Thermochimica Acta
Elsevier Publishing Company, Amsterdam
Printed in Belgium

EVALUATION OF THERMAL ANALYSIS EQUIPMENT FOR THE DETERMINATION OF VAPOR PRESSURE AND HEAT OF VAPORIZATION

GERALD P. MORIE, TROY A. POWERS, AND CLYDE A. GLOVER
Research Laboratories, Tennessee Eastman Company, Division of Eastman Kodak Company, Kingsport, Tennessee 37662 (U. S. A.)

(Received July 8th, 1971)

ABSTRACT

A rapid, relatively simple method for determining vapor pressure and heat of vaporization on small amounts of organic compounds is described. A DuPont 900 differential thermal analyzer (DTA), a Perkin-Elmer Model DSC-1B differential scanning calorimeter (DSC), and a Thomas-Hoover (T-H) melting point apparatus were evaluated in this work. Vapor pressure data for a wide variety of organic liquids were obtained by measuring the boiling points of the liquids at pressures ranging from 20 to 735 torr. A computer was used to rapidly plot the experimental data. The average deviations of boiling points from the literature values were 2.3°C for the DTA, 1.2°C for the DSC, and 1.5°C for the T-H. The vapor pressure data were used to solve the Haggenmacher equation for heat of vaporization (ΔH_v). The deviations of the experimental values for ΔH_v from the literature values were 5.5%, 8.3%, and 3.3% for the DTA, DSC, and T-H methods, respectively.

INTRODUCTION

Differential thermal analysis (DTA) is a routine technique for the determination of boiling points. Boiling points at atmospheric[1,2], subatmospheric[3,4], and super-atmospheric pressures[5] have been measured by this thermal technique. Differential scanning calorimetry (DSC) has also been used to determine boiling points, and a detailed procedure has been written by the manufacturer[6]. The temperature-vapor pressure dependence of a few liquids has been measured by DTA[3,7,8]. Most of the previous work was done with custom-made equipment or with commercially available equipment which had several modifications. Usually, the technique was evaluated with water or a few normal hydrocarbons.

Thermal techniques have also been used to measure heats of vaporization at or near the normal boiling points for numerous compounds. Usually, this has involved an area measurement of the boiling endotherm. However, some evaporation of the compound always occurs before the boiling point is reached. Thus, the exact amount of compound in the instrument at the time the boiling point is attained is unknown. This problem is overcome when the Clapeyron equation is used to calculate the heat of vaporization. However, this equation assumes ideal gas behavior, which may be in error for many compounds.

The purpose of our work was to make vapor pressure and heat of vaporization measurements on a wide variety of compounds having different intramolecular and intermolecular attractions. Two popular, commercial thermal analysis instruments were compared for this purpose. Only modifications in the sample assembly of each instrument were made. Vapor pressure curves were quickly obtained on very small samples. The data obtained were compared with those in the literature and with boiling points obtained by the classical inverted capillary technique[9] performed on a Thomas–Hoover melting point apparatus. Vapor pressures and heats of vaporization were calculated by a computer, and vapor pressure curves were plotted by a Cal Comp plotter. The Haggenmacher method[14], which corrects for liquid volume and nonideal gas behavior, was used to calculate the heat of vaporization.

EXPERIMENTAL

Apparatus

A DuPont Model 900 differential thermal analyzer, a Perkin–Elmer Model 1B differential scanning calorimeter, and a Thomas–Hoover melting point apparatus (A. H. Thomas Company, Catalog No. 6406-K) were used in this work. The sample chambers of neither the DTA nor the DSC would maintain a reduced pressure as they were received from the manufacturers. Therefore, vacuum chambers, which are shown in Figs. 1–3, were devised. These chambers were evacuated to a given pressure and isolated from the system; then, the pumping was discontinued. A steady pressure was maintained long enough to determine the transition temperature at that pressure.

A U-type open-end mercury manometer was used for all pressure measurements.

Materials

Carborundum boiling chips were ground and passed through a 325-mesh sieve.

Toluene, hexane, chlorobenzene, and ethyl propionate were purified by preparative gas chromatography. Eastman reagent-grade nitrobenzene was used as received, and octyl alcohol and acetic acid were purified by distillation.

Procedure

Differential scanning calorimetry — Each sample was placed into a volatile-sample pan into which Carborundum powder had previously been added, a lid was placed on the sample pan, and then a pin hole was made in the lid so that the container was unrestricted. A similar pan containing only Carborundum powder was used for a reference. A sensitivity of 8 mcal/sec, full-scale deflection, and a heating rate of 10°C/min were used. Temperature calibration of the DSC was achieved by comparing the temperature of the boiling endotherm at ambient pressure with the boiling point given by the literature vapor pressure curve. Boiling points were measured as a function of pressure using the extrapolated onset of the endotherm as the boiling point.

Differential thermal analysis — The sample was mixed with Carborundum powder, and then a 1-mm-I.D. capillary was packed with the mixture to a depth of

3–5 mm. Dry Carborundum powder was used for a reference material. The instrument was operated at 30°C/min and a sensitivity of 0.04 mV/ in of chart paper. Although the DTA cannot be easily adjusted using a melting point of boiling point standard, the deviation of the experimental boiling points of toluene at various pressures from the literature values was used to correct subsequent experimental data.

Thomas-Hoover apparatus — The classical inverted capillary boiling point method[9], which was originally described by Siwoloboff[10], was used, and the boiling points were observed visually.

Treatment of the data — Standard vapor pressure (P) plots of ln P *versus* $1/K$ were made with an IBM Model 1130 computer and CalComp plotter. A least squares fit of each set of data to a straight line was made; the plots are shown in Figs. 4–10. To obtain a measurement of the accuracy for the method, we plotted the data as log P *versus* temperature (°C) and compared then with the literatures values[11]. The heat of vaporization was calculated by the Haggenmacher method modified by Fishtine[12].

RESULTS AND DISCUSSION

Characteristic thermograms are shown in Figs. 11 and 12. The equilibrium boiling point is taken as the intercept of the extrapolated onset of the endotherm and the extrapolation of the baseline as shown in these figures. It has previously been shown that a small sample size is best for these boiling endotherms[8]. When small samples are used, the sample usually completely evaporates before an endotherm peak occurs. Thus, normal endotherms with a peak and return to baseline do not usually occur.

Dilution of the sample with an inert material increases the surface area of the sample and reduces superheating. In addition, a better match of thermal conductivity and specific heat of the sample and reference are attained. Previous investigators used Carborundum[7] boiling chips and small diameter glass beads[8] for this inert support. We evaluated both materials and found that more reproducible, more well-defined thermograms resulted when Carborundum powder was used.

In our study, liquid → vapor transitions were measured. Calibrations made with a liquid → vapor transition were found to be more accurate than those made with a solid → liquid transition.

Standard vapor pressure graphs of the natural logarithm of the pressure versus the reciprocal of the absolute temperature were made. The data, shown in Figs. 4–10, were plotted by an IBM 1130 computer equipped with a CalComp plotter. The correlation coefficient for the best straight line was greater than 0.999 for all sets of data. A comparison of the experimental data with those in the literature can be made using the vapor pressure curves or the statistical summary shown in Table I. The experimental data compare well with the literature data; however, the difference between the slopes of the DSC data and the literature data is greater than the differences between the slopes of the literature data and either the DTA data or the T-H data. The standard error of the slope (or estimated standard deviation of the slope) given in Table II is a measure of the dispersion of the points about the line[13].

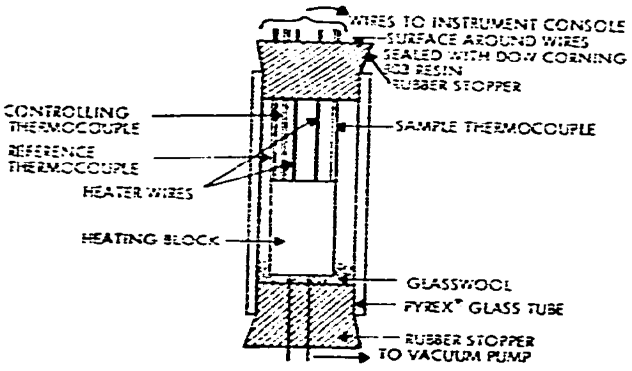

Fig. 1. DTA vacuum chamber.

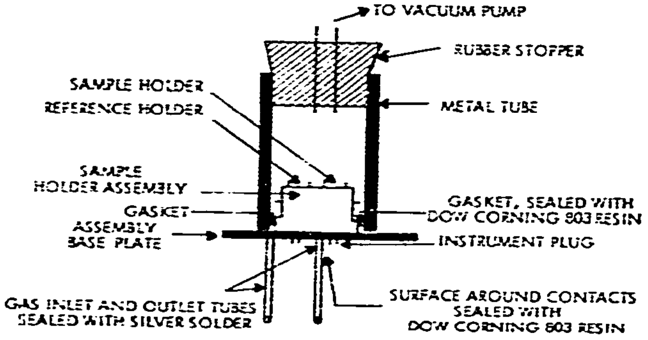

Fig. 2. DSC vacuum chamber.

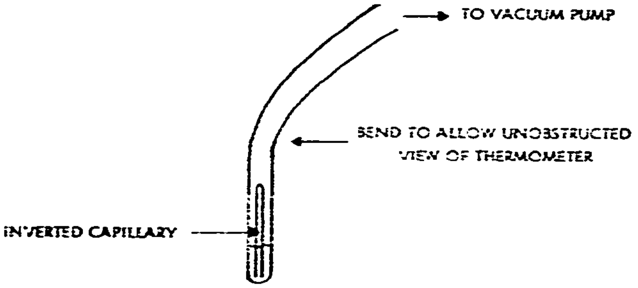

Fig. 3. Modification of T–H boiling setup for use under reduced pressure.

To obtain a measure of accuracy in terms of temperature, we plotted boiling point (°C) *versus* log P and listed the deviations of the experimental boiling points from the literature values in Table II. For each method, an average of the deviations at all pressures was calculated; these averages are also listed in Table II.

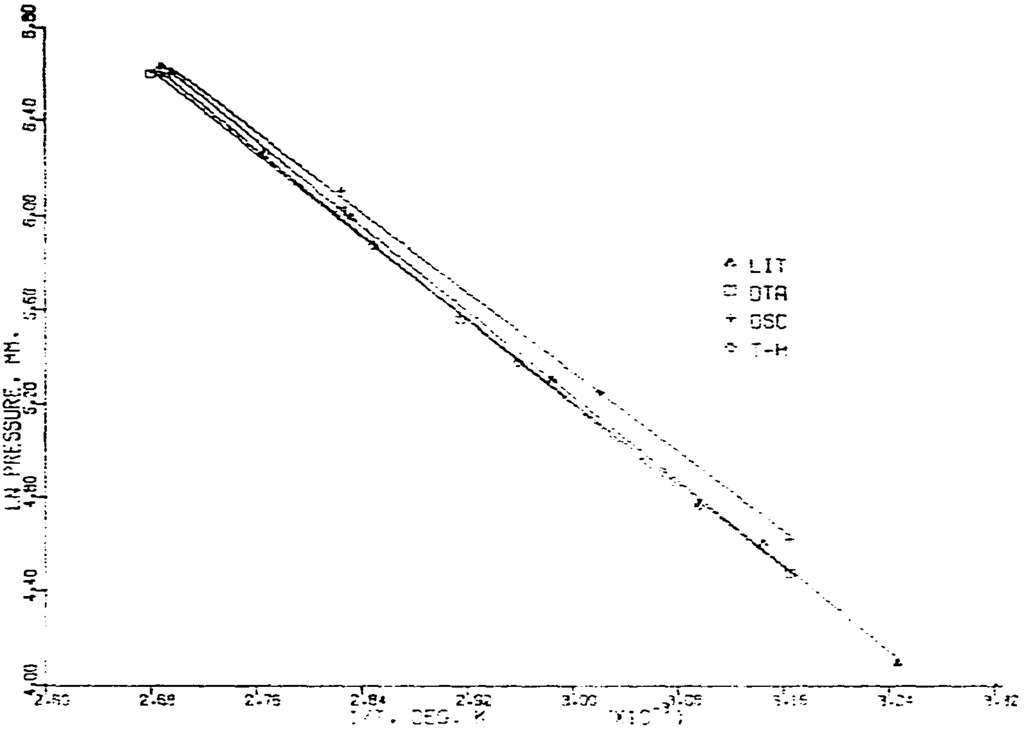

Fig. 4. Vapor pressure of toluene.

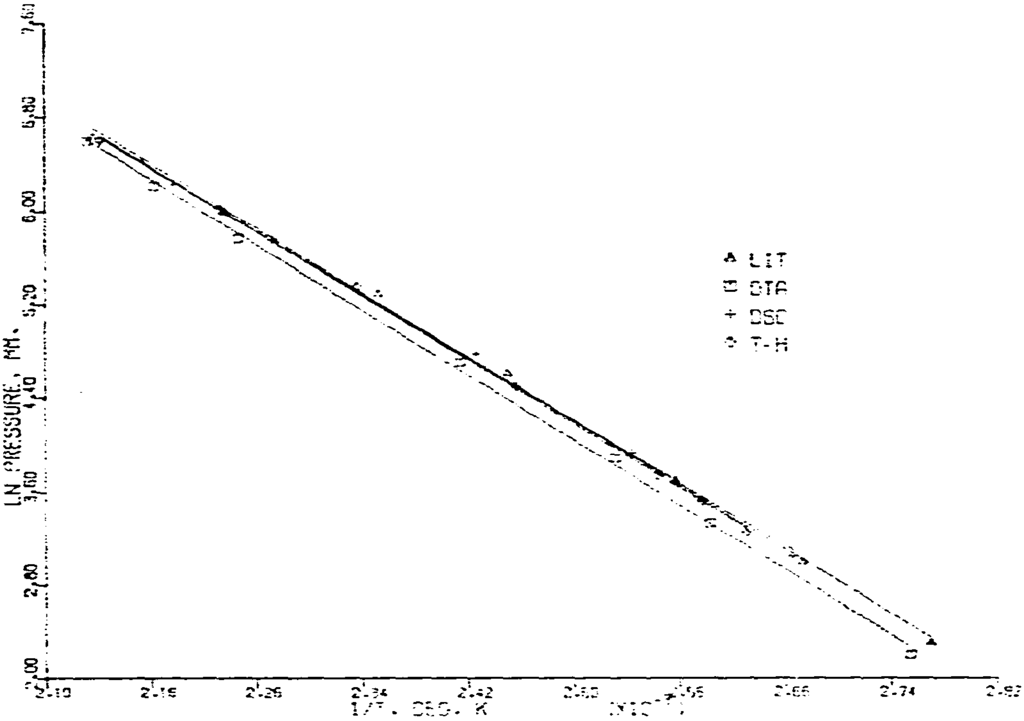

Fig. 5. Vapor pressure of octyl alcohol.

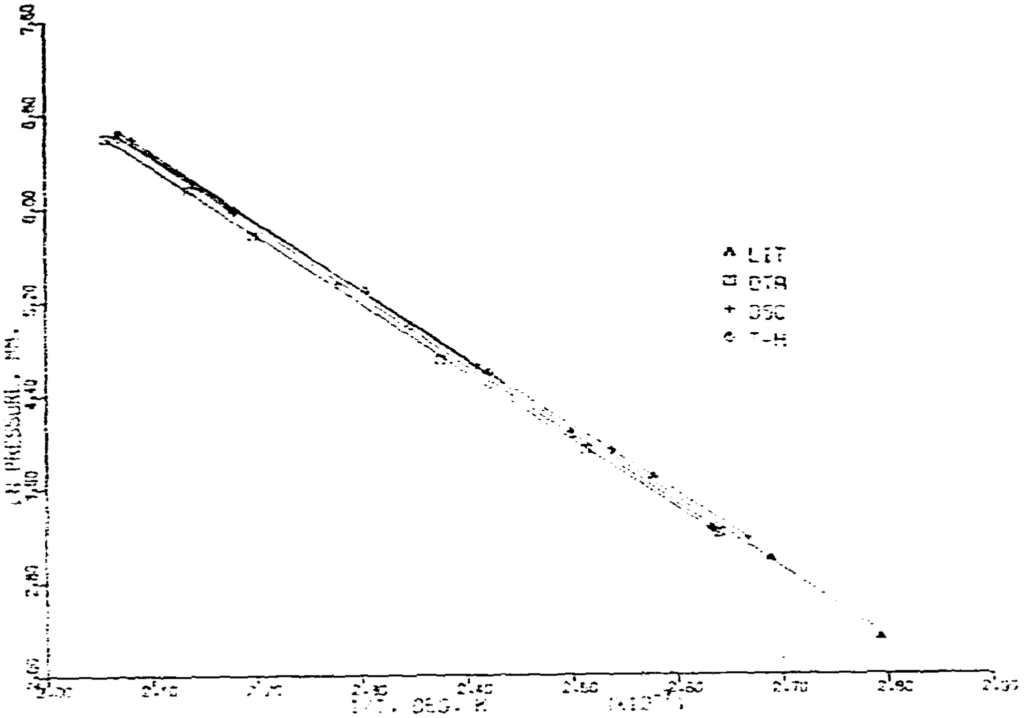

Fig. 6. Vapor pressure of nitrobenzene.

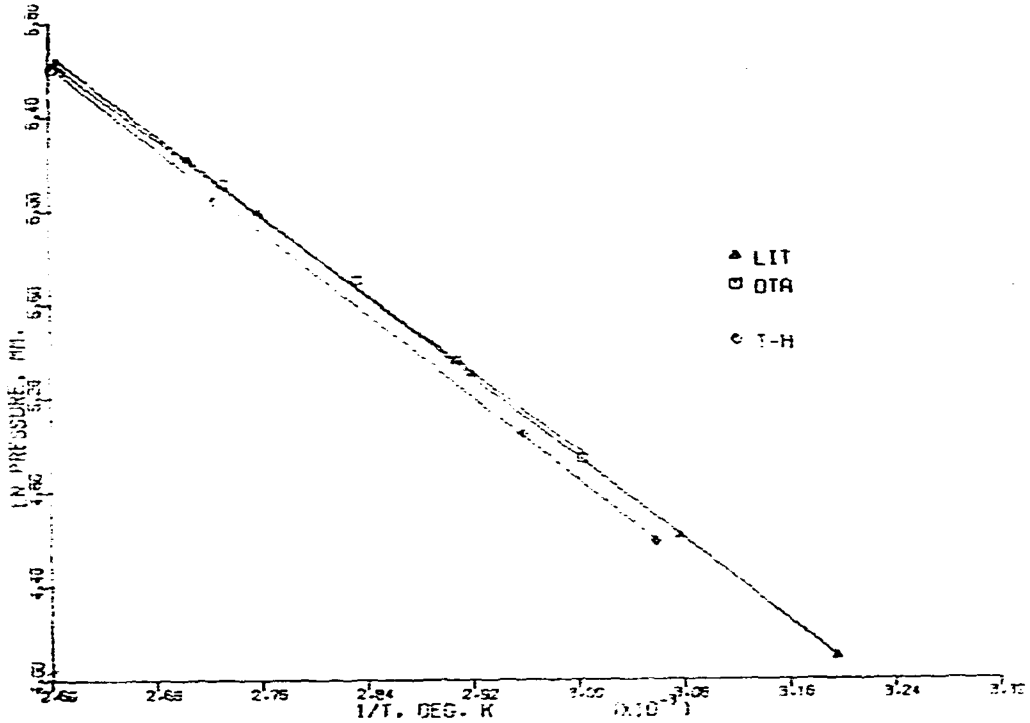

Fig. 7. Vapor pressure of ethyl propionate.

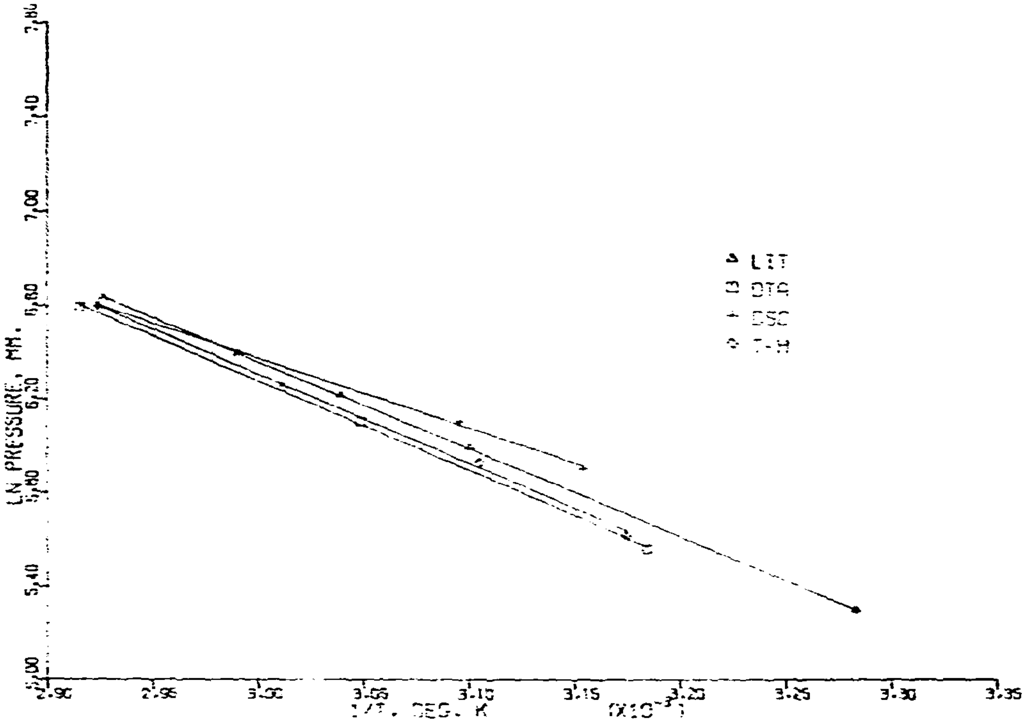

Fig. 8. Vapor pressure of hexane.

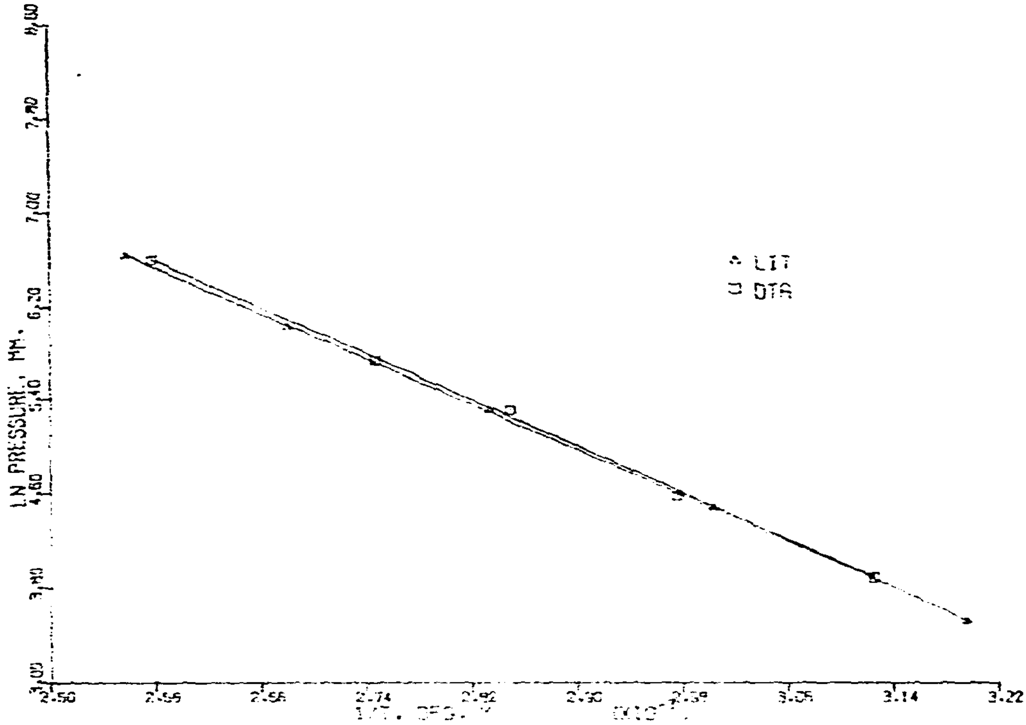

Fig. 9. Vapor pressure of acetic acid.

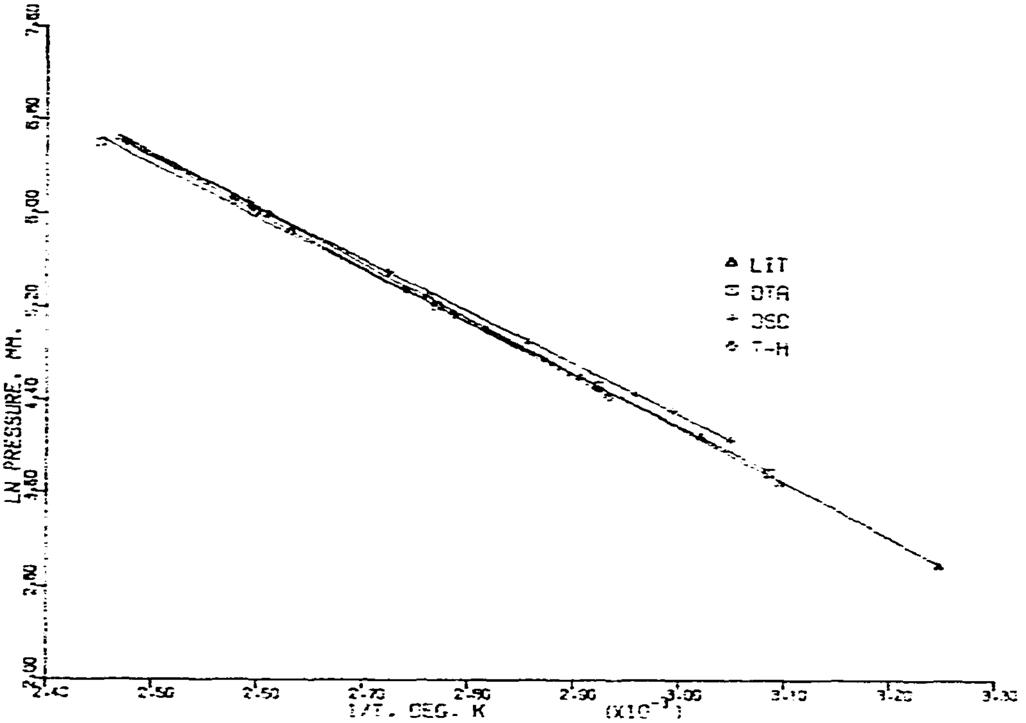

Fig. 10. Vapor pressure of chlorobenzene.

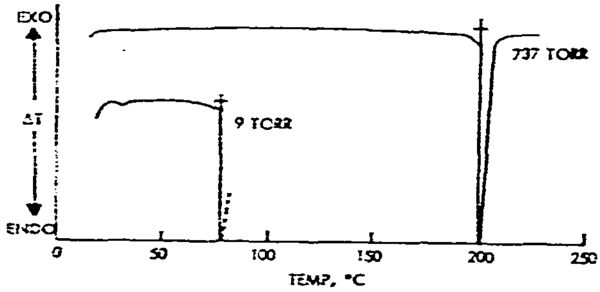

Fig. 11. DTA thermograms of octyl alcohol.

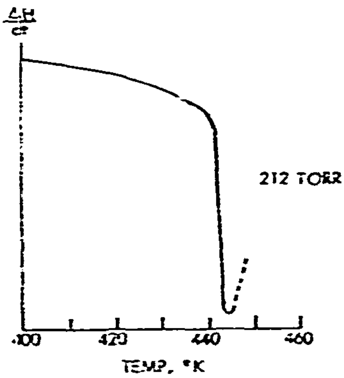

Fig. 12. DSC thermogram of nitrobenzene.

TABLE I

STATISTICAL COMPARISON OF DTA, DSC, AND T–H DATA

Compound		*Literature*	*DTA*	*DSC*	*T–H*
Acetic acid	slope	—4867	−5018		
	slope error, %	5.7	8.9		
Chlorobenzene	slope	−4689	−4508	−4427	−4686
	slope error, %	4.1	4.2	3.7	4.3
Ethyl propionate	slope	−4519	−4468	−4238	−4523
	slope error, %	5.2	8.8	9.0	8.6
Hexane	slope	−3747	−3897	−2999	−3858
	slope error, %	6.9	20.0	18.9	10.7
Nitrobenzene	slope	−5934	−5901	−5794	−5957
	slope error, %	8.0	5.0	9.3	3.4
Octyl alcohol	slope	−6868	−7028	−6714	−6836
	slope error, %	9.5	9.6	10.8	6.5
Toluene	slope	−4327	4332		.−4443
	slope error, %	5.1	4.8		4.9

TABLE II

COMPARISON OF DTA, DSC, AND T–H BOILING POINT DATA AT VARIOUS PRESSURES

	Average deviation from literature, °C		
Compound	*DTA*	*DSC*	*T–H*
Acetic acid	1.2		
Chlorobenzene	1.6	0.9	1.6
Ethyl propionate	1.0	2.0	1.5
Hexane	2.7	1.0	1.2
Nitrobenzene	3.3	1.8	1.1
Octyl alcohol	4.0	0.5	1.0
Toluene	Standard*	Standard*	2.3
Average	2.3	1.2	1.5

*Used to calibrate method.

The heat of vaporization (ΔH_v) can be estimated from vapor pressure data using a form of the Clapeyron equation:

$$\frac{\mathrm{d}\log P}{\mathrm{d}(1/T)} = \frac{\Delta H_v}{2.303\,R(V_g - V_l)} \tag{1}$$

where T = temperature, °K, V_g = molar volume of the gas, V_l = molar volume of the liquid.

However, many organic vapors with different intermolecular and intramolecular attractions may deviate considerably from ideal gas behavior. Haggenmacher[14] proposed the use of the following equation for calculating the change in volume (ΔV):

$$\Delta V = \sqrt{(1-P)/T_r^3} \tag{2}$$

where P_r and T_r are the reduced pressure and temperature.

The Antoine equation, which corrects for nonideal gas behavior, was used as the vapor pressure function.

$$\log P = A - B/(t+C) \tag{3}$$

where A, B, and C are constants of the Antoine equation, and t is the temperature in °C. Differentiation and rearrangement of Eqn. 3 gives:

$$\frac{\mathrm{d}\log P}{\mathrm{d}(1/T)} = -\frac{T^2 B}{(t+C)^2} \tag{4}$$

Eqns. 2 and 4 can be substituted into Eqn. 1 to yield

$$\Delta H_v = \frac{2.303\, R T^2 B \sqrt{1-P_r/T_r^3}}{(t+C)^2} \tag{5}$$

This equation should be used at or below the atmospheric boiling point of any liquid.

The experimental data were used to obtain the constants for the Antoine equation. Since $T_r = T/T_c$, the value for T_c (critical temperature) listed in the literature was used to solve Eqn. (5). All of these steps were done with the aid of a second computer program. The values obtained for ΔH_v at the highest pressure used are listed

TABLE III

HEAT OF VAPORIZATION AND DEVIATION FROM LITERATURE VALUES

	ΔH_v			
Compound	*Literature*	*DTA*	*DSC*	*T–H*
Acetic acid, 118°C	9.189	9.062		
Error (all temp), %		3.10		
Chlorobenzene, 132°C	8.556	8.001	8.329	8.838
Error (all temp), %		3.46	5.44	1.55
Ethyl propionate, 99°C	8.204	7.972	7.281	8.577
Error (all temp), %		2.86	5.40	2.26
Hexane, 69°C	6.886	6.951	4.712	5.979
Error (all temp), %		4.63	16.70	8.02
Nitrobenzene, 210°C	10.476	11.703	11.413	10.852
Error (all temp), %		7.44	6.93	2.01
Octyl alcohol, 195°C	11.420	12.054	11.193	11.658
Error (all temp), %		4.03	1.96	2.41
Toluene, 110°C	8.011	7.103		8.335
Error (all temp), %		12.90		3.30
Average error, %		5.5	8.3	3.3

in Table III for each compound and experimental technique. Similar calculations were made with the literature data. The deviation from the literature values was calculated for each technique at all temperatures studied. The average deviation from the literature values, or mean error if the literature values are assumed to be correct, are listed in Table III for each compound and thermal method used.

An average relative error of 5.5% for ΔH_v was obtained with the DTA data. This is sufficiently accurate for most applications, and since the DTA apparatus requires less attention than the Thomas–Hoover apparatus, the former is probably the better technique for this particular measurement.

In conclusion, there is no significant difference in precision among the three methods. Similarly, the three techniques studied require about the same amount of time. It should be pointed out that the Thomas–Hoover method, in which visual observations are used, requires constant attention, and that corrosive materials may be detrimental to the DSC sample chamber.

AKNOWLEDGMENTS

The authors gratefully acknowledge the helpful discussions and computer programming assistance of Dr. H. W. Patton. Appreciation is expressed to Dr. W. H. Seaton and Mr. R. L. Boys for calculations and assistance.

REFERENCES

1 D. A. Vaassalo and J. C. Hardin, *Anal. Chem.*, 34 (1962) 132.
2 J. Chin, *Anal. Chem.*, 27 (1955) 1102.
3 A. A. Krawetz and T. Tovarog, *Rev. Sci. Instrum.*, 33 (1962) 1465.
4 I. M. Sarasohn, *DuPont Thermogram*, 2 (1965).
5 A. M. Wisnewski, R. J. Calhoun and L. P. Witnauer, *J. Appl. Polym. Sci.*, 9 (1965) 3935.
6 *Thermal Analysis Newsletter No. 7*, Perkin-Elmer Corp., 1967.
7 E. M. Barrall II, R. S. Porter and J. F. Johnson, *Anal. Chem.*, 37 (1965) 1053.
8 H. R. Kernme and S. I. Kreps, *Anal. Chem.*, 41 (1969) 1869.
9 N. D. Cheronis and J. B. Entrickin, *Semimicro Qualitative Analysis*, Thos. Y. Crowell Co., 1947, p. 60.
10 A. Siwoloboff, *Ber.*, (1886) 795.
11 J. H. Perry (Ed.), *Chemical Engineer's Handbook*, McGraw-Hill, New York, 1963, pp. 3-47 to 3-59.
12 S. H. Fishtine, *Ind. Eng. Chem.*, 55 (1963) 49.
13 W. Mendenhall, *Introduction to Statistics*, Wadsworth, Belmont, California, 1963, p. 222.
14 J. E. Haggenmacher, *Ind. Eng. Chem.*, 40 (1948) 436.