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A MODIFIED METHOD FOR THE DETERMINATION OF HEAT OF VAPORIZATION OR HEAT CAPACITY OF SELECTIVE LIQUIDS USING AN EMPIRICAL DIFFERENTIAL SCANNING CALORIMETRY SCAN TECHNIQUE

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ABSTRACT

An empirical single scan-method for ΔH_v determination has been developed which is accurate, precise and faster than existing methods. The proposed method utilizes dependent C_p area ratio measurements and differential scanning calorimetry. Alternately, true C_p measurements can be obtained when ΔH_v has been previously determined by classical techniques.

INTRODUCTION

In a standard differential scanning calorimetric (DSC) experiment involving liquids, it is assumed for practical purposes that all the heat energy supplied to the

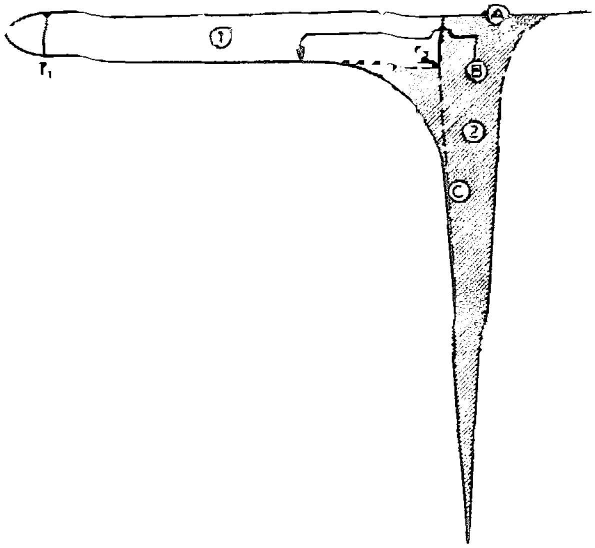

Fig. 1. Theoretical DSC scan showing a DSC stable (heat capacity) area (1) and a DSC dynamic (ΔH_v) area (2). Shaded parts represent the B.P. endotherm (or dynamic) area. A = blank baseline; B = sample pan baseline; T_1 = measured starting temperature; T_2 = extrapolated B.P.

system will be absorbed: (1) to heat the sample from ambient temperature to the boiling point, and then (2) to boil the sample at a relatively constant rate until the sample is completely vaporized. In (2), it is further assumed that a standard *sample pan-puncture* method[1,2] is used to prevent any adverse vapor-liquid equilibrating pressurization phenomena.

In actuality, however, the total scan area can be pictured as arising from a DSC stable area (1) and a DSC dynamic area (2). In graphic terms, this can be pictured as a routine DSC thermogram (Fig. 1) which is segmented into a DSC stable (heat capacity) area (1) and a DSC dynamic (ΔH_v) area (2).

DISCUSSION

The points given in Fig. 1 give rise to the empirical relation.

$$\Delta H_v = \frac{\text{Area 2}}{\text{Area 1}} (C_p)(T_2 - T_1) \tag{1}$$

where ΔH_v is in cal g^{-1} and T is in °C.

As noted in eqn (1), if the empiricism is valid, determination of the ΔH_v (if the dependent C_p is known) is possible, which easily leads to a calculation of vapor pressure from Clausius–Clapeyron relations. Alternately, C_p determinations using the attached method would be possible if ΔH_v is known by separate DSC experiments. Currently, ΔH_v studies (with accompanying vapor-pressure values) by instrumental

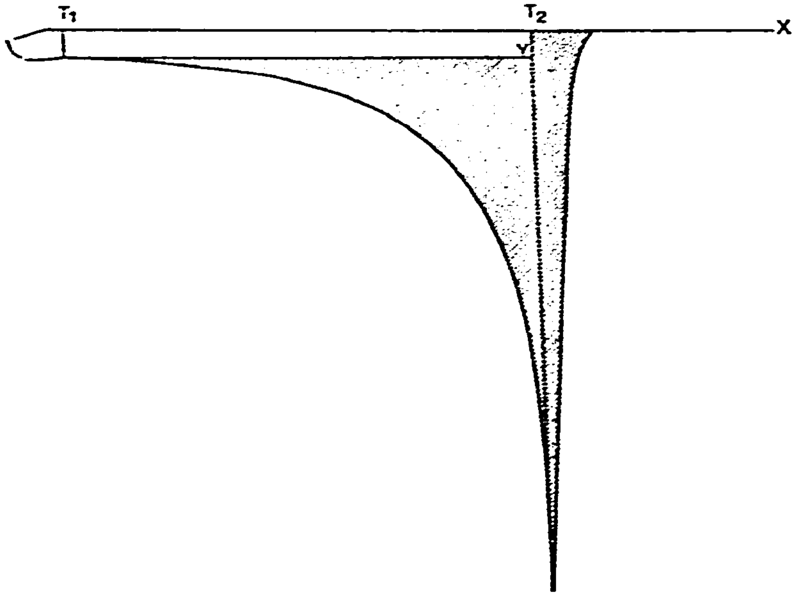

Fig. 2. DSC thermogram for 1-butanol using the parallelogram designation method (graphic); T axis, 20°C in.$^{-1}$, program rate, 10°C min^{-1}, Y axis, 1.0 (mcal sec^{-1}) in.$^{-1}$. C area = 133, ΔH_v area = 374.

thermal techniques[1,2] require time-consuming multiple experimentations; and heat-capacity measurements[3,5] require careful sample weight control, hermetic seal control, and heat-sink contact control and result in C_v values for liquids which have an unknown relation to desired C_p values. The proposed method shows few of the hazards mentioned above.

During the course of the experimental variations of the method (tape sealing of the cap pinhole vs. capping of the pinhole with a loose lid), it became apparent that two interpretations of the sample baseline were possible. Method 1, "The Parallelogram Method" (Fig. 2), shows a sample baseline (Y) drawn parallel to the blank-pan baseline (X) from T_1 to T_2. This method is applicable usually when no attempt is made to cover the pinhole or when such an attempt was ineffective (such as taping with liquids of boiling point >85–90 °C) causing immediate baseline drift. Method 2, "The Extension Method" (Fig. 3), used a sample baseline (Y) extended tangentially from its own initial straight segment (temporary stable sample line with a constant

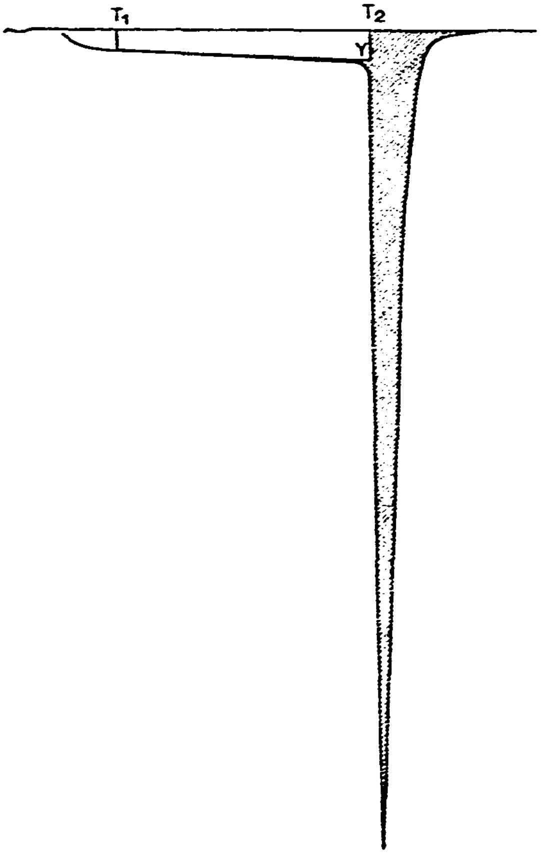

Fig. 3. DSC thermogram for methylene dichloride, graphically interpreted as a baseline extension method (taped puncture hole). Cooled by CO_2 to −40 °C, ending temperature for baseline 80 °C. Temperature scale 20 °C in.$^{-1}$; 10 °C in.$^{-1}$ rate; Y axis 1.0 (mcal sec^{-1}) in.$^{-1}$. C area = 103; ΔH, area = 468.

slope). It may be noted that Methods 1 and 2 concur where the temporary stable sample line slope is approximately parallel to the blank baseline.

It was further noted that the usual practice of lightly taping the pinhole during experiments in which the temperature of the B.P. transition was below 100°C was effective as a general practice as was merely covering the pinhole with an empty lid for liquids with a B.P. above 100°C.

EXPERIMENTAL

All experiments were performed using the DuPont 990 TA system with cell base II and an atmospheric DSC cell compartment. The constantan disc contacts were modified by use of Dow Corning heat sink compound No. 340.

The experimental instrument details are presented in Table 1.

TABLE 1

INSTRUMENT PARAMETERS

Temperature limits	*Chosen to suit the specific properties of the investigative liquids*
Start	At least 50°C below B.P.
End	At least 50°C above B.P.
Y' range	1.0 (mcal sec^{-1}) in.$^{-1}$
Heating rate	10°C min^{-1}
Mode	Return to start
Cell base II	DSC calibrated
	IX
	Derivative OFF
Sample sealing	Hermetic cold-weld seal

While aluminum pans presented little difficulty because of sample–pan interaction, most experiments were conducted in gold pans to ensure against interactions which had been noted to occur in earlier work[4] for heat-capacity determinations.

Sample containment during the initial heating stages was attained by covering the sample pinhole made with a 22-gauge needle with a 2–3 mm square of Scotch magic tape placed over the hole in both the sample and blank pans. Bubble seepage or sample vapor reaction caused by higher temperatures was overcome by using a loose lid positioned on top of the pinhole with both sample and blank pans instead of magic tape during sample run and blank runs and was necessary only with temperatures above 100°C or when sample seepage through the tape was noticeable (by a rapidly changing sample baseline slope).

Experimentally, for low-boiling liquids, a blank scan is determined by performing a heat profile throughout a general temperature range determined by the compound under investigation. The blank determination utilizes cold-weld hermetically sealed pans with the puncture hole in the sample pan as a standard. After completion of the heat scan and cooling, 5–10 μl of sample is introduced into the sample pan and the scan is repeated after applying the square of magic tape over the needle hole. The scan is analyzed as shown in Figs. 2 and 3 and the dependent ΔH_v or C_p value calculated by use of eqn (1). For higher boilers, the procedure is identical except needle holes are placed in both sample and blank pans and an inverted pan cap placed over the top lid of both pans.

After completion of the current work, a similar study of ΔH_v by Staub and Schnyder[6] appeared which suggested that simple lead balls (or BB shot) might be useful instead of the tape or extra inverted lids over the pinhole. We found this method to be inferior to that described in this work.

The empirical value of the experimental method is its simplicity and the fact that weights of sample are unnecessary, unlike experiments in which heat capacity values are to be determined[4,5].

RESULTS

The determining factor in the usefulness of the described method is the geometric assignment and measurement of dependent C_p areas vs. endothermic B.P. areas as shown in Fig. 1. While in its simplest case, these areas can be graphically assigned, we found precision and accuracy were best served by using a plane polarizing planimeter. The planimeter method eliminated the need to idealize irregular shapes into geometric sections, although great care must be exercised in utilizing the planimeter.

In the standards used to evaluate the method, the coefficient of variations (Tables 2–4) ranged from 0.60–1.91% in multiple determinations of both ΔH_v and C_p when experimental data (recorded thermograms) based upon coordinate values obtained by standard DSC procedures[1,4] were used.

TABLE 2

EXPERIMENTAL C_p AND ΔH_v DETERMINATIONS[a] FOR 1-BUTANOL

Run No.[b]	C_p *(cal g^{-1} °C^{-1})*	ΔH_v *(cal g^{-1})*
1	0.573	143.4
2[c]	0.581	141.4
3[c]	0.584	140.7
4	0.556	147.6
5	0.582	141.2
6	0.574	143.4
7	0.571	143.6
Mean	0.574	143.0
Standard deviation	0.0095	2.342
Coefficient of variation (%)	±1.65	±1.64
Confidence limit (95%)	$0.574 \pm 0.008_7$	$143.0 \pm 2.16_6$
Literature value[7]	0.582 (30 °C)	141.3

[a] Using dependent coordinate C_p or ΔH_v values determined by a different method. [b] Single determination values. [c] Taped pinhole.

TABLE 3

EXPERIMENTAL C_p AND ΔH_v DETERMINATIONS[a] FOR XYLENE

Run No.[b]	C_p	ΔH_v
1	0.411	81.0
2	0.414	80.4
3	0.409	81.5
4	0.414	80.5
5	0.416	80.1
6	0.413	80.7
Mean	0.412_8	80.7
Standard deviation	0.0024	0.4938
Coefficient of variation (%)	±0.58	±0.61
Confidence limit (95%)	$0.412_8 \pm 0.002_5$	$80.7 \pm 0.51_8$
Literature value[7]	0.411 (25 °C)	81.0

[a] See Table 2. [b] Singlet determinations using inverted cap seal method.

TABLE 4

EXPERIMENTAL C_p AND ΔH_v DETERMINATIONS[a] FOR 2,2-DIMETHOXYPROPANE

Run No.[b]	C_p	ΔH_v
1	0.582	80.6
2	0.577	81.4
3	0.560	83.9
4	0.589	79.8
5	0.573	82.0
6	0.592	79.4
7	0.571	82.2
Mean	0.577	81.3
Standard deviation	0.011	1.549
Coefficient of variation (%)	±1.90	1.91
Confidence limit (95%)	0.577±0.010	81.3±1.43
Literature value[7]	0.579 (50 °C)	81.1

[a] See Table 2. [b] Singlet determinations using tape seal method.

The accuracy evaluations of butanol, xylene and 2,2-dimethoxypropane (Tables 2–4) for C_p and ΔH_v were, respectively: 98.6%, 101.2%; 100.4%, 99.6%; 99.8%, 100.2%.

During the course of the investigation, it was noted that chloroform anomalously failed to give values or thermograms within normally accepted experimental variation. This was true either in aluminum or gold pans, by a taped or non-taped closure method, or by the "parallelogram" or "straight baseline" interpretation. After similar experiments with carbon tetrachloride and methylene chloride, it was concluded that the anomaly was the result of the peculiar halogenrelated dielectric associated with $CHCl_3$ which is not evident with either CCl_4 or CH_2Cl_2.

The results of this series of experiments appear in Table 5.

TABLE 5

C_p AND ΔH_v VALUES FOR SOME SELECTED LOW AND HIGH BOILERS

Compound	C_p *(cal g^{-1} °C^{-1})*		ΔH_v *(cal g^{-1})*	
	Exp.^{a} *value*	*Lit.*^{8} *value*	*Exp.*^{a} *value*	*Lit.*^{8} *value*
CH_2Cl_2	0.287^b	0.288 (15°C)	79.3^b	78.6
CCl_4	0.208	0.201 (20°C)	44.8	46.4
$CHCl_3$	0.429^c 0.437^c	0.226 (15°C)	31.1^c 30.5^c	59.0
N,N-Dimethyl aniline	0.426^d	0.418 (20°C)	79.1^d	80.8
Distilled H_2O	0.997^e	1.000 (15°C)	541.4^e	539.6

[a] Except for $CHCl_3$, the experimental value is an average of duplicate determinations differing by not more than 2%, relative. [b] For CH_2Cl_2, average is for one taped, "extended-baseline" method and one non-taped, "parallelogram" method. [c] Singlet determination by pan cap method. [d] Taped-pan method. [e] Non-taped method.

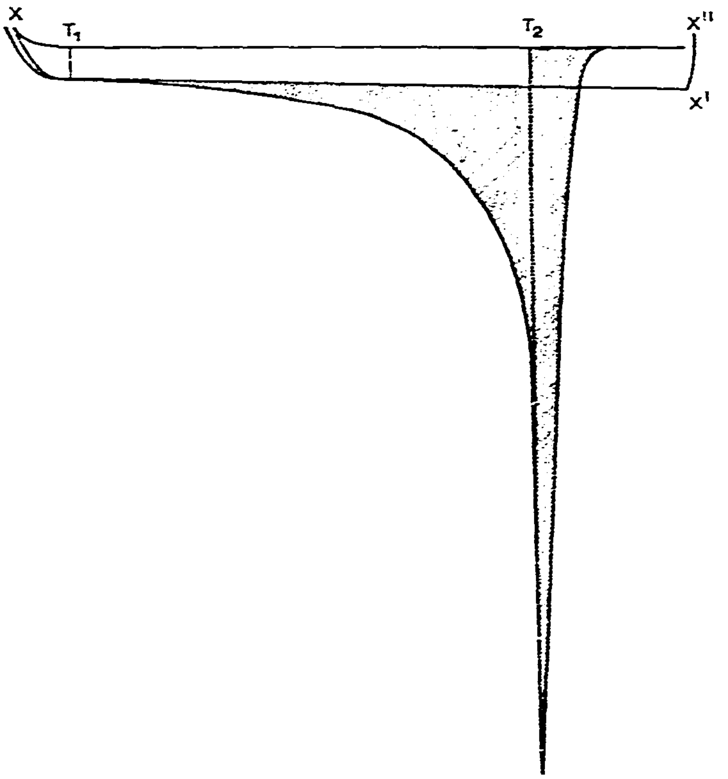

Fig. 4. Dual DSC thermogram of toluene with heat capacity determination circumscribed on a B.P. (ΔH_v) experiment, showing the full Carnot cycle area.

The advantages of the proposed empirical approach suggested by this work are:

1. A reduction in the number of determinations required in ΔH_v experiments, if C_p is known or has been determined by other methods. No Clausius–Clapeyron plot necessary.
2. Solves the problem of sample containment (in cold-weld hermetic capsules) in true C_p determinations.
3. Eliminates sample weighings in C_p determinations, if ΔH_v is known or has been experimentally obtained by other means.
4. True C_p values can be obtained and not C_v values as is the case in DSC determinations at the present time (since the sample is not subjected to pressure changes).

As further proof of the validity of the empirical approach described, as well as the presumed relationship between assigned areas in the two different methods given, a different approach was tested for a relatively high boiler shown in Fig. 4. In this figure, the procedure was such that the "parallelogram picture" was reproduced by instrumental means in the same manner as by graphic means. The area circumscribed by X, X′, X″ showed the normal Carnot cycle that would appear in a DSC heat capacity method. T_1 and T_2 were chosen in the manner described above.

The procedure followed to produce the instrument-generated parallelogram (Fig. 4) was:

a. Scan an empty pan baseline (X, X″).

b. Scan with a sealed (cold-weld, gold) capsule to inscribe area X, X′, X″.

c. Cool, then carefully puncture the same sample capsule and rescan as a boiling point thermogram.

d. The areas attributed to C_p and B.P., and all calculations and measurements are assigned as previously described.

e. Sample weight is not needed if C_p or ΔH_v is known, but can be used if C_p or ΔH_v is not known.

For toluene (Fig. 4),

$$\Delta H_v = \frac{431 \text{ area counts (punctured)}}{190 \text{ area counts (sealed)}} \times 0.421\,(C_{p50})^8 \times 90\,^\circ\text{C}\,(T_2 - T_1) =$$

$$= 86.0 \text{ cal g}^{-1}$$

$$C_p = \frac{190}{431} \times 86.5^8 \text{ cal g}^{-1} \times \frac{1}{90^\circ} = 0.424 \text{ cal } ^\circ\text{C}^{-1} \text{ g}^{-1}$$

The accuracy denoted by the above for

$$\Delta H_v = \frac{86.0}{86.5} \times 100 = 99.4\% \qquad \text{and} \qquad \text{for } C_p = \frac{0.424}{0.421} \times 100 = 100.7\%.$$

Values obtained using the weight of sample and the standard methods of calculation[2,3] are:

$$C_{p50^\circ} = \frac{60 \times 1.055 \times 0.40}{10 \times 6.06} = 0.418$$

$$\Delta H_v = \frac{431}{190} \times 0.418 \times 90^\circ = 85.3$$

The deviations are well within experimental error.

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