

## Subambient applications of differential thermal analysis for the determination of vapor pressure<sup>1</sup>

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(Received 2 October 1991; accepted 27 February 1992)

### Abstract

Differential thermal analysis (DTA) has been shown to be a useful technique for determining the vapor pressure of pure liquids. Incorporation of a subambient cooling accessory into existing commercial instrumentation allows rapid determination (in less than 2 h) of vapor pressure curves of pure liquids over wide pressure (5–760 Torr) and temperature (–180–450°C) ranges using a small amount (less than 1 ml) of sample. Vapor pressure curves of several compounds, for which only atmospheric pressure boiling points were available, have been established with this technique.

### INTRODUCTION

In the early 1960s, differential thermal analysis (DTA) was identified as a useful technique for studying phase transitions of organic materials over a wide temperature range. Several years later, the use of DTA for establishing vapor pressure curves for pure liquids over wide temperature and pressure ranges was reported [1–4]. Since that time, differential scanning calorimetry (DSC) has replaced DTA as the method of choice for most phase transition studies. Despite the superiority of DSC for the investigation of many thermal events, a DTA cell equipped with a glass capillary specimen holder and thermocouple temperature sensor continues to be a more suitable configuration for measurement of boiling temperatures.

In a 1976 review of parameters affecting the determination of vapor pressure by thermal analysis techniques, Seyler [5] concluded that the DTA glass capillary configuration allows attainment of equilibrium boiling condi-

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<sup>1</sup> Presented at the 20th Annual NATAS Conference, Minneapolis, MN, 20–26 September 1991.

tions which cannot be achieved with the use of other specimen holder designs. The lack of widespread familiarity and the resulting limited use of this valuable technique for the determination of vapor pressure were noted by Charles [6].

DTA is one of three methods used routinely in our laboratories for the determination of vapor pressure of pure liquids. The small specimen size and minimal time required to establish a vapor pressure curve have resulted in DTA being the technique preferred over the Knudsen effusion method or the isoteniscope. Recent incorporation of an accessory which simplifies cooling of the apparatus to liquid nitrogen temperature ( $-180^{\circ}\text{C}$ ) has extended the temperature range over which this technique can be used and enhanced significantly the applicability of this method to our work. Vapor pressure curves for perfluoroisobutene (boiling point  $7^{\circ}\text{C}$ ) and perfluorocyclobutene (boiling point  $0.2^{\circ}\text{C}$ ) have been established using this subambient procedure.

## EXPERIMENTAL

### *Apparatus*

The basic experimental technique used in these experiments has been described previously [1,3]. The major differences between this procedure and those used by Vassallo and Harden [1] and Kemme and Kreps [3] were the use of a computer to control data acquisition and the incorporation of a Dewar flask (available from TA Instruments) designed to cool rapidly the specimen cell block for subambient operations through the use of liquid nitrogen. The pressure readout device was an absolute manometer with a precision of 0.1 Torr. Instrument calibration was checked using Freon 113 (1,1,2-trichloro-1,2,2-trifluoroethane, boiling point  $48^{\circ}\text{C}$ ) and Freon 114 (1,2-dichloro-1,1,2,2-tetrafluoroethane, boiling point  $4^{\circ}\text{C}$ ).

### *Temperature control*

Prior to measuring vapor pressures at very low temperatures, the ability of the DTA equipment to control the rate of temperature increase was investigated. Kemme and Kreps recommended a heating rate of  $5^{\circ}\text{C min}^{-1}$  for accurate determination of vapor pressure. Therefore, it was critical that the cooled cell block did not self-warm at a faster rate.

The cell block was cooled to  $-180^{\circ}\text{C}$  and allowed to self-warm. The observed temperature rise was less than  $3^{\circ}\text{C min}^{-1}$ , indicating that temperature control could be maintained using the desired heating rate of  $5^{\circ}\text{C min}^{-1}$ .

### Sample preparation

To load specimens that boil below room temperature into the glass capillary tubes, special handling techniques were developed. Compounds that boil below room temperature are usually received in lecture bottles equipped with valves. A small amount of sample (several milliliters) is transferred from the lecture bottle to a Reacti-Vial equipped with a screw cap and rubber septum. The vial is precooled to a temperature below the boiling point of the compound under study. The specimen in the vial will remain a liquid provided the cap does not leak. Transfer of the specimen from the vial to the glass capillary tube is accomplished by cooling the cell block with the capillary in place and discharging the proper amount of liquid using a precooled microsyringe.

### RESULTS

Table 1 contains the experimental temperatures and pressures for Freon 113 and Freon 114. Differences between literature values of boiling temperatures [7] and the present results are listed at each experimental pressure. The data are in good agreement. A plot of the vapor pressure vs. temperature curves for these compounds is shown in Fig. 1, where the symbols are experimental points and the lines are the literature values.

TABLE 1

Vapor pressure data for Freon 113 and Freon 114

Freon 113				Freon 114			
$T$ (°C)		$\Delta T$	$P$ (Torr)	$T$ (°C)		$\Delta T$	$P$ (Torr)
Exp.	Lit.			Exp.	Lit.		
46.8	47.6	0.8	761.4	3.1	3.3	0.2	767.3
46.3	47.5	1.2	759.1	-11.2	-11.0	0.2	424.1
46.3	47.5	1.2	759.0	-18.4	-17.8	0.6	300.0
35.7	38.2	2.5	549.3	-25.8	-25.9	-0.1	213.2
28.4	29.6	1.2	400.0	-32.2	-32.2	0.0	149.2
24.2	25.1	0.9	334.8	-39.2	-39.7	-0.5	100.0
18.7	19.8	1.1	270.0	-42.8	-43.7	-0.9	80.0
11.6	12.8	1.2	200.1	-47.6	-48.6	-1.0	60.0
5.3	6.3	1.0	150.0	-53.6	-55.3	-1.7	40.0
-3.4	-2.1	1.3	100.0	-57.7	-59.7	-2.0	30.0
-7.4	-6.5	0.9	80.0	-62.8	-65.8	-3.0	19.9
-12.8	-12.0	0.8	60.0				
-19.7	-19.1	0.6	40.2				
-24.3	-24.1	0.2	30.0				
-29.0	-29.2	-0.2	21.9				
-30.3	-31.3	-1.0	19.1				

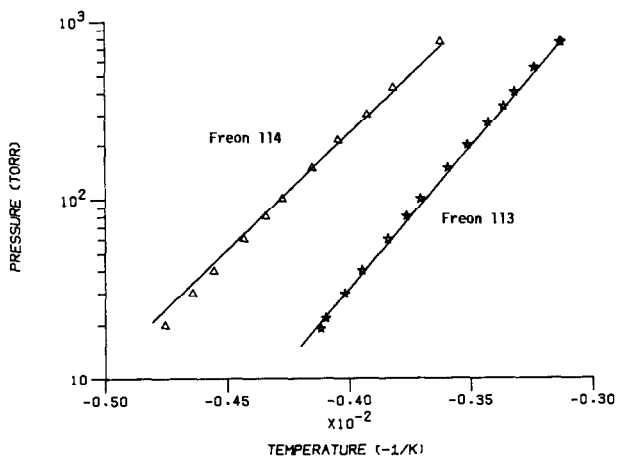


Fig. 1. Literature vs. experimental vapor pressure data for Freon 113 and Freon 114.

The largest difference between the literature values and the experimental data (3°C) is observed for Freon 114 below  $-60^{\circ}\text{C}$ . The source for the Freon 114 literature data provided only a Clausius–Clapeyron equation and an experimental temperature range; neither raw data nor the experimental method were given. Citation of a Clausius–Clapeyron instead of an Antoine equation (preferred for expressing vapor pressure data as a function of temperature) requires that the literature values be used with caution. The absence of raw literature data prevents assessment of how

TABLE 2

Vapor pressure data for perfluoroisobutene

Antoine constant			
<i>A</i>			6.61628
<i>B</i>			809.878
<i>C</i>			209.730
Standard deviation			0.0021
Calculated boiling point ( $^{\circ}\text{C}$ )			7.08
Temperature ( $^{\circ}\text{C}$ )	Pressure (Torr)		Difference (%)
	Experimental	Calculated	
7.2	763.0	763.68	0.09
-8.0	400.0	399.58	-0.10
-17.8	250.3	249.24	-0.42
-27.2	150.3	151.12	0.54
-36.2	89.0	88.96	-0.05
-43.4	55.5	55.87	0.66
-50.1	35.2	34.90	-0.86
-55.4	23.4	23.36	-0.15
-60.9	14.9	14.95	0.33

TABLE 3  
Vapor pressure data for perfluorocyclobutene

Antoine constants			
<i>A</i>			6.71893
<i>B</i>			799.118
<i>C</i>			208.050
Standard deviation			0.0034
Calculated boiling point (°C)			0.16
Temperature (°C)	Pressure (Torr)		Difference (%)
	Experimental	Calculated	
0.2	758.0	761.43	0.45
–14.2	400.3	394.98	–1.33
–23.0	250.1	251.50	0.56
–32.0	150.3	151.28	0.65
–38.6	100.4	100.69	0.29
–44.1	70.2	69.95	–0.36
–49.0	50.1	49.50	–1.20
–50.5	44.0	44.34	0.77
–53.6	35.0	35.07	0.21

well the cited equation fits the experimental values. On the basis of the number of data points generated in the present work and the self-consistency of the data set, it is felt that the values generated by the DTA method reflect accurately the vapor pressure of Freon 114 in this temperature range.

Vapor pressure data generated for perfluoroisobutene and perfluorocyclobutene are given in Tables 2 and 3. Each data set was fitted to an Antoine equation. The Antoine constants are listed at the top of the tables and the percentage difference between the experimental and calculated pressures is given at each experimental temperature. Antoine plots of both data sets show the slight curvature characteristic of this type of plot, reflecting the change in heat of vaporization (slope of the curve) as a function of temperature.

## CONCLUSION

A modified DTA technique for measuring vapor pressure has been shown to be a quick easy method requiring a very small specimen. The use of a low temperature accessory extends the use of the method to subambient temperatures.

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