An Improved Transpiration Method for the Measurement of Very Low Vapor Pressures

Philip C. Hansen and Charles A. Eckert*

Department of Chemical Engineering, University of Illinois, Urbana, Illinois 61801

The transpiration technique for measuring very low vapor pressures has been improved by the use of better catalysts and a longer path length IR cell. Accurate data may now be obtained to pressures as low as 3 mPa much more rapidly than by the classical effusion techniques. Results are reported for anthracene (313–363 K), triphenylmethane (303–358 K), dibenzofuran (303–343 K), 9-fluorenone (298–343 K), and dibenzothiophene (303–348 K).

Introduction

Relatively little characterization has been done traditionally on nonvolatile, heavy-end components. However, many such materials are becoming increasingly important from both an economic and environmental viewpoint, and separation processes will have to be developed for such chemicals. Thus it is becoming increasingly important to have a rapid and reasonably accurate method to measure the vapor pressure of materials of very low volatility. Our immediate interest in such measurements is to use these data to evaluate enhancement factors for supercritical extraction processes (*1*), but they also will be useful in the development of predictive methods.

In the pressure range below 1 Pa, a number of variations on the effusion technique have been used. The modified Knudsen cell used by Murray et al. (*3*) requires a highly sensitive microbalance, a precise effusion hole, and high vacuum. Torsion effusion is based on suspending an effusion cell from a long thin wire and uses the direct proportionality of the vapor pressure on the torque exerted on the wire by the effusing molecules. DeKruif and Van Ginkel (*4*) report a detailed and complicated apparatus for such measurements. The inclined piston effusion method balances the weight of a free piston against the exerted pressure of the sample vapor (*5*). As with the other methods a high vacuum is required. The gas saturation method has received attention recently (*6*–*8*) and is challenging the more common effusion methods in the measurement of accurate vapor pressure data in the millipascal range.

Because of the difficulties of such methods, good data have been sparse, and some investigators have developed estimation techniques. The AMP equation (*9*) uses a group contribution method to predict pure component vapor pressures within a factor of 2. Another method, the SWAP technique (*10*), uses a single datum and principles similar to the AMP method to predict a vapor pressure curve. Data so obtained are claimed to be valid to 20% at the boiling point.

In this paper we present a rapid (a datum in a few hours, compared to days for effusion methods) and accurate improvement of the gas saturation or transpiration method, capable of measuring vapor pressures to much lower levels. Here we go down to 3 mPa, but the apparatus as presented is applicable to 100 μPa. The experimental method involves converting an equilibrium concentration of an organic sample, saturated in a gas stream, to carbon dioxide and other gases. Carbon dioxide in the effluent is analyzed and the sample vapor pressure, P^s, is found by

$$P^s = [CO_2]P/n \tag{1}$$

where P is pressure in the apparatus (near atmospheric) and n is the number of carbon atoms in a molecule of the sample. The major improvement made over current methods is the use of a 20-m path length infrared spectrophotometer to measure carbon dioxide concentrations as low as 50 ppb.

We have used this improved gas saturation method to measure vapor pressure data for anthracene, triphenylmethane, dibenzofuran, 9-fluorenone, and dibenzothiophene. As a group, oxygen-containing compounds have not been treated as completely by existing group contribution methods as other substituted organics. The addition of a carbonyl and a ketone type compound to the data will undoubtedly aid in incorporating various oxygen-containing organics into group contribution methods that provide useful vapor pressures with a minimum of effort.

Experimental Section

Apparatus. The gas saturation apparatus is shown schematically in Figure 1. The apparatus is constructed of stainless steel and glass; plastics, Teflon, and other materials used to seal connections have vapor pressures in the measurement range and are not used upstream of the catalytic convertor. An open end manometer measures the saturator outlet pressure. Column heights are measured to ±0.025 mm with a Gaertner cathetometer tube. Pressure is also measured at the saturator inlet to monitor operating conditions.

The purifier removes carbon dioxide from supply oxygen. Trace hydrocarbons are converted to carbon dioxide and water vapor in a catalytic (Pd coated on Al_2O_3) furnace at 770 K. The oxygen is then cleaned with Drierite and Ascarite. This purification step removes 0.43 ppm carbon dioxide from the supply oxygen.

A Hallikainen controller thermostats the temperature bath fluid within ±0.01 K. Temperature is measured with mercury-filled total immersion glass thermometers, calibrated with a platinum resistance thermometer traceable to N.B.S. Temperature is recorded to 0.01 ± 0.005 K.

The saturator is composed of four 9.5 mm × 230 mm stainless steel tubes. The demister is a 9.5 mm × 150 mm stainless steel tube packed with glass wool to remove entrained solids. The tubing connecting the temperature bath to the catalytic converter is always kept at temperatures above the bath temperature.

The catalytic convertor is a 25-cm schedule 40 stainless steel pipe machined to accept four thermocouple fittings. Alumel–chromel thermocouples monitor the convertor temperature. The convertor is packed with alumina pellets. A more detailed discussion of different catalysts is given elsewhere (*11*). Heat is supplied with a muffle furnace capable of temperatures in excess of 1250 K.

The infrared analyzer is a MIRAN-1A of Foxboro Analytical. A single beam instrument, it is fitted with a gas cell variable in path length from 0.75 to 20.25 m in 1.5-m increments. When the longest path length is used, carbon dioxide can be measured to 50 ppb. Calibration of the infrared spectrophotometer is accomplished by using Air Products primary standards. These carbon dioxide in nitrogen mixtures are certified to ±1% in carbon dioxide concentration.

0021-9568/86/1731-0001$01.50/0

Table I. Summary of Experimental Vapor Pressure Data

	P^s, mPa				
	anthracene	triphenylmethane	dibenzofuran	9-fluorenone	dibenzothiophene
T, K					
298.15				16.5	
303.15		3.13	487.4	30.8	36.3
308.15		3.52	781.8	55.7	64.7
313.15	5.80	7.38	1280	91.7	112.2
318.15	10.5	16.3	2128	149.7	192.0
323.15	19.3	34.3	3200	269.7	361.7
328.15	39.0	53.4	4679	455.7	636.1
333.15	67.5	97.8	7246	812.6	1044
338.15	98.7	179.3	12780	1256	1770
343.15	168.8	342.3	19710	2394	2338
348.15	305.6	580.8			3433
353.15	525.2	857.9			
358.15	914.7	1527			
363.15	1224				
mean dev from eq 2	5.7%	9.9%	4.6%	5.5%	7.0%
A	5359	5578	4132	4818	4762
B, K^{-1}	17.88	18.75	16.30	17.36	17.27
Δh^{sub}, kJ mol^{-1}	102.6	106.8	79.1	92.2	91.2

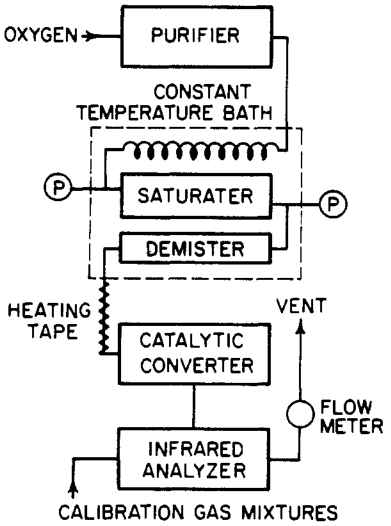

Figure 1. Schematic of experimental apparatus.

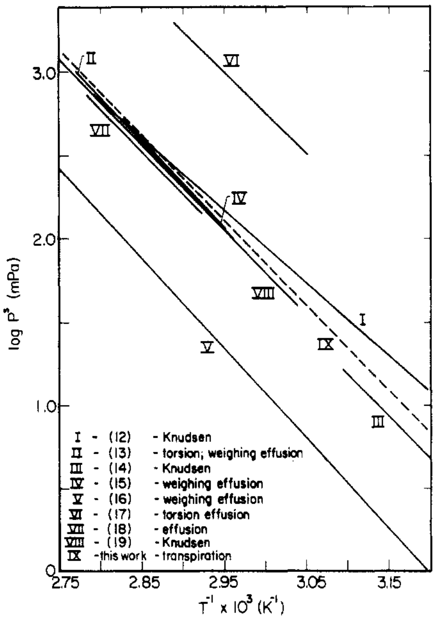

Figure 2. Comparison of the experimental data from different investigators (by different methods, given in parentheses) for the vapor pressure of anthracene.

Materials. The oxygen carrier gas is Air Products rated at 99.994% pure. The purification section removes 0.43 ppm carbon dioxide improving the carrier gas purity to five nines.

Anthracene and dibenzofuran are Aldrich "Gold Label" quality pure to 99.9%. These compounds were used as received.

Vacuum sublimation was used to purify triphenylmethane, 9-fluorenone, and dibenzothiophene (Aldrich, 97% pure as received). Purity of 99.5+% for triphenylmethane and dibenzothiophene was verified by elemental analysis and melting point range. 9-Fluorenone was purified to 99+% verified by the same methods.

All compounds used as sample solids are further purified in the experimental pretreatment procedure, as discussed in the next section.

Procedure. The saturator is cleaned with distilled ethanol and baked at 550 K for 12–24 h. About 40 g of the solid to be studied is packed into the saturator, which is then flushed at a low flow (1 cm^3/s) at a temperature above the highest experimental temperature for 3 days to strip off any residual volatile impurities. Very heavy impurities, if present, do not interfere in the experiment. For the run the purification convertor is set to 770 K and the main catalytic convertor to 1250 K, and the flow rate increased 10–20 cm^3/s for 60–90 min. Then the gas mixture is directed to the infrared gas cell, which has a volume of 5.6 L; to ensure complete exchange, 30 L are passed through the cell. The absorbance of the mixture is recorded and compared with that for pure oxygen. This difference gives the carbon dioxide concentration relative to the calibration gas.

Results and Discussion

In order to test the apparatus, measurements were made for the vapor pressure of anthracene in the temperature range 313–363 K (1 mPa–2 Pa). Some values are averages of 2–5 data at a single temperature. Many previous studies on anthracene have been reported (*12–19*), and the results of this work are compared with these in Figure 2 over the range 313–363 K. Note that all other data reported in this temperature range were made by some variation of an effusion method—a more involved and tedious process than transpiration. With the exception of some older data that scatter somewhat, the results presented here are in very good agreement with those of other investigators. Our data have been fit by a nonweighted least-squares method to the Clausius–Clapeyron equation.

$$\log P^s \text{ (mPa)} = B - A/T \text{ (K)} \tag{2}$$

The coefficients found are reported in Table I, and the average deviation of the data from the straight line is less than 6%. Possibly a better fit could be obtained from a higher order equation, but the data probably do not justify more than two adjustable parameters.

From the *A* parameter, we evaluate the enthalpy of sublimation of anthracene as 102.6 ± 1.3 kJ mol^{-1}. Kudchadker et al. (*20*) have reviewed 13 such measurements ranging from 84 to 105 kJ mol^{-1} and selected a most probable value of 100.9 kJ mol^{-1}. DeKruif (*13*) compared several data sets graphically and reports that the vast majority of the data from 300 to 400 K yield values in the range 97–105 kJ mol^{-1}.

The greatest uncertainties in the measurement are probably due to oxidation and to the IR analysis. Temperature control is far too good to contribute uncertainty, and the sample preparation, with the extensive purging of volatiles, also contributes negligibly. Pressure measurements may have slight effects, but substantially less than 1%. We found that great care had to be taken in the catalyst bed to ensure complete combustion—including temperature homogeneity and precautions to minimize flow channelling. It is extremely difficult to oxidize a trace organic completely. With our efforts we believe we did achieve 99+% combustion. In the IR measurement the calibration was good to only ±1% at best, and at low absorbances (lowest pressures) the reading uncertainty was as much as ±5%. Presumably greater accuracy at lower pressures could be achieved by using a longer path length cell, but this would also require the availability of very accurate calibration mixtures in the ppb range.

Table I also presents similar results for triphenylmethane, dibenzofuran, 9-fluorenone, and dibenzothiophene. Again in a few cases multiple runs at the same temperature have been averaged.

The mean absolute percent deviations for all the data sets of this work ranged from 4.6% to 9.9%. The triphenylmethane data show the greatest deviation at the three lowest temperatures. Omitting these values reduces the standard deviation for the set to 5.1%, with h^{sub} still 107 kJ mol^{-1}. The mean absolute percent deviations are then within the stated uncertainty of 6% for the experimental measurements.

Literature vapor pressure data for comparison for dibenzofuran, triphenylmethane, 9-fluorenone, and dibenzothiophene as solids are scarce at best. Culbertson and Bent (*21*) and Aihara (*22*) report data for triphenylmethane at 300–364 K and 325–349 K, respectively. Their values for h^{sub} are 100.8 and 100.1 kJ mol^{-1}, respectively. Differences are 5.6% and 6.3% from our value of 106.8 kJ mol^{-1}.

Dibenzofuran and 9-fluorenone have previously been measured as liquids only. Edwards and Prausnitz (*23*) measured vapor pressures of dibenzothiophene from 336 to 366 K, and report h^{sub} as 90.7 kJ mol^{-1}. Our h^{sub} value of 91.2 kJ mol^{-1} is in good agreement, but the absolute values of P^s are about 10% lower.

Conclusions

Low vapor pressure data for nonvolatile compounds seldom exist and the reported values disagree greatly depending on the method used. For very low vapor pressures, 1 Pa–1 mPa and lower, an improved method has been developed to replace Knudsen or torsion effusion.

We have presented vapor pressure data for anthracene, triphenylmethane, dibenzofuran, 9-fluorenone, and dibenzothiophene. The mean deviation of these data is within the experimental uncertainty. Enthalpy of sublimation data have been obtained and agree well with limited literature values. The gas saturation method provides a rapid means of obtaining good data, and virtually eliminates interfering impurities. Experimental uncertainties are largest at the lowest pressures, where concentrations and absorbance readings are least accurate.

The oxygen-containing compounds (dibenzofuran and 9-fluorenone) data presented here will be helpful in extending present group conribution and other predictive methods. Oxygen is a substituent for which few model compounds have been studied.

Acknowledgment

The capable assistance of Joseph Ritter, Michael Shulman, and Mark Bessermann in preparing compounds and making measurements is very much appreciated.

Registry No. Anthracene, 120-12-7; triphenylmethane, 519-73-3; dibenzofuran, 132-64-9; 9-fluorenone, 486-25-9; dibenzothiophene, 132-65-0.

Literature Cited

(1) Johnston, K. P.; Eckert, C. A. *AIChE J.* **1981**, *27*, 773.
(2) Johnston, K. P.; Ziger, D. H.; Eckert, C. A. *Ind. Chem. Fundam.* **1982**, *21*, 191.
(3) Murray, J. J.; Pottie, R. F.; Pipp, C. *Can. J. Chem.* **1974**, *52*, 557.
(4) DeKruif, C. G.; Van Ginkel, C. H. D. *J. Chem. Thermodyn.* **1977**, *9*, 725.
(5) Osborn, A. G.; Douslin, D. R. *J. Chem. Eng. Data* **1975**, *20*, 229.
(6) Macknick, A. B.; Prausnitz, J. M. *J. Chem. Eng. Data* **1979**, *24*, 175.
(7) Sinke, G. C. *J. Chem. Thermodyn.* **1974**, *6*, 311.
(8) Bender, R.; Bieling, V.; Maurer, G. *J. Chem. Thermodyn.* **1983**, *15*, 585.
(9) Abrams, D. S.; Massaldi, H. A.; Prausnitz, J. M. *Ind. Eng. Chem. Fundam.* **1974**, *13*, 259.
(10) Smith, G.; Winnick, J.; Abrams, D. S.; Prausnitz, J. M. *Can. J. Chem. Eng.* **1976**, *54*, 337.
(11) Hansen, P. C. Ph.D. Dissertation, University of Illinois, Urbana, 1985.
(12) Wiedemann, H. G.; Vaughan, H. P. *Proc. Toronto Symp. Therm. Anal.* **1970**, 233.
(13) DeKruif, C. G. *J. Chem. Thermodyn.* **1980**, *12*, 243.
(14) McEachern, D. M.; Sandoval, O. *J. Phys. E* **1973**, *6*, 155.
(15) Bradley, R. S.; Cleasby, T. G. *J. Chem. Soc.* **153**, 1690.
(16) Hoyer, Von H.; Peperle, W. *Z. Electrochem.* **1958**, *62*, 61.
(17) Burdurov, S. *Izv. Khim. Bulg. Akad. Nauk* **1960**, *7*, 281.
(18) Kelly, J. D.; Rice, F. O. *J. Phys. Chem.* **1964**, *68*, 3794.
(19) Taylor, J. W.; Crookes, R. J. *J. Chem. Soc., Faraday Trans. 1* **1976**, *72*, 723.
(20) Kudchadker, S. A.; Kudchadker, A. P.; Zwolinski, B. J. *J. Chem. Thermodyn.* **1979**, *11*, 1051.
(21) Culbertson, G. R.; Bent, H. E. *J. Am. Chem. Soc.* **1936**, *58*, 2000.
(22) Aihara, A. *Bull. Chem. Soc. Jpn.* **1959**, *32*, 1242.
(23) Edwards, D. R.; Prausnitz, J. M. *J. Chem. Eng. Data* **1981**, *26*, 121.

Received for review December 6, 1984. Accepted August 12, 1985. This project has been financed in part with federal funds as part of the program of the Advanced Environmental Control Technology Research Center, University of Illinois, at Urbana-Champaign, which is supported under cooperative agreement CR 806819 with the Environmental Protection Agency. The contents do not necessarily reflect the views and policies of the Environmental Protection Agency nor does the mention of trade names or commercial products constitute endorsement or recommendation for use. Additional funding was provided by the Phillips Petroleum Co., Arco Oil and Gas Co., Exxon Research and Engineering Co., General Foods Corp., and the National Science Foundation.