{CuSO}_4 \cdot 3\text{H}_2\text{O}(\text{c}) + 2\text{H}_2\text{O}(\text{l})$
- $2\text{H}_2\text{O}(\text{l}) \rightarrow 2\text{H}_2\text{O}(\text{g})$
- $\text{CuSO}_4 \cdot 3\text{H}_2\text{O}(\text{c}) \rightarrow \text{CuSO}_4 \cdot \text{H}_2\text{O}(\text{c}) + 2\text{H}_2\text{O}(\text{g})$
- $\text{CuSO}_4 \cdot \text{H}_2\text{O}(\text{c}) \rightarrow \text{CuSO}_4(\text{c}) + \text{H}_2\text{O}$

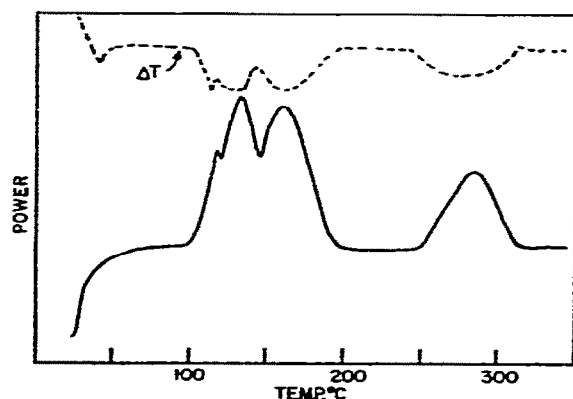


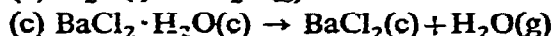
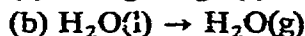
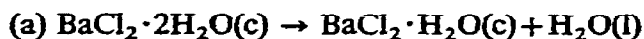
Fig. 5. Calorimeter power curve for the dehydration of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$.

The curves in Fig. 5 were due to the above reactions. The first two peaks were due to reactions(a)–(c), while the last peak was caused by reaction (d). This is a well known system and has been studied by a number of investigators^{15–17}. Only recently,

Wendlandt¹⁸ has detected the presence of liquid water in this system [reaction (a) above] by means of electrical conductivity measurements.

The ΔH values obtained for the dehydration reaction are given in Table IV. These values are given in kcal/mole of water and in kcal/mole of compound. The agreement between the values found here and the literature values is quite good.

The calorimeter was also used to obtain the ΔH of dehydration of $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$. This compound dehydrates according to the reactions¹⁵:



The first peak in the power curve was due to reactions (a) and (b) and the second, by reaction (c). The ΔH values are given in Table IV. The ΔH values obtained were in good agreement with the literature values.

TABLE IV

HEATS OF REACTION AND/OR FUSION AS DETERMINED BY THE DELTATHERM CALORIMETER (HEATING RATE OF 5°/MIN)

Sample	Sample mass (g)	Area (in ²)	Heat absorbed (cal)	ΔH (cal/g)	
				Found	Lit.
CuSO ₄ ·5H ₂ O	0.777	18.18 ^a	161.4	12.9 ^b	71 ^c
		6.03	53.5	17.2 ^b	
				69 ^c	
CuSO ₄ ·5H ₂ O	0.760	17.60 ^a	156.3	12.8 ^b	
		5.92	52.6	17.3 ^b	
				70 ^c	
CuSO ₄ ·5H ₂ O	0.710	16.29 ^a	144.7	12.7 ^b	
		5.60	49.7	17.5 ^b	
				70 ^c	
BaCl ₂ ·2H ₂ O	1.657	12.26	108.9	25.2 ^c	26.83 ^c
BaCl ₂ ·2H ₂ O	0.835	10.43	92.6	27.1 ^c	
Lead ^d	1.503	0.944	8.38	5.6	5.5
Lead	1.503	0.944	8.38	5.6	

^aFirst two peaks. ^bKcal/mole of water. ^cKcal/mole of compound

For a ΔH_f determination, the fusion of lead was investigated. The results obtained are shown in Table IV. As can be seen, the results obtained agreed very well with the reported values.

CONCLUSIONS

As can be seen from the results reported here, the Deltatherm dynamic adiabatic calorimeter is a versatile and useful instrument. It is capable of operation in the temperature range of 50–800°C. A high temperature version of the instrument,

capable of operation to a maximum temperature of 1200°C, is currently being developed. The calorimeter is stated to have an accuracy and precision for C_p and/or heat of reaction studies of $\pm 1\%$. It is anticipated that the calorimeter will be widely used for the investigation of various chemical systems, especially in the higher temperature ranges.

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