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AN IMPROVED METHOD OF MEASUREMENT OF VAPORIZATION HEAT OF VOLATILE LIQUIDS WITH A DIFFERENTIAL SCANNING CALORIMETER

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ABSTRACT

An improved method is presented to measure the latent heat of vaporization of volatile liquids at atmospheric pressure on a differential scanning calorimeter. Individual measurement errors of 8–10-mg samples were reduced to less than 2% and the average error of five runs on benzene and toluene was less than .01%.

MATERIALS AND METHODS

Introduction

A Perkin-Elmer, model DSC-1B, differential scanning calorimeter was used in this study. It uses samples in the 1–10-mg range. Two methods[1] are available to measure the heat of vaporization of volatile liquids. Measurement errors of these methods are rather large and this investigation improved the equipment arrangement and established a procedure to yield good measurements.

The first available method (Programmed Temperature Method) consists of sealing the volatile sample in a pan and making a pinhole in the cover, see Fig. 1a. The sample pan is then placed in the calorimeter and the temperature is programmed to rise and pass through the boiling point of the liquid. Since the rate of vaporization is a function of temperature it is necessary to make a correction for the substantial amount of sample vaporized before reaching its boiling point. This correction can be made by using a thermal conductivity effluent analysis accessory to determine the amount of sample vaporized at temperatures below the boiling point. Fig. 2 shows the recorded curves of differential power and effluent thermal conductivity. From these curves the latent heat of vaporization is calculated.

The major difficulties of this method of obtaining accurate data are: (1) unknown sample loss occurring between weighing the sample, placing it in the calorimeter, and during purging the system; (2) a small sample mass as limited by maximum peak height of differential power curve on the recorder; and (3) the necessity of making six integrations for each determination. This sample loss in (1) can be excessive even at room temperature. Consider, for example, acetone sealed in a volatile sample pan with a .02-in hole in the cover at room temperature. The acetone was found to vaporize at about .25 mg/min in a calm balance case. This rate would increase substantially in the calorimeter where a purge gas is flowing and the temperature becomes substantially higher than room temperature. Thus, even when using a large sample of 10 mg, evaporation alone would introduce a minimum of 2.5% error for every minute between weighing and the time the effluent analyser becomes effective. Moreover, the effluent analyser cannot be used until the air is purged from the system and after the carrier gas-flow rate has reached a steady state. This operation usually takes about 4 min. Therefore, a minimum uncertainty of 5–10% would result for the largest possible sample size. In addition, such a large sample can not be actually used because the differential power recorder would go off scale even if temperature is programmed through the boiling point on the least sensitive range setting. Therefore, it was necessary to use only small samples, which in turn increased the uncertainty on evaporated mass and also amplified the integration error.

The second method (Isothermal Mini-putter Method) is similar to the first one except that a small ball (.031-in diameter) is placed tightly on the cover hole (.006-in diameter, see Fig. 1b) to stop vaporization. The runs are to be made isothermally. The ball was found to reduce the vaporization rate to about half of

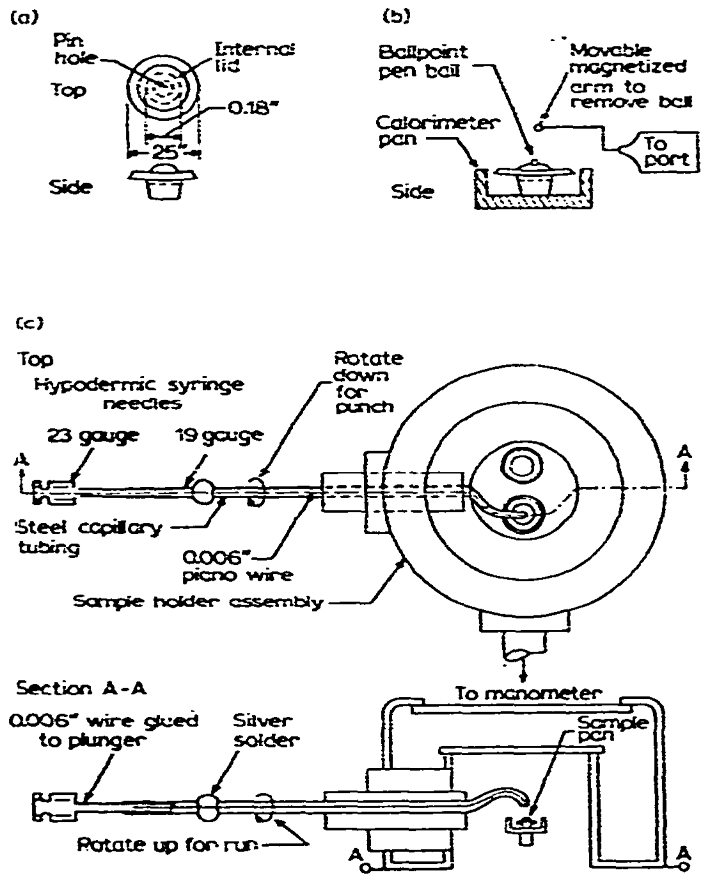

Fig. 1. (a) Volatile sample pan; (b) sample pan with ball; (c) apparatus used to puncture sample pans.

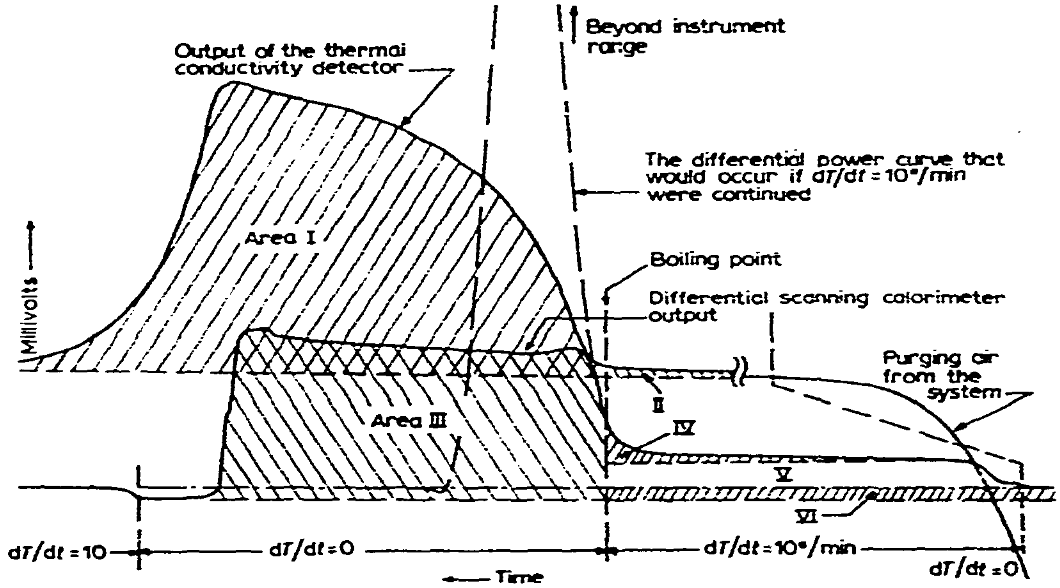

Fig. 2. Area I, proportional to sample mass evaporated at boiling point; II, proportional to sample mass evaporated before reaching boiling point; III, energy to evaporate sample (area I) at boiling point; IV + VI, energy to evaporate sample (area II) before reaching boiling point; V, sensible heat to raise sample temperature.

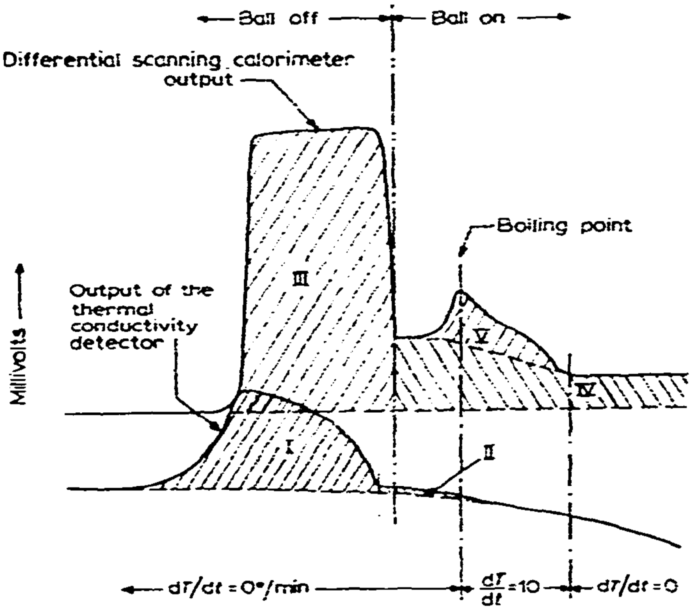

Fig. 3. Area I, proportional to sample mass evaporated at boiling point after removing the ball; II, proportional to sample mass evaporated before reaching boiling point; III, energy to evaporate sample (area I) at boiling point; IV, energy to heat the sample and ball to reach boiling point; V, energy to evaporate sample (area II) before reaching boiling point.

that of the previous method but an additional uncertainty about the proper baseline was resulted (Fig. 3). Experimental data are shown in Table I which indicates an improvement but the error was still rather large.

TABLE I

HEAT OF VAPORIZATION OF BENZENE MEASURED BY TWO METHODS

Method	*Sample mass (mg)*	ΔH_{vap} *(cal/g)*	*Deviation from lit.*[2] (%)
1[a]	7.868	127	+35
2[b]	8.976	84.2	−10.6

[a]Method 1 — Programmed Temperature Method, .006-in diameter hole. [b]Method 2 — Isothermal Mini-putter Method, .006-in hole with a .031-in ball.

To improve the measurement precision, the new method consists of better arrangements and procedures to prevent sample loss and to increase the integration accuracy.

Equipment modifications

A puncture device was designed and installed as shown in Fig. 1c. It consists of a sharpened .006-in diameter wire in a syringe and could be manipulated externally to puncture a very thin external cover and an internal lid of a sealed sample pan. Here the equipment temperature may be either programmed or held constant. However, only isothermal runs were made in this study.

To facilitate puncturing, the aluminum sample-pan covers supplied by Perkin–Elmer were thinned by sanding with a very fine (No. 400) sand paper. To improve the reproducibility an aluminum cover with the sample sealed in was held on a holding rod connected to a 100-r.p.m. motor. Fifty light strokes with the sand paper was found adequate.

A Leeds and Northrop Speed-O-Max G recorder was connected to the DSC unit and was used to drive a Perkin–Elmer 194-B Integrator which counts 6000 times per minute. This arrangement provided a printed read-out, eliminated tedious graphical integrations and improved reproducibility and precision of results.

Procedures

The cover, an internal lid, and a sample pan are cleaned with methylene chloride and then weighed on a Cahn electric balance. A volatile sample is fed to the pan and the internal lid and the thinned external lid cover are placed and sealed. This sealed pan is weighed again on a Cahn balance to measure the mass of sample. The external lid is thinned according to a procedure described earlier and the pan is weighed to observe if a leakage exists.

The sample pan is then placed in the DSC unit together with a reference pan. After the system has been purged and the sample holder is brought to the desired pressure (760 mm Hg) the temperature is programmed manually up to the sample boiling point. A zero baseline is then established on the recorder chart with a calorimeter sensitivity or range setting (*e.g.* 4 mcal/sec on Fig. 4) at which vaporization is to be conducted.

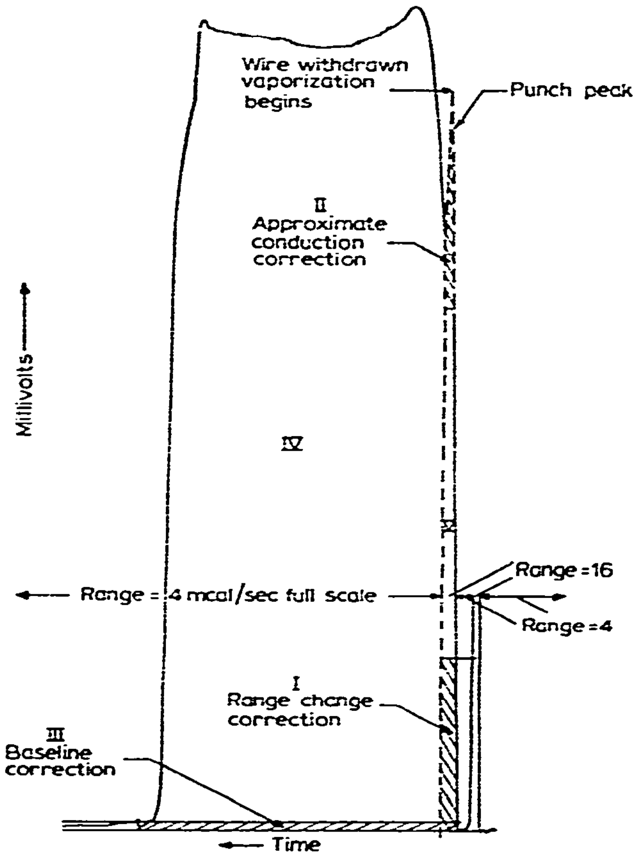

Fig. 4. Area I, range change correction due to baseline shift; II, correction for energy dissipated during punching operation; III, correction for baseline shift; IV, energy to evaporate sample at boiling point after punching; V, energy to evaporate sample during punching.

During punching, the thermal load would be high due to contact of the punch wire. Therefore, the range must be set high at 16 (or 32) mcal/sec. Since a change of setting would cause a shift of baseline, this shift magnitude should be recorded on the recorder chart before punching. Return the range to the previous low-range setting and print the integrator reading *a*. As quickly as possible, change the range to 16 (or 32), rotate the punch-wire guide into position, punch a hole in the sample pan, withdraw the wire from the hole while observing for any expelled liquid, and then rotate the punch-wire guide back to its original position. When the DSC recorder pen *approaches the mid-scale, the range is switched back to the low setting (e.g. 4 mcal/sec* on Fig. 4) and simultaneously print the integrator reading *b*. The difference (*b*−*a*) corresponds to the punch-peak area in Fig. 4. Allow all of the sample to vaporize and the pen would return to a new baseline. Print the integrator reading *c* and mark the position of the recorder pen on recorder chart when integrator print is made. The difference $(c-b)$ corresponds to areas III and IV. To determine area II or the conduction correction during punching, set range on 16 (or 32), zero the recorder, print the integrator reading *d*, punch a hole in the pan, and print the integrator reading *e* when the pen return to zero. The difference $(e-d)$ is the area II. This completes the run.

The latent heat of vaporization is thus calculated as follows:

ΔH_{vap} (in cal/g) $= [(c-b-60t_{\mathrm{v}}C_{\mathrm{Bv}}) + (b-a-e+d-60t_{\mathrm{p}}C_{\mathrm{Bp}})(R_{\mathrm{p}}/R_{\mathrm{v}})](K_{\mathrm{v}}/m)$, where

a,b,c,d,e = count readings from the integrator
t_{v} = vaporization time reading from recorder chart (min)
t_{p} = punch time reading from recorder chart (min)
C_{Bv} = base-line correction from chart for vaporization (%)
C_{Bp} = base-line correction from chart for punching (%)
R_{v} = range for vaporization, mcal/sec
R_{p} = range for punching, mcal/sec
K_{v} = calibration constant of DSC at R_{v}, mcal/integrator readout digit
m = mass of sample, mg

RESULTS AND DISCUSSIONS

The punch operation can result in expelling liquid sample. Data of runs with visually observable expelling were discarded. Table II shows the results of many

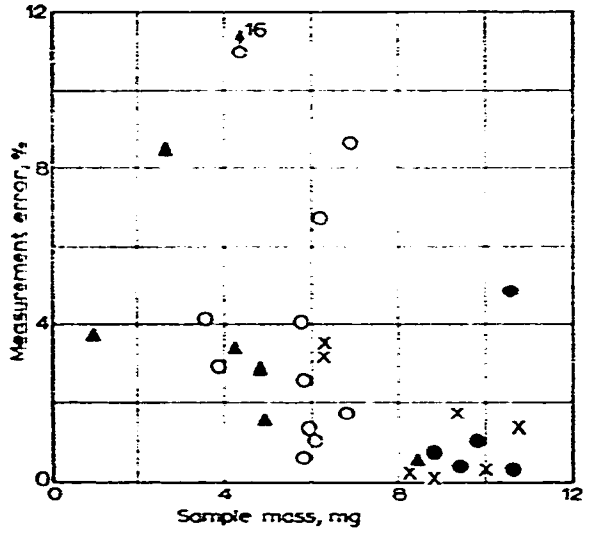

Fig. 5. Measurement error *vs.* sample mass of various internal lid configurations of Table II: ○, no; ●, loose; ▲, tight; x, sealed foil.

internal lid configurations. The sealed aluminum foil as proposed appears to be the best arrangement. The expelling may be due to condensed liquid on inside surface of the external lid or adhesion of liquid to the punch wire during withdrawal. The sealed foil as an internal lid prevents condensation on inside of the external lid, and any liquid adhered to the wire may be wiped by the foil as well as the external lid during withdrawal.

Fig. 5 shows the per cent errors relative to mass of liquid samples used for various internal lid configurations of Table II. The general trend of an increased

TABLE II

MEASUREMENTS OF IMPROVED METHOD WITH VARIOUS INTERNAL LID CONFIGURATIONS

Internal lid configuration	*Sample*[a,b]	*Sample*	ΔH_{vap} (*mcal/mg*)[c]	*% Error (c) of measured* ΔH_{vap}
A. No internal lid	BZ-28	9.424	93.83	−.3
	BZ-29	10.600	93.94	−.2
	BZ-38	10.516	98.73	−4.8
	BZ-39	8.824	94.85	+.7
	BZ-41	9.861	95.12	+1.0
B. Loose internal lid (.17-in dia.)	BZ-48	5.900	92.87	−1.3
	BZ-55	4.148	109.4	+16.2
	BZ-60	6.816	95.74	+1.7
	BZ-61	4.840	96.47	+2.5
	BZ-64	6.032	93.18	−1.0
	BZ-65	6.910	86.02	−8.6
	BZ-63	6.204	100.45	+6.7
	BZ-91	5.832	93.62	+.6
	BZ-67	3.864	91.37	−2.9
	BZ-88	5.828	97.89	+4.0
(.18-in dia.)	BZ-21	3.480	90.28	−4.1
C. Internal lid pressed tight (with forceps)	BZ-24	8.404	93.69	−.5
	BZ-89	4.18	91.03	−3.3
	BZ-90	2.648	86.3	−8.4
(with rod)	BZ-42	.972	97.59	+3.7
	TOL12	4.824	89.2	+2.8
	TOL14	4.912	88.1	+1.5
D. Sealed aluminum foil internal lid	BZ-83	6.336	97.36	+3.4
	BZ-95	8.844	94.12	−.02
	BZ-97	10.072	93.91	+.25
	TOL19	6.220	89.5	+3.1
	TOL20	9.416	85.30	−1.7
	TOL22	8.128	87.01	+.2
	TOL23	10.788	87.90	+1.3

[a] All sample numbers beginning with the letters BZ are made from spectro-grade benzene. [b] All sample numbers beginning with the letters TOL are made from reagent-grade toluene. [c] The lit.[2] values used are: benzene ΔH_{vap} = 94.14 mcal/mg, toluene ΔH_{vap} = 86.8 mcal/mg.

precision for a larger sample mass does exist as expected. Runs with internal lids pressed tightly or sealed did show better results than loose internal lids or no lid. The use of a sealed aluminum foil is preferred because a small force is required in punching. This protects the DSC heater unit under the sample pan and results less frequent expelling of liquid also. The five runs with sealed aluminum foil and 8- to 10-mg sample showed an error range of measured ΔH_{vap} as -1.7 to $+1.3\%$. The average error of these runs is less than 0.01%. This shows that further improvement of measurement accuracy can be made by making repeated runs as in any other measurement or analysis work.

CONCLUSION

An improved method with modifications and procedure is proposed for a DSC or similar calorimetric unit to measure the latent heat of vaporization of volatile liquids. With a sample mass of 8 to 10 mg, the measured latent heats showed less than 2% error.

ACKNOWLEDGMENT

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