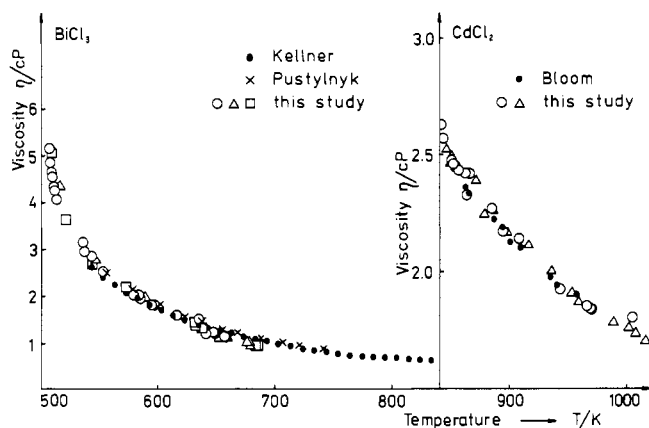


Table III. Values of Constants in Arrhenius and VTF Equations Calculated for Data in Tables I and II

	Arrhenius equation $\eta = Ae^{B/T}$			VTF equation $\eta T^{-1/2} = Ae^{B/(T-T_0)}$			
	$\ln A$	$B$	correlation coeff	$\ln A$	$B$	$T_0, K$	correlation coeff
$CdCl_2$	$-1.47 \pm 0.05$	$2019 \pm 42$	0.9936	$-3.97 \pm 0.02$	$559 \pm 103$	$475 \pm 2.5$	0.9971
$BiCl_3$	$-4.68 \pm 0.09$	$3137 \pm 50$	0.9953	$-6.14 \pm 0.05$	$1312 \pm 214$	$215 \pm 2.5$	0.9971

Figure 1. The temperature dependence of viscosity of molten  $BiCl_3$  and  $CdCl_2$ .

refilling with helium were carried out as previously described (6, 9).

### Results and Discussion

The results of our measurements are reported in Tables I and II. They are compared with data of previous authors on Figure 1. The agreement of all sets of values is satisfactory.

Due to the supposed structural rearrangements occurring in both salts with increasing temperature, one should expect the dependences rather nonconforming to the Arrhenius law. Our experimental results show a small departure from this law only in the lowest temperature region of existence of the liquid phases. This departure is more distinct in the  $BiCl_3$  than in the  $CdCl_2$  case.

The three-parameter equation of Vogel-Tamann-Fulcher (VTF) type (10-12)

$$\eta / T^{1/2} = Ae^{B/(T-T_0)} \quad (2)$$

where  $\eta$  is the viscosity coefficient,  $T/K$  is the temperature,  $T_0/K$  is the temperature of the ideal glass transition, and  $A$  and  $B$  are constants, does not approximate the experimental data better than the Arrhenius law.

Table III reports the values of constants and correlation coefficients calculated by fitting our results for both Arrhenius and VTF equations. The reported  $B$  and  $T_0$  values correspond to the highest correlation coefficient for the logarithmic form of eq 2 when all our experimental data in the full temperature range are used.

It should be noted that the dependences on temperature of the viscosities of both salts demonstrate the structural anomalies different than the ultrasonic velocities. In the case of  $CdCl_2$  the latter property depends on temperature according to the non-linear law (1), whereas the same dependence for  $BiCl_3$  is linear (13). So ultrasonic properties indicate the more distinct structural rearrangement in molten  $CdCl_2$  than in  $BiCl_3$  whereas viscosity data suggest the opposite conclusion.

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## Development of an Apparatus To Measure Vapor Pressures at High Temperatures and Its Application to Three Higher-Boiling Compounds

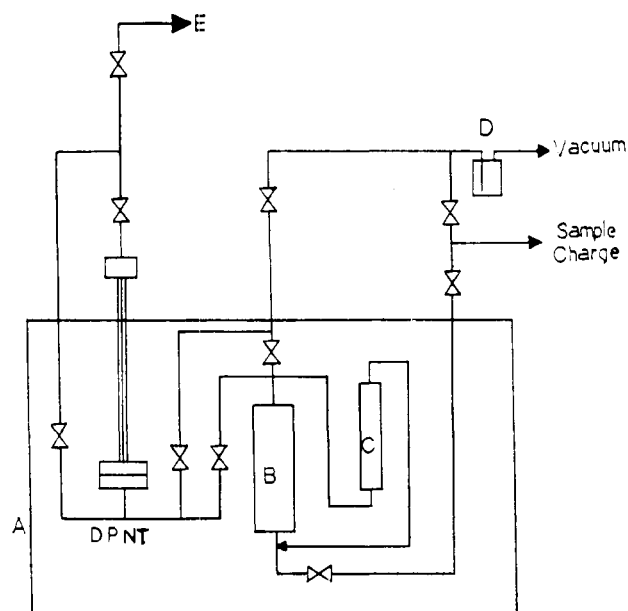
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An apparatus to measure vapor pressures of aromatic hydrocarbons up to moderately high temperatures is described. With this apparatus, the vapor pressures of tetralin, *m*-cresol, and biphenyl were measured up to 600.7 K. The measurements are found to be in agreement with selected literature values, measurements of which have been conducted previously.

### Introduction

An accurate knowledge of vapor pressures is needed for several theoretical and practical reasons. Such data are needed to establish pure-component limits in binary systems and liquid-activity coefficients in multicomponent systems, for the calculation of enthalpy of vaporization, etc. Also, vapor pressure data are needed to obtain enhancement factors which help in



**Figure 1.** High-temperature, vapor pressure apparatus: (A) high-temperature bath; (B) equilibrium cell; (C) magnetic pump; (D) cold trap; (E) to pressure measuring and supply system (see Figure 2).

the study of molecular interactions between unlike pairs.

### Experimental Section

**Apparatus.** The apparatus used in this work is similar in design to that described by Carruth (1), Chen et al. (4), and Hwang et al. (9) for lower temperature vapor pressure measurements but is designed and constructed specifically for high-temperature measurements. It can be used either in the elution mode (1) (for vapor pressures below ca. 15 mmHg) or in the static mode (for vapor pressures above ca. 15 mmHg). For this work only the static method was used.

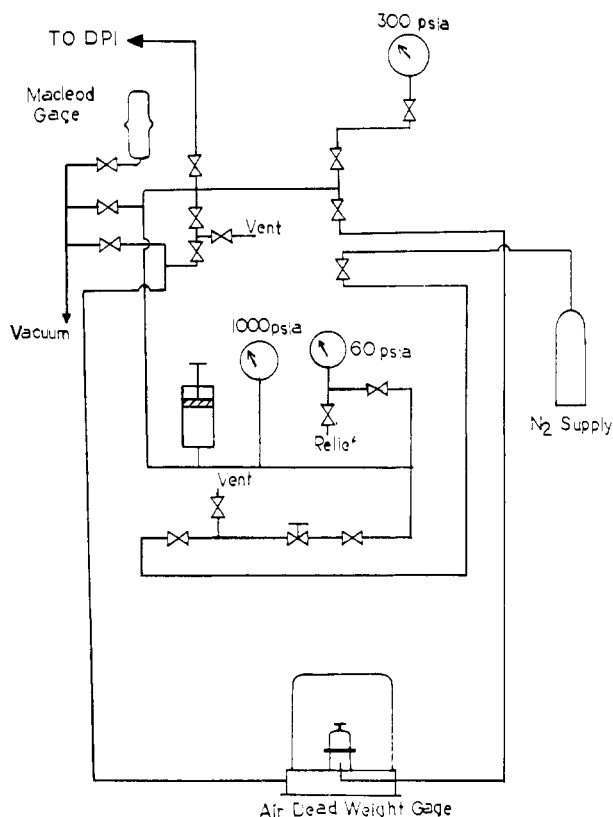
Figure 1 shows the schematic diagram of the experimental apparatus. The equilibrium cell (EC) consists of a 75-cm<sup>3</sup> sampling cylinder made from 316 stainless steel. It is rated for ca. 10 MPa at 673 K. This pressure rating is adequate for aromatic compounds, because all of these compounds have critical pressures of less than ca. 6 MPa.

To hasten the establishment of equilibrium, the vapor phase is circulated through the liquid phase by a high-temperature magnetic pump. This pump is similar in design to that described by Ruska et al. (13) and was fabricated in our machine shop.

Twelve 500-W strip heaters strapped around the bath tank are the main heat source to the bath fluid (Monsanto's Therminol 66). The amount of heat needed is regulated via three-phase 220-V power transformers. The fine control is achieved by a 100-W immersion heater which takes its input from a Hallikainen Model 1358A Thermotrol temperature controller. The Thermotrol takes its input from a thermopile sensor and, by use of proportional and reset functions, provides a time-modulated electrical output to the 100-W heater. A temperature control of  $\pm 0.01$  K is achieved for the bath fluid.

The temperature of the bath was measured (very close to the EC) with a Leeds and Northrup platinum resistance thermometer (PRT), which had been calibrated against an NBS standard. The resistance of the PRT is measured with a Leeds and Northrup Model 8067 Mueller bridge and a Model 9828 DC null detector. The accuracy of temperature measurement is better than  $\pm 0.01$  K (expressed on IPTS-68).

The pressure in the EC is measured with a Ruska Instruments Corp. (RIC) Model 2439-702-8100 differential pressure null transducer (DPNT). The null position of the DPNT diaphragm



**Figure 2.** Pressure supply and measuring system.

is indicated as an analogue signal on a Ruska Instruments Corp. (RIC) Model 2416-708 differential pressure null indicator (DPNI). The DPNT diaphragm's balancing pressure is measured with an RIC Model 2465 gas-lubricated-piston, dead-weight gauge. Before vapor pressure measurements are started, the zero calibration of the DPNT is carried out by exposing both of its chambers to the same stepwise variation in pressure at different temperatures. The null position of the zero potentiometer is recorded for each temperature and pressure. The sensitivity of the DPNT is  $\sim 0.02$  mmHg per unit of the DPNI dial. The piston-cylinder assembly of the air dead-weight gauge is enclosed in a bell jar which is evacuated after placement of the appropriate weights on the piston. The small pressure (0.1–0.2 mmHg) in the bell jar is measured with a MacLeod gauge to an accuracy of  $\pm 0.01$  mmHg. The pressure reading of the dead-weight gauge is corrected for ambient temperatures, thermal expansion (or contraction) of the piston (whose diameter and properties are provided by the Ruska Instrument Corp., Houston, TX), the local value of acceleration of gravity, and the pressure in the bell jar after it has been evacuated. Figure 2 shows the pressure measuring and supply system.

**Materials.** All compounds were purchased from Aldrich Chemical Co. with a minimum purity of 99+%. Tetralin and *m*-cresol were used without further purification. Biphenyl was further purified by zone refining technique to a purity of  $99.99 \pm 0.05\%$ . The purity was estimated by the freezing-point method developed by Taylor and Rossini (15).

**Procedure.** One of the major sources of error in vapor pressure measurements is due to incomplete degassing of the compound whose vapor pressure is being determined. Therefore, before the compound is charged, it is thoroughly degassed outside the EC. This involves several (usually 6–8) alternate freezing and thawing cycles under vacuum. When no bubbles are observed during the thawing of the compound, ca. 45 cm<sup>3</sup> of the compound is charged into the EC. The valve connecting the degassing bottle and the EC is then closed. The magnetic pump is turned on, and the compound allowed to reach thermal

Table I. Vapor Pressure Data

	temp, K	press., mmHg	100( $\Delta P/P$ )
<i>m</i> -cresol	388.14	30.90	-0.15
	394.40	43.42	0.21
	400.61	58.87	0.09
	406.55	77.15	0.08
	416.07	114.18	-0.48
	429.44	190.04	0.36
	441.05	280.75	-0.06
	460.48	509.67	-0.13
	476.55	797.95	0.12
	489.87	1120.83	0.03
	507.92	1712.33	0.02
	530.42	2746.44	-0.24
	551.31	4109.20	0.27
	574.91	6173.04	-0.12
594.16	8408.70	0.03	
tetralin	355.45	13.03	
	398.96	78.76	
	423.30	168.16	
	473.26	630.07	
	523.81	1929.96	
	540.36	2610.90	
biphenyl	396.15	15.30	0.12
	416.96	35.80	-0.54
	437.84	74.72	0.90
	454.43	123.36	-0.27
	474.02	214.51	-0.42
	496.81	386.42	-0.03
	518.80	646.96	0.62
	531.06	835.14	-0.17
	547.24	1158.79	-0.27
	569.29	1765.23	-0.03
	588.34	2469.95	0.18
600.70	3001.56	-0.08	

$$^a \Delta P/P = (P_{\text{exptl}} - P_{\text{calcd}})/P_{\text{exptl}}$$

equilibrium. When the pressure of the system has stopped changing, it is recorded as the "provisional" vapor pressure. The system is then evacuated to vaporize  $\sim 2\text{--}3 \text{ cm}^3$  of the sample (the vaporized sample condenses in the cold trap). The vapor pressure of the sample is measured again after allowing for establishment of equilibrium. If the vapor pressure values before and after evacuation are identical, degassing of the sample is considered complete.

The temperature of the bath is then changed to the next requisite value. After allowing for thermal equilibrium ( $\sim 1$  h after the bath temperature has stabilized), the pressure of EC is measured every half hour. When the vapor pressure is constant over a period of 2–3 h, the system is at equilibrium. The bath temperature is then changed to the next desired value, and the above process is repeated for each temperature.

## Results and Discussion

Vapor pressures under the following conditions were measured: (1) tetralin, from 355.45 to 540.36 K; (2) *m*-cresol, from 388.14 to 594.16 K; and (3) biphenyl, from 396.15 to 600.70 K. The experimental data points are presented in Table I.

A comprehensive compilation of vapor pressures has been presented by Ohe (11). Most of the vapor pressures are reported only up to the normal boiling point of the respective compounds. Glaser and Ruland (6) report smoothed vapor pressure data for several aromatic hydrocarbons for temperatures approaching the critical point. These authors have also reported the normal boiling point and the critical point for each compound.

Figures 3–5 are drastic reductions of the original figures used

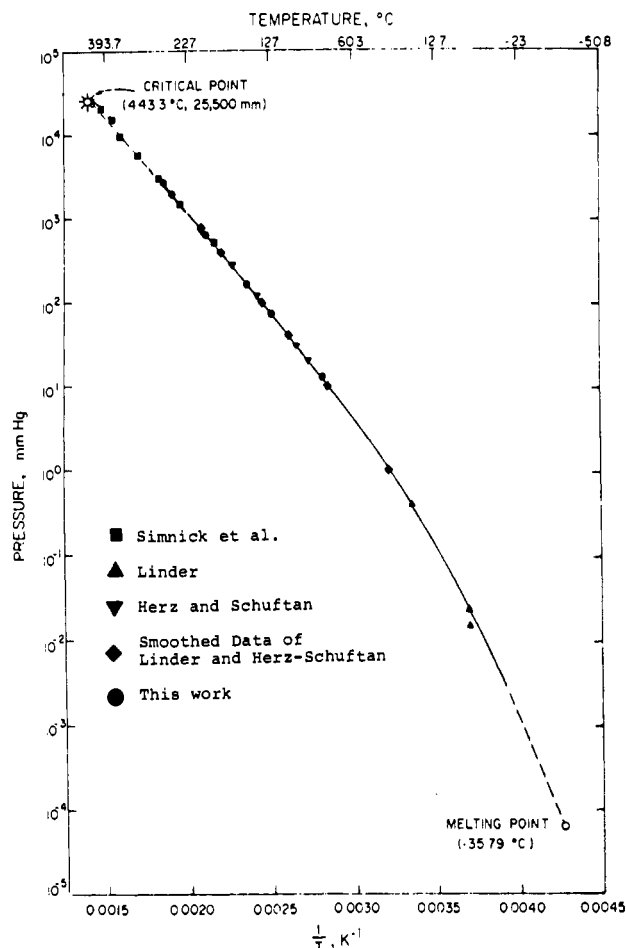
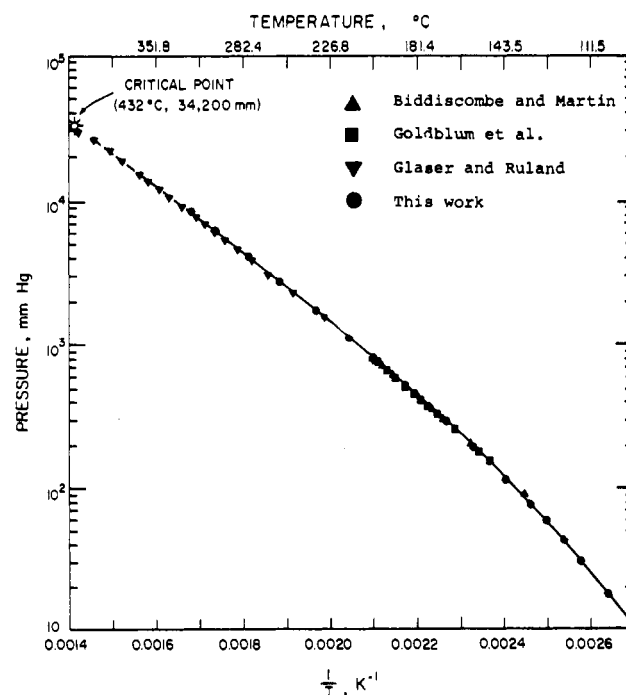


Figure 3. Vapor pressure of tetralin.

Figure 4. Vapor pressure of *m*-cresol.

for the graphical comparisons between experimental vapor pressure data obtained in this work and those reported in the literature.

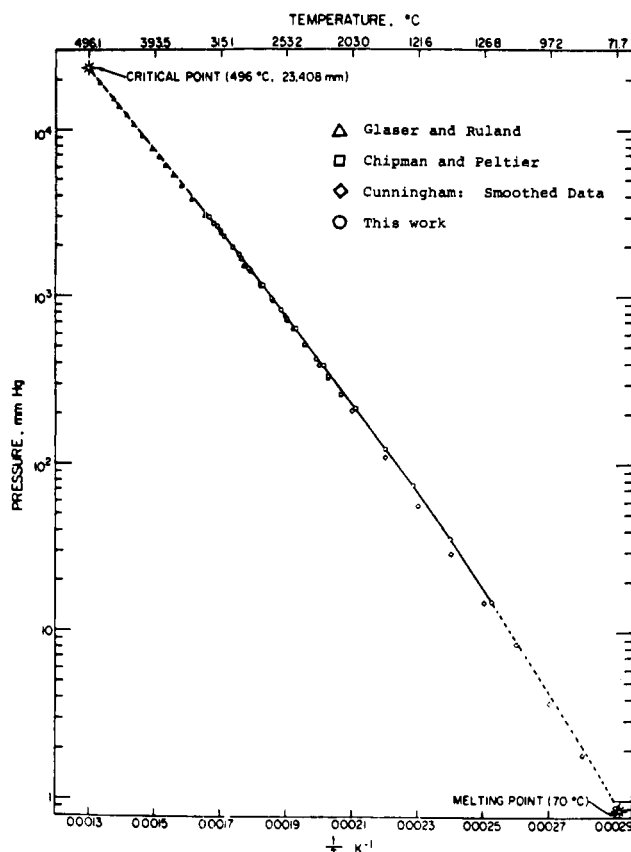


Figure 5. Vapor pressure of biphenyl.

Chebyshev polynomials (12, 16) are used to analytically represent *m*-cresol and biphenyl vapor pressure data obtained during this investigation. The 6th-order polynomial functions are then used to analytically compare the data obtained in this work with those reported in the literature. The constants in Chebyshev polynomials are estimated by using standard regression techniques. These constants for *m*-cresol and biphenyl are tabulated in Table II, along with the average root mean square (rms) error for the polynomial fit. For tetralin, the number of experimental points taken in this work do not justify a Chebyshev polynomial fit of the data. The original vapor pressure vs.  $1/T$  plot for tetralin, of which Figure 3 is a drastic reduction (by a factor of 4), shows the extent of the agreement of this work with previous measurements.

For *m*-cresol, the vapor pressure reported by Goldblum et al. (7) differs from this work by a root mean square average of 1.5%. At the lowest temperatures, their values are higher by ca. 3%, whereas at higher temperatures they are lower by ca. 1%. Vapor pressures reported by Glaser and Ruland (6) are lower by ca. 3%. Vapor pressures reported by Biddiscombe and Martin (2) differ from this work by an rms average of 1.9%.

For biphenyl, data of Chapman and Peltier (3) are lower than this work by an rms average of 6.5%. The difference is largest at temperatures lower than 493.9 K, where the average dif-

Table II. Constants for Chebyshev Polynomial<sup>a</sup>

	<i>m</i> -cresol	biphenyl
$A_0$	2977.155	2580.441
$A_1$	874.063	806.938
$A_2$	-24.124	-8.785
$A_3$	7.321	2.870
$A_4$	-2.681	-1.651
$A_5$	1.480	0.553
$A_6$	-0.669	-0.683
rms <sup>b</sup>	0.20	0.39
$T_{\max}$ , K	595.70	600.75
$T_{\min}$ , K	388.10	396.10

<sup>a</sup> The Chebyshev polynomial is defined as  $T \log P = A_0/2 + \sum_{i=1}^n A_i E_i(x)$  where  $E_1(x) = x$ ,  $E_2(x) = 2x^2 - 1$ ,  $E_{i+1} = 2xE_i - E_{i-1}$ , and  $x = [2T - (T_{\max} + T_{\min})] / [T_{\max} - T_{\min}]$ . <sup>b</sup> rms =  $([100(P_{\text{exptd}} - P_{\text{calcd}})/P_{\text{exptd}}]^2/N)^{1/2}$ .

ference is ca. 10%. For temperatures above  $\sim 539.16$  K, the average difference is  $\sim 2\%$ . The values of Glaser and Ruland are lower by an rms average of 6.3%.

As is apparent from the above comparisons, there is, in general, some disagreement between data reported by different investigators. Most of these data either are reported up to the normal boiling point of the compound or are measured for temperatures above the normal boiling point. The apparatus described in this paper is capable of measuring vapor pressures from about the triple point of the substance up to moderately high temperatures or the temperature where significant decomposition begins.

#### Acknowledgment

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