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PARAMETERS AFFECTING THE DETERMINATION OF VAPOR PRESSURE BY DIFFERENTIAL THERMAL METHODS

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ABSTRACT

Use of differential thermal methods for the determination of vapor pressures is an established technique of general applicability which is suitable for consideration as a standard procedure. The effects of several experimental criteria including sample quality, heating rate, sample size, sample vessel, test configuration, and thermodynamic interference are discussed. The practicality of this method as a general standard procedure can only be realized when these effects are considered.

INTRODUCTION

In 1962 Krawetz and Tovrog[1] suggested that the vapor pressure function for pure liquids could be determined using differential thermal analysis (DTA). Since then much attention has been directed toward variations in design of experiments and equipment (including use of differential scanning calorimetry (DSC)) which served to improve accuracy and extend the range of investigation[2–4]. Today vapor pressure determinations using differential thermal methods can routinely be obtained in the range of 10^{-1} to 10^4 torr. The successful application of this method is, however, contingent upon resolution of the effects of several critical parameters affecting the determination.

The purpose of this paper is therefore to review the use of differential thermal methods as a standard, routine procedure for vapor pressure determinations. Emphasis will be placed on the discussion of effects of experimental parameters such as sample quality, sample vessel, test configuration, heating rate, sample size, temperature and pressure ranges, and thermodynamic interferences.

METHODS

The determination of vapor pressures by differential thermal methods is one approach to a general procedure referred to as the "boiling point" method. This method includes the use of differential thermal instrumentation (DSC or DTA) to measure the isothermal boiling temperature of a pure liquid as a function of pressure. The boiling temperature is taken to be the extrapolated onset temperature of the boiling endotherm (Fig. 1). In this manner pressure, rather than temperature, is the independent variable, and the temperature equilibrium conditions of isothermal boiling are readily obtainable within a dynamically heated environment. The measured cell pressure therefore equals the vapor pressure of the material undergoing isothermal boiling.

A complete vapor pressure function for a pure liquid can be generated by a plot of pressure–boiling temperature data points as log P vs. $1/T$ (K) (Fig. 2) or log P vs. T (°C) on an appropriate Cox chart[5]. If it is assumed that the vapor behaves as an ideal gas, the vapor pressure function will be a straight line described by the Clausius–Clapeyron equation[6] with a slope of $-\Delta H/2.303R$. ΔH represents the enthalpy of vaporization and is assumed to be constant over the measured temperature range. R is the ideal gas constant equal to 1.987 cal K^{-1} mol^{-1}. A variety of experimental designs for vapor pressure determinations have been described in the lit-

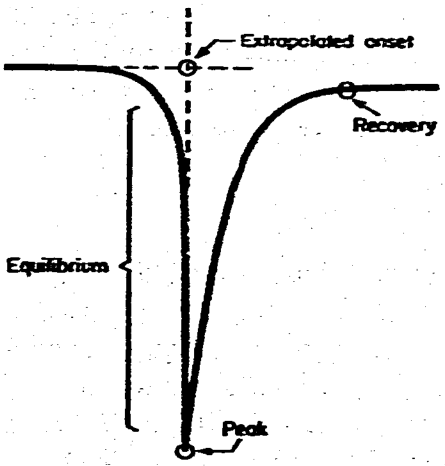

Fig. 1. Isothermal boiling endotherm.

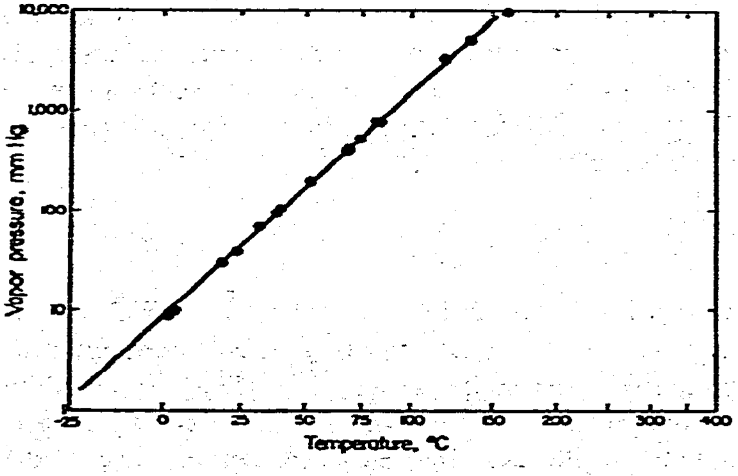

Fig. 2. Classical vapor pressure curve; Spectro Grade isopropyl alcohol.

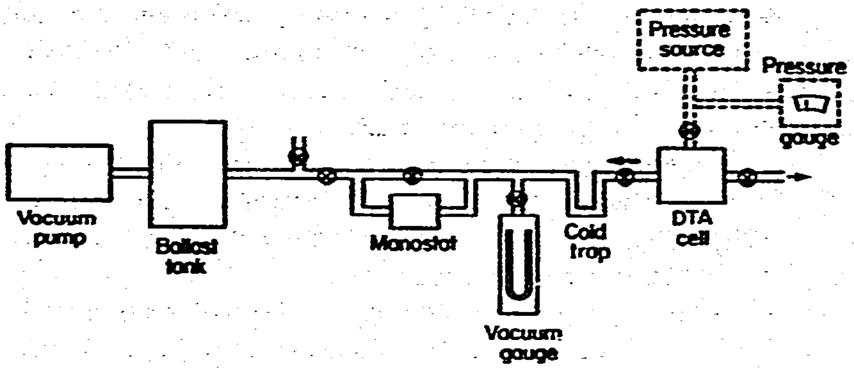

Fig. 3. Instrumental arrangement for vapor pressure studies by differential thermal methods.

erature[4,7]. A typical instrumental arrangement is illustrated in Fig. 3. The essential components include a stable, controllable vacuum and/or pressure generating source with the appropriate metering devices attached to a differential thermal cell.

DISCUSSION

Pressure stabilization and measurement represents the greatest source of experimental error using the design described above. A typical operating range for this apparatus extends from 10^{-1} to 10^4 torr. The measurement and control of temperature is accomplished with the differential thermal instrumentation and is therefore limited by the capabilities of the specific unit utilized.

Besides the obvious equipment limitations, there exists a group of experimental parameters whose effects on the determination of a vapor pressure function can result in serious errors. The effects of the experimental parameters must be evaluated and specified before the technique can be considered as standard procedure for general applications.

At the onset, sample quality must be considered. In order for a measurement to be valid, a sample must undergo isothermal boiling within the temperature range of the instrument. Secondly, any decomposition accompanying or preceding isothermal boiling invalidates the results of the analysis. Thus the presence of impurities, whether induced or inherent, cannot be tolerated above 5% of a soluble non-ionic species[4,12]. The presence of impurities may be detected by a non-linear vapor pressure function, by a non-isothermal boiling endotherm (temperature continues to increase during boiling), or multiple-endothermic transitions.

The generation of impurities through thermal decomposition is of particular concern when super-atmospheric pressure data are to be used. When confined, many organic liquids will decompose rapidly at temperatures slightly above their atmospheric boiling temperature. A second concern when using super-atmospheric pressures is non-ideal gas bahavior of the vapors which can result in a non-linear vapor pressure function. Use of super-atmospheric pressures nevertheless remains an integral part of the procedure. This is especially necessary when instrumental limitations restrict differential thermal analyses below room temperature. Therefore, substitution of a limited number of super-atmospheric boiling temperature data points may be required to complete a vapor pressure analysis.

A thermodynamic phenomenon, the triple point, can introduce difficulties in determining data points at pressures where the boiling temperature approaches the melting temperature, i.e., $(T_{bp}-T_m)$ is small[6]. Considerable deviation from the linear vapor pressure function will be observed in such cases.

Because a linear heating rate is employed in differential thermal methods, the effect of the heating rate on the observed boiling temperature must be evaluated.

TABLE 1

EFFECT OF HEATING RATE ON OBSERVED BOILING TEMPERATURE

Heating rate (°C min^{-1})	$T_{b.p.}$ (°C)
0.5	99.32
1.0	99.73
2.0	99.91
5.0	100.00
10.0	100.03
15.0	99.93
20.0	99.92

Kemme and Kreps[4] (Table 1) concluded from their data for water at 760 torr that for heating rates of 2 to 20°C min^{-1} there was no appreciable change in the observed boiling temperature. However, when very slow heating rates are employed, sample loss through rapid pre-boiling vaporization can become significant and can prejudice the analysis. Therefore, for the sake of convenience, accuracy, and economy, rates of 10 to 20°C min^{-1} are routinely employed. As a consequence, use of such heating

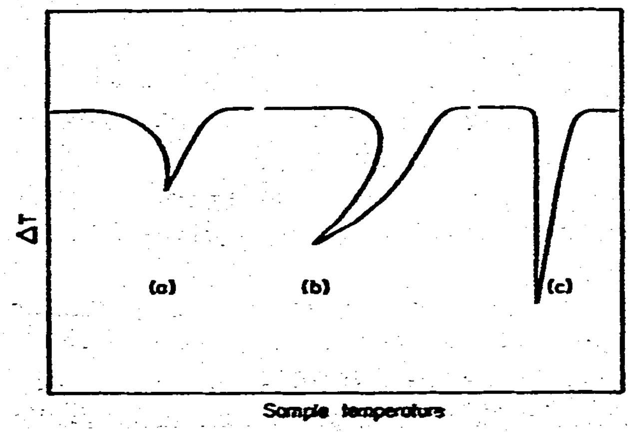

Fig. 4. Effect of sample size on observed endotherm. (a) Insufficient sample; (b) excess sample; (c) optimum sample size.

rates permits a complete vapor pressure function based on five data points to be generated within several hours. This represents a significant time reduction over many other techniques.

Sample size is a variable which can exert significant influence on the observed boiling endotherm[4]. For samples that are too small, insufficient sample remains at the boiling point to establish reflux conditions necessary for attainment of isothermal boiling. Too large a sample results in super-heating and partial self-cooling (Fig. 4) before isothermal boiling is approached. A standard sample size cannot, however, be prescribed because it is a function of the test configuration and the latent heat of the system. As a result, the optimum sample size must be individually determined for each instrument used. For many commercial instruments a 1–15 μl sample is typical.

A final group of experimental parameters which may be generalized as sample test configuration, includes the use of an inert diluent, the type and size of the sample vessel, and the use of DTA vs. DSC. The general types of test vessel configurations commonly used are illustrated in Fig. 5. The pan configurations are typical of DSC

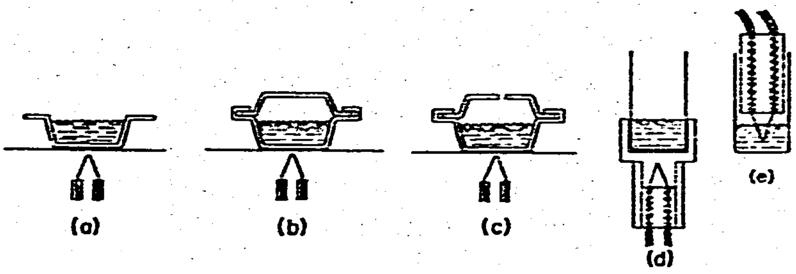

Fig. 5. Sample vessel configurations. (a) Open pan; (b) hermetically sealed pan; (c) sealed pan with pinhole; (d) open capillary; (e) capillary with inserted thermocouple.

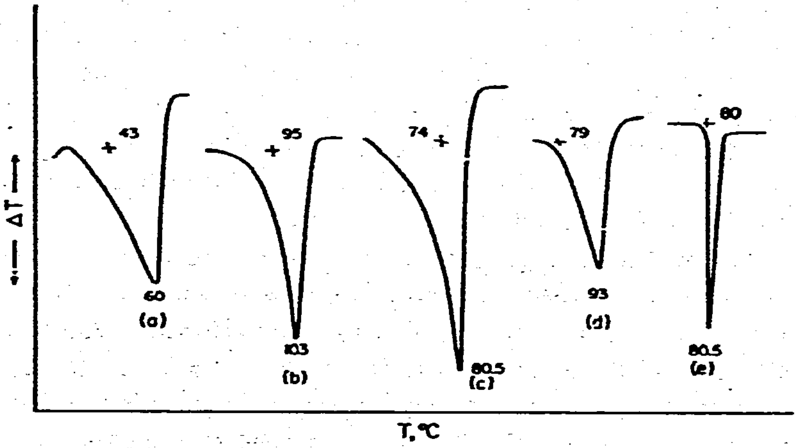

Fig. 6. Observed boiling endotherms with different sample vessel configurations. (a) Open pan; (b) hermetically sealed pan; (c) sealed pan with pinhole; (d) open capillary; (e) capillary with inserted thermocouple.

and quantitative DTA instrumentation while the capillary configurations are typical of DTA instrumentation. The series of endotherms illustrated in Fig. 6 were obtained for Spectro Grade isopropyl alcohol at 750 torr using the different vessel configurations as identified.

Using the shape and temperature of the boiling endotherm as the principal criteria for comparison of the results obtained from the capillary and pan vessels, the capillary will, for the most part, be more satisfactory. Use of metallic pans necessitates caution, in that reactions between the sample and the pan may occur, especially with aluminum pans. A second consideration when using pans is that the combination of the larger surface area-to-volume ratio of pans and a minimal vapor head can result in considerable sample loss and difficulty in achieving isothermal boiling. These complications are especially prevalent with an open pan and produce unsatisfactory boiling data with this configuration.

Unsatisfactory results are also obtained with a hermetically sealed pan. Vaporization of a fraction of the sample prior to boiling serves to self-pressurize the vessel. The sample pressure ($Ps = Pc + dP$) becomes greater than the cell pressure ($dP > 0$) and a boiling point elevation is encountered. Examination of the hermetic pan with a pinhole suggests a resemblance to an effusion vessel with the pinhole serving as the orifice. As such, the pinhole dimension becomes critical. For a very small pinhole diameter, the laws of effusion are not applicable and the pinhole approximates a short capillary tube[8]. This approximation allows achievement of equilibrium conditions in a differential thermal cell using a "pan" sample vessel. A pinhole size of less than 0.88 mm (0.035 in.) is generally satisfactory for 6.35 mm (0.25 in.) diameter commercial pans.

Generally the glass capillary is very good because the small surface area-to-volume ratio and the long vapor column promote rapid achievement of equilibrium boiling conditions. Partial refluxing in the capillary reduces loss of sample through diffusion and enhances isothermal boiling. Both the open capillary and the inserted thermocouple capillary result in sharp boiling endotherms. However, if the annular space in the thermocouple inserted capillary becomes smaller than the mean free path of the vapor, a pressure gradient is established which will alter the isothermal boiling temperature[4]. This would most likely be encountered in the case of larger bore capillaries which utilize a thermocouple centering sleeve. Reduction in the length of the centering sleeve is usually sufficient to eliminate this complication.

The second portion of sample test configuration considerations includes the use of inert diluents such as glass beads or powdered ceramic (alumina or Carborundum). The curves in Fig. 7 are measurements of Spectro Grade isopropyl alcohol at 755 torr in the various test vessels with the addition of 5 mg of 100 μm glass beads. Note that in the case of the hermetic pan with a pinhole, although sizeable vaporization occurs prior to boiling, isothermal boiling is eventually achieved, whereas without the inert diluent, equilibrium conditions were only approximated. Also, in the case of the open capillary, a much narrower onset to peak interval is encountered with addition of the inert diluent. The use of an inert diluent serves several functions regardless of

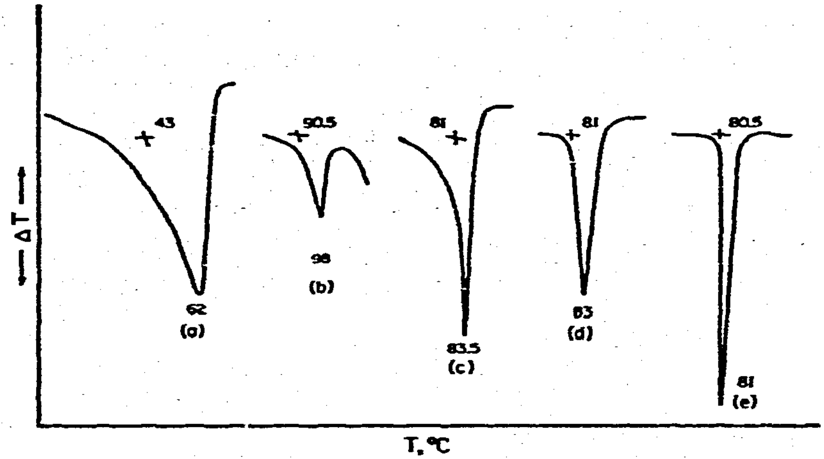

Fig. 7. Observed boiling endotherms with different sample vessel configurations plus inert diluent. (a) Open pan; (b) hermetically sealed pan; (c) sealed pan with pinhole; (d) open capillary; (e) capillary with inserted thermocouple.

the sample vessel used. It increases the liquid surface area, reduces vaporization before boiling by retention of sample through surface tension[9], and acts as nucleation sites for boiling which minimizes superheating. The inert diluent also provides a better match of heat transfer characteristics between the sample and reference portions of a cell, especially after boiling. When the considerations cited above are taken into account, accurate vapor pressure functions for pure liquids may be determined. Figures 8 and 9 illustrate the vapor pressure functions of distilled water and Spectro Grade isopropyl alcohol, respectively. The solid curves represent literature values[10,11] while the data points were determined using a 4-mm thermocouple inserted capillary with 5 µl of sample dispersed over 5 mg of 100-µm glass beads. A heating rate of 10°C min^{-1} was employed for all determinations with a Du Pont 990 thermal

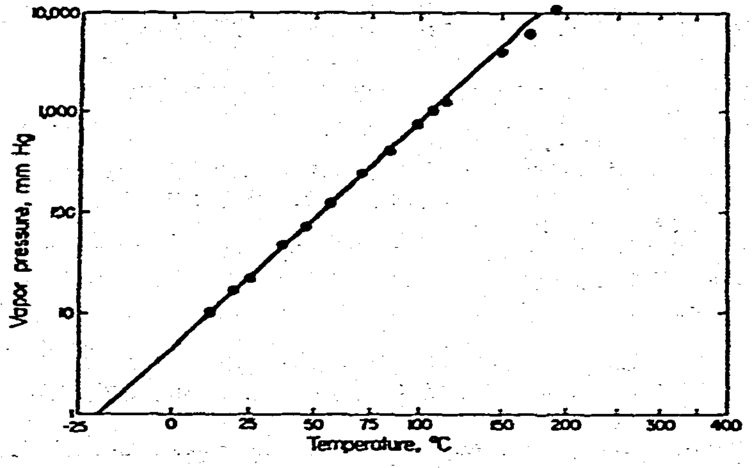

Fig. 8. Vapor pressure curve of distilled water. ———, literature curve; ●, experimental data.

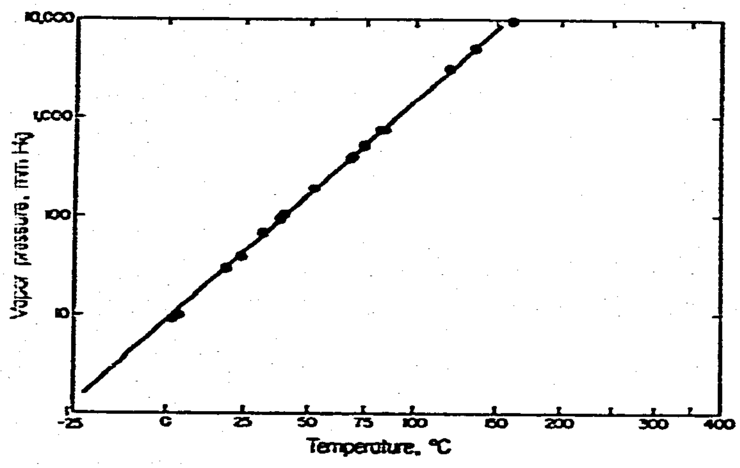

Fig. 9. Vapor pressure curve of spectro grade isopropyl alcohol. ———, literature; ● experimental data.

analyzer. All data points represent single determinations having a temperature resolution of 0.5°C and agree within 2.6% of published values.

CONCLUSION

The use of differential thermal methods for the determination of vapor pressure functions of pure materials is a method of general applicability which is suitable for use as a standard procedure. The practicality of this method as a general standard can only be realized when considerations are given to the effects of several experimental parameters on vapor pressure determinations. It is recommended that a standard method for the determination of vapor pressures by differential thermal methods include: (1) an optimum sample size blended with an appropriate quantity of inert diluent; (2) a sample vessel of either a glass capillary or a metallic hermetic pan with a standard pinhole (approx 0.88 mm); and (3) a heating rate of 10–20°C min^{-1}.

REFERENCES

1 A. A. Krawetz and T. Tovrog, *Rev. Sci. Instrum.*, 35 (1962) 1465.
2 A. M. Wisnewski, R. J. Calhoun and L. P. Witnauer, *J. Appl. Polym. Sci.*, 9 (1965), 3935.
3 E. M. Barrall, J. Gernert, R. S. Porter and J. F. Johnson, *Anal. Chem.*, 35 (1963) 1837.
4 H. R. Kemme and S. I. Kreps, *Anal. Chem.*, 41 (1969) 1869.
5 G. P. Morie, T. A. Powers and C. A. Glover, *Thermochim. Acta*, 3 (1972) 259.
6 I. M. Sarasohn, *DuPont Thermogram*, 2 (1965).
7 D. A. Vassalo and J. C. Harden, *Anal. Chem.*, 34 (1962) 132.
8 E. E. Hughes and S. G. Lias, *Nat. Bur. Stand. Tech. Note*, 70 (1960).
9 E. M. Barrall, R. S. Porter and J. F. Johnson, *J. Phys. Chem.*, 68 (1964) 2810.
10 E. W. Washburn, *International Critical Tables of Numerical Data Physics, Chemistry and Technology*, Vol. 3, McGraw-Hill, New York, p. 210.
11 T. E. Jordan, *Vapor Pressure of Organic Compounds*, Interscience, New York and London, 1954, p. 63.
12 W. F. Sheehan, *Physical Chemistry*, Allyn and Bacon, Boston, 1970, pp. 291–354.