

ΔH_m^{id}	heat of mixing for an ideal solution ($\Delta H_m^{\text{id}} = 0$), J mol ⁻¹
ρ	gas density, mol cm ⁻³
ϕ	isothermal Joule-Thomson coefficient, defined by eq 5, J mol ⁻¹ Pa ⁻¹
Ω_a, Ω_b	constants in eq 19-21, dimensionless
ω	acentric factor, eq 26, dimensionless (ω_1 and ω_2 refer to acentric factors for CH ₄ and CO ₂ , respectively)

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Investigation of Vapor Pressures and Heats of Vaporization of Condensed Aromatic Compounds at Elevated Temperatures

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A high-temperature static apparatus is used to investigate vapor pressures in the range 1-2780 mmHg over the temperature range 425-640 K for three aromatic compounds similar to those which are often found in coal liquids: fluorene, dibenzofuran, and dibenzothiophene. The experimental vapor pressure data of fluorene and its homomorphs cited above have been fitted to Chebyshev polynomials. The values of dp/dT calculated from the Chebyshev polynomials, the compressibility factors of saturated vapor and liquid estimated from three-parameter corresponding states correlation, and the acentric factors determined from their experimental vapor pressure data presented in this paper were used to evaluate the heats of vaporization of the aromatic compounds mentioned above from the Clapeyron equation.

Introduction

The purposes of this article are (I) to investigate the vapor pressures of some commercially important substances found in coal liquids, viz., fluorene, dibenzofuran, and dibenzothiophene, and (II) to determine the heats of vaporization of fluorene and the homomorphs mentioned above. The determination of vapor pressures of some oxygen- and sulfur-containing coal-derived liquids is an important consideration from not only the purely scientific standpoint but also a commercial standpoint. Hydrocarbon fractions derived from the liquefaction of coal are composed largely of hydrogen-deficient condensed-ring molecular systems. Since many of the pure compounds that are members of these systems are low vapor pressure solids at room temperature, the amount of reliable physical and thermodynamic data available for them, compared to that for alkane hydrocarbons (1), is sparse. Vapor pressure

is an important physical property required in designing coal-liquid processing and separation plants. The idea of choosing these condensed aromatic compounds is that the thermodynamic properties are virtually unknown, especially at high temperatures. Moreover, it is interesting and valuable to study the properties of the coal-related compounds belonging to the same family or homomorphs (2) which will help to generate best correlations for better prediction of physical properties. No experimental vapor pressure values are reported in the literature for these compounds in the temperature range of the present investigation. However, Edwards and Prausnitz (3) report vapor pressure measurements in solid and liquid dibenzothiophene at fairly low temperatures. The experimental data of vapor pressures were fitted to Chebyshev polynomials and values of dp/dT were calculated. No literature measurements of heats of vaporization over the range of temperatures were found for these compounds. For design of coal-conversion processes these data are very much necessary. The following paper presents the calculated values of heats of vaporization from our experimental vapor pressure data over a range of temperature. The Clapeyron equation was used to calculate the heat of vaporization. The compressibility factors of saturated vapor and liquid needed for the above calculation were estimated from Pitzer's three-parameter corresponding states correlation using the acentric parameters obtained from this study.

Experimental Vapor Pressure Measurements

Materials. All compounds studied were purchased from Aldrich Chemical Co. with the following purities: fluorene, 98%; dibenzofuran, 98%; and dibenzothiophene, 95%. These substances were purified by 48 passes in a zone refiner to a purity of 99.99%. The purity was estimated by the freezing-point

Table I. Vapor Pressure and dp/dT of Fluorene

T, K	$p, \text{ mmHg}$	$dp/dT, \text{ mmHg/K}$	T, K	$p, \text{ mmHg}$	$dp/dT, \text{ mmHg/K}$
424.81	12.53	0.48	524.66	271.64	6.67
427.72	13.93	0.53	533.05	332.66	7.89
437.06	19.77	0.71	551.57	508.16	11.27
444.05	25.23	0.88	567.86	724.44	15.26
451.67	32.81	1.10	572.41	794.33	16.58
458.72	41.11	1.36	591.02	1158.78	23.00
462.11	46.34	1.49	600.24	1393.16	26.78
476.42	72.44	2.20	625.78	2218.20	38.51
489.72	107.65	3.08	636.94	2691.53	43.48
512.56	199.53	5.18	639.39	2779.71	44.49

method of Taylor and Rossini (4).

Apparatus and Procedure. The measurement of vapor pressure was carried out with a high-temperature static apparatus, described earlier (5). Some modifications were made to the apparatus to include a degassing and charging system and in the experimental procedure to improve the accuracy and extend the pressure measurements to the lower region as low as 1 mmHg. A commercial-mixture high-temperature inorganic salt (Draw Temp 275 manufactured by E. F. Houghton Co.) was used as a bath fluid. A temperature control of ± 0.01 K was achieved for the bath fluid. The temperature near the equilibrium cell was measured in IPTS-68 with an accuracy of ± 0.01 K by means of a Leeds and Northrup platinum resistance thermometer calibrated against an NBS standard. The pressure measurements were made with a high-temperature Ruska differential-pressure null detector and a Ruska gas-lubricated dead-weight gauge Model 2465. For pressure measurements below 20 mmHg down to 1 mmHg a calibrated Ruska Model DDR 6000 digital quartz pressure gauge has been used. The overall accuracy of the pressure measurement is estimated to be 0.01% of the measured value.

In precise vapor pressure measurements at elevated temperatures there are three important things to be taken care of apart from the precise pressure and temperature measurements. They are (1) proper degassing of the compound, (2) attainment of thermal equilibrium, and (3) degradation or decomposition of the compound. One of the major sources of error in vapor pressure measurement is due to incomplete degassing of the compound whose vapor pressure is being determined. Therefore, the compound is thoroughly degassed in a degassing system outside the equilibrium cell by alternate freezing and thawing cycles under vacuum. This procedure was repeated 8–9 times until we obtained concordant values of vapor pressure at the same temperature. About 45 cm³ of the degassed sample was charged into the cell. The thermal equilibrium of the compound in the equilibrium cell was established by a magnetic pump (6) which continuously stirred the vapor phase and the liquid phase of the compound in the cell. Adequate time (~ 1 –2 h) was given during pressure measurements at each temperature to make sure that the system had attained equilibrium conditions. The decomposition occurs in polynuclear aromatic compounds at some high temperature, usually before reaching their respective critical temperatures, and is probably one reason that data at high temperature are so scarce. Hence, during the vapor pressure measurements at high temperatures one has to make sure that the degradation has not occurred. The procedure as discussed by Wiczorek et al. (7) has been used in the present measurements to confirm that thermal decomposition had not occurred in the temperature range reported in this paper.

Results and Discussion

Vapor pressures under the following conditions were measured: (1) fluorene, from 424.81 to 639.39 K; (2) dibenzofuran, from 435.35 to 618.05 K; and (3) dibenzothiophene, from

Table II. Vapor Pressure and dp/dT of Dibenzofuran

T, K	$p, \text{ mmHg}$	$dp/dT, \text{ mmHg/K}$	T, K	$p, \text{ mmHg}$	$dp/dT, \text{ mmHg/K}$
435.35	38.90	1.25	523.56	380.19	8.21
444.44	51.52	1.55	536.48	501.19	10.26
454.54	69.18	1.96	543.48	575.44	11.54
466.20	95.50	2.57	552.49	691.83	13.39
473.93	117.49	3.07	564.97	870.96	16.33
483.09	147.91	3.75	574.71	1047.13	18.92
495.05	199.53	4.81	595.95	1513.56	25.50
500.00	223.87	5.31	609.76	1905.46	31.50
507.61	269.15	6.14	618.05	2187.76	37.26
512.82	301.99	6.77			

Table III. Vapor Pressures and dp/dT of Dibenzothiophene

T, K	$p, \text{ mmHg}$	$dp/dT, \text{ mmHg/K}$	T, K	$p, \text{ mmHg}$	$dp/dT, \text{ mmHg/K}$
424.81	3.53	0.14	500.00	52.48	1.61
428.82	4.17	0.17	515.46	83.18	2.41
435.54	5.49	0.22	525.76	111.69	3.11
440.53	6.67	0.27	549.45	208.93	5.30
444.84	7.94	0.31	568.18	331.13	7.84
455.79	12.02	0.44	588.23	524.81	11.68
463.39	15.85	0.56	596.66	630.96	13.63
471.25	20.89	0.71	600.96	691.83	14.70
482.62	30.20	0.98	607.53	794.33	16.40
491.16	39.81	1.26			

424.81 to 607.53 K. The values of experimental vapor pressures of the condensed aromatic compounds fluorene, dibenzofuran, and dibenzothiophene are presented in Tables I–III, respectively.

Chebyshev polynomials (8) of the following form have been used for representation of the vapor pressure curves of the polynuclear aromatic compounds studied

$$T \log p = a_{0/2} + a_1 E_1(x) + a_2 E_2(x) + \dots + a_s E_s(x) + \dots + a_n E_n(x) \quad (1)$$

where $E_s(x) = \cos(s \cos^{-1} x)$ is the Chebyshev polynomial in x of degree s , and where x is a function of temperature, varying between the limits 1 and -1 , defined as

$$x = \frac{2T - (T_{\max} + T_{\min})}{T_{\max} - T_{\min}} \quad (2)$$

T_{\max} and T_{\min} being thermodynamic temperatures, respectively, just above and just below the extreme temperatures of the measured values. The first few Chebyshev polynomials are

$$E_1(x) = x \quad E_2(x) = 2x^2 - 1 \quad E_3(x) = 4x^3 - 3x \quad (3)$$

and are evaluated from the equation $E_{s+1}(x) - 2xE_s(x) + E_{s-1}(x) = 0$.

The values of $T \log p$ were fitted by Chebyshev polynomials up to order 8. The values of dp/dT obtained from the best fit have been presented in the tables along with their respective vapor pressures and temperatures in Tables I–III, respectively, for all of the compounds. The constants of Chebyshev polynomials for the best fit, the respective limits of the temperatures, namely, T_{\max} and T_{\min} , and the percent root mean square deviation (rms) in pressure

$$p_{\text{rms}} = \left[\frac{\sum (p_{\text{expt}} - p_{\text{calcd}})^2}{p_{\text{expt}}^2} (100)^2 / n \right]^{1/2} \quad (4)$$

have been tabulated in Table IV for fluorene and its homomorphs, respectively. The residuals $\Delta \log p = \log p_{\text{expt}} - \log p_{\text{calcd}}$ for the investigated compounds are shown in Figure 1. Critical parameters estimated by the method described by Wilson et al. (9) for these coal-derived liquids have been tab-

Table IV. Constants of Chebyshev Polynomials for $T \log p$

coeff	fluorene ^a	dibenzofuran ^b	dibenzo- thiophene ^b
A_0	2671.155	2752.968	1993.863
A_1	868.324	685.243	764.925
A_2	-0.673	1.556	0.592
A_3	0.863	0.682	0.118
A_4	-0.021	0.161	-0.308
A_5	-0.904	0.271	0.195
A_6	-0.380	-0.016	0.267
A_7	0.170	0.274	-0.522
A_8		0.053	0.167
T_{\max} , K	639.40	618.10	607.60
T_{\min} , K	424.80	435.30	424.80
p_{rms}	0.27	0.23	0.21

^a Seventh order. ^b Eighth order.

Table V. Estimated Critical Parameters Used for Fluorene and Its Homomorphs

compd	T_c , K	p_c , atm	Z_c	ω	T_b , K
fluorene ($C_{13}H_{10}$)	870.0	46.4	0.352	0.334	570.44
dibenzofuran ($C_{12}H_8O$)	837.8	40.0	0.293	0.380	557.86
dibenzothiophene ($C_{12}H_8S$)	899.3	39.4	0.282	0.390	605.32

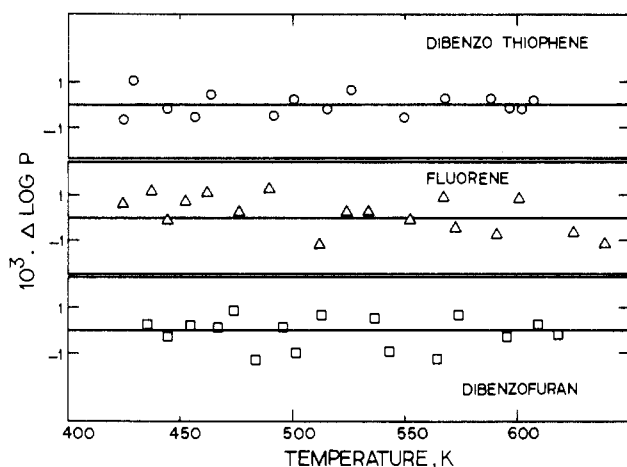


Figure 1. Residuals in $\log p$ (i.e., $\Delta \log p = \log p_{\text{expt}} - \log p_{\text{calcd}}$) for fluorene, dibenzofuran, and dibenzothiophene.

ulated in Table V. The coefficients for the polynomials which cover the temperature range investigated whose limits are represented by T_{\max} and T_{\min} are given in Table IV. A good fit was obtained by using an eighth-order polynomial for dibenzothiophene and dibenzofuran, and percent root mean square (rms) deviations of 0.21 and 0.23, respectively, were obtained. For fluorene, a seventh-order polynomial was chosen to give a 0.27% rms deviation. Since fluorene and its homomorphs were unstable in the highest temperature range, it was not possible to continue the vapor pressure measurement up to their respective critical temperatures. But when we extended the same curve, fitting $T \log p$ (fourth-degree polynomials) up to the critical temperature (i.e., $T_{\max} = T_c$ estimated), we got rms deviations of 0.38%, 0.31%, and 0.26%, respectively, for fluorene, dibenzothiophene, and dibenzofuran. It did not produce any spurious results between the temperature limit of the data and T_c . The corresponding coefficients of the polynomials are tabulated in Table VI. The values of dp/dT in the investigated range of temperature calculated from the corresponding order of polynomials are given in Tables I–III, respectively.

Comparison with Existing Data. Mortimer and Murphy (10) have conducted some vapor pressure measurements in the region 434.15–573.55 K. Our present measurements in liquid fluorene are in the region 424.81–639.39 K. Figure 2 shows the excellent comparison of both data. Our data are in good

Table VI. Constants of Chebyshev Polynomials for $T \log p$

coeff	fluorene ^a	dibenzofuran ^a	dibenzo- thiophene ^a
A_0	4653.304	4557.371	4035.935
A_1	1901.149	1640.962	1644.529
A_2	61.485	76.436	-208.371
A_3	25.367	26.239	-84.673
A_4	4.171	4.315	-17.579
T_{\max} , K	870.0	837.8	899.3
T_{\min} , K	424.8	423.5	424.8

^a Fourth order.

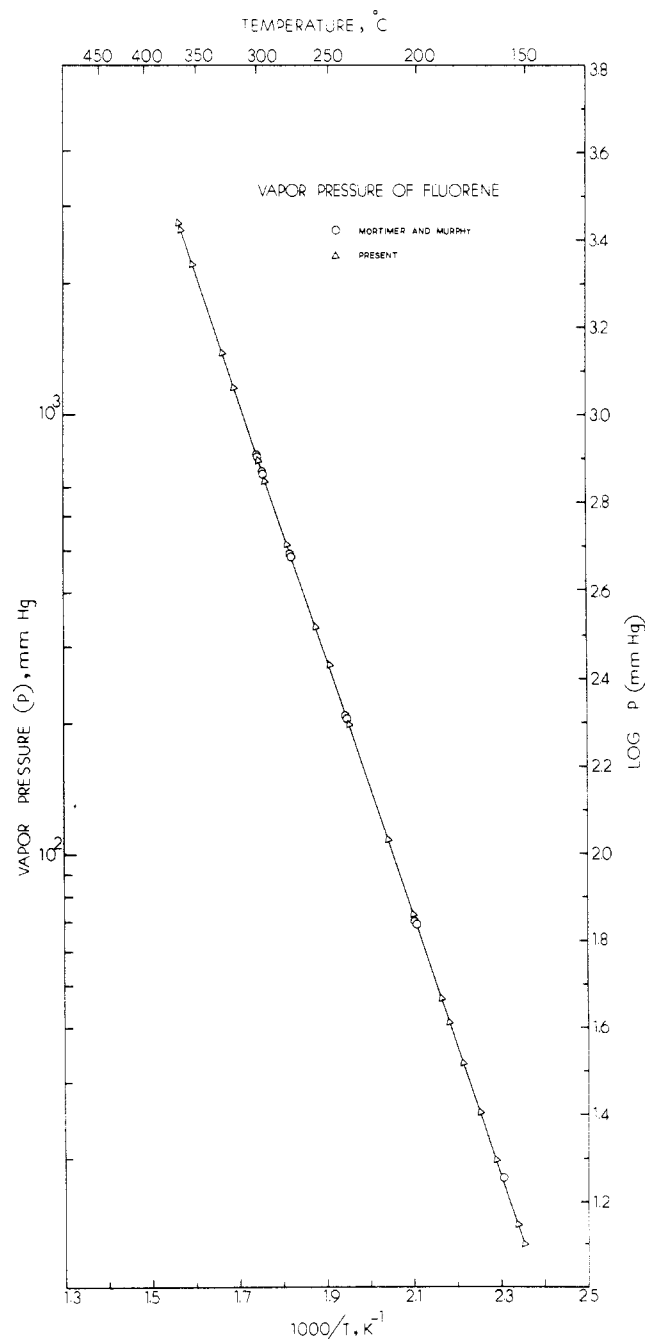


Figure 2. Vapor pressures of fluorene.

agreement with the data of Mortimer et al. In the case of dibenzothiophene no experimental vapor pressure values are reported in the literature in the range of the present investigation (424.81–607.53 K). However, Edwards and Prausnitz (3) have reported vapor pressure measurements in the temperature range 373.75–404.90 K for liquid dibenzothiophene. Although Edwards and Prausnitz's data are at lower temperatures than

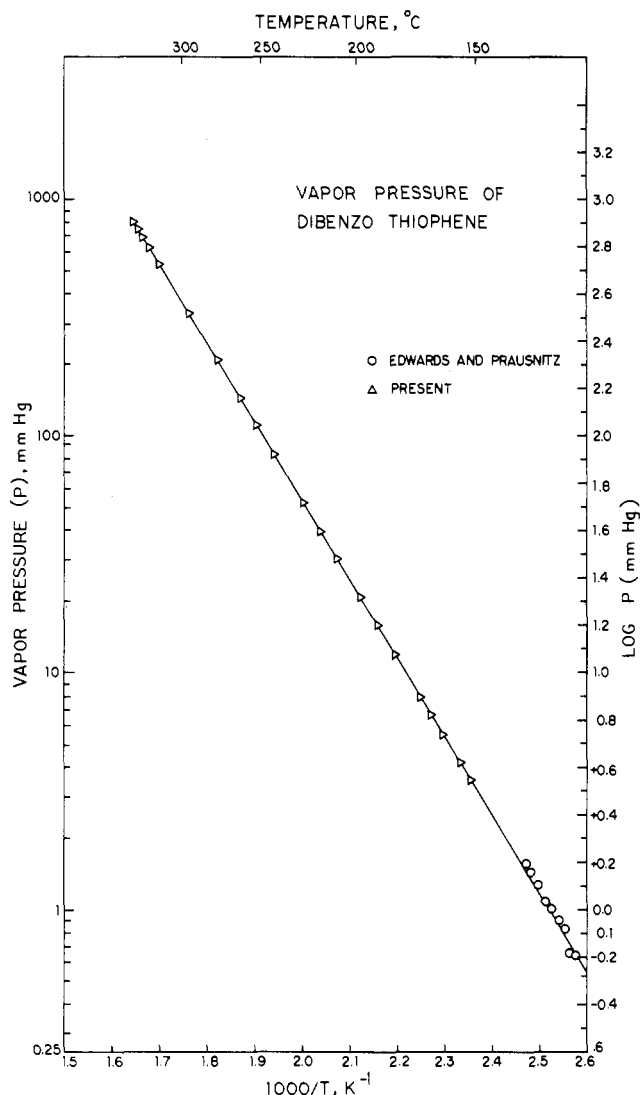


Figure 3. Vapor pressures of dibenzothiophene.

our measurements, we have shown them in Figure 3 to compare with our present data. Their data show considerable scatter around our present curve. For dibenzofuran sufficient data are not available for comparison. The vapor pressures of dibenzofuran have been measured in the temperature range 435.35–618.05 K and are shown in Figure 4.

Heat of Vaporization. Heats of vaporization of fluorene and its two homomorphs dibenzofuran and dibenzothiophene were calculated from the Clapeyron equation:

$$dp/dT = \Delta H_v / [(RT^2/p)\Delta Z] \quad (5)$$

where $\Delta Z = Z_{sat}^v - Z_{sat}^l$ and Z_{sat}^v is the compressibility factor of saturated vapor, Z_{sat}^l is the compressibility of saturated liquid, ΔH_v is the heat of vaporization, p is the vapor pressure, and T is the temperature. Since no experimental data of critical parameters T_c and p_c and compressibility factors of vapor and liquid along the saturated curve were available, we have estimated those parameters using the method described by Wilson et al. (9), and they are tabulated in Table V. ω is the acentric factor defined as $\omega = -\log p_{r, vap} - 1.0$, where $p_{r, vap}$ is the reduced vapor pressure

$$p_{r, vap} = p_{vap} / p_c$$

at reduced temperature T_c , $T/T_c = 0.7$.

The values of acentric factors for the compounds investigated were calculated from the experimental vapor pressures discussed formerly in this paper. Pitzer's (11) three-parameter

Table VII. Coefficients of Polynomial for Compressibility Factors $Z^{(0)}$ and $Z^{(1)}$ for Saturated Vapor and Liquid at Reduced Temperature Ranges between $T_r = 0.94$ and $T_r = 0.56$

coeff	vapor		liquid	
	$Z^{(0)}$	$Z^{(1)}$	$Z^{(0)}$	$Z^{(1)}$
A_0	1.0329	4.8701	0.8930	-0.3242
A_1	-0.5760	-25.4854	-5.2910	1.5098
A_2	1.7942	48.1356	11.7974	-2.1798
A_3	-1.7863	-37.6756	-11.8799	0.8856
A_4		10.1178	4.6733	

Table VIII. Heats of Vaporization (kJ/mol) of Fluorene, Dibenzofuran, and Dibenzothiophene

T, K	fluorene	dibenzo-	
		dibenzofuran	thiophene
425.15	57.4	48.8	64.5
435.15	57.1	48.7	64.0
445.15	56.9	48.6	63.6
455.15	56.7	48.5	63.3
465.15	56.5	48.5	63.1
475.15	56.2	48.2	62.9
485.15	56.0	48.1	62.8
495.15	55.8	47.9	62.7
505.15	55.5	47.8	62.6
515.15	55.3	47.7	62.6
525.15	55.1	47.5	62.5
535.15	54.8	47.4	62.5
545.15	54.6	47.3	62.4
555.15	54.3	47.1	62.3
565.15	54.1	47.0	62.1
575.15	53.8	46.9	61.8
585.15	53.6	46.8	61.5
595.15	53.3	46.7	61.0
605.15	53.1	46.6	60.4
615.15	52.9	46.5	59.7
625.15	52.6	46.5	
635.15	52.4		

corresponding states correlation was used to evaluate the compressibility factor of saturated vapor and liquid.

In these calculations the linear form for the acentric factor was used $Z = Z^{(0)} + \omega Z^{(1)}$ where $Z^{(0)}$ is the compressibility factor for a simple fluid, $Z^{(1)}$ is the compressibility factor correction for deviation from a simple fluid, and ω is the acentric factor. The coefficients of the polynomial

$$Y = A_0 + A_1 T_r + A_2 T_r^2 + A_3 T_r^3 + A T_r^4 \quad (6)$$

used to calculate $Z^{(0)}$ and $Z^{(1)}$ for saturated vapor and liquid at reduced temperature ranges between $T_r = 0.94$ and $T_r = 0.55$ are tabulated in Table VII and discussed by Wiecezorek et al. (12). The coefficients of Chebyshev polynomials tabulated in Table VI have been used to calculate dp/dT which in turn have been used to calculate ΔH_v , the heat of vaporization. Heats of vaporization, calculated from experimental vapor pressure data, and estimated values of the compressibility factors for vapor and liquid are listed in Table VIII. They are estimated to be accurate to ± 1.5 kJ/mol.

No accurate experimental data of heat of vaporization for these polynuclear aromatic compounds are available at these elevated temperature ranges. However, the heat of vaporization of fluorene (58.1 kJ/mol) reported (13) at slightly lower temperature ranges is about 7% higher than our present value (54.1 kJ/mol). The heat of vaporization reported by Mortimer et al. (10) at the boiling point of fluorene (52.4 kJ/mol) is well within the accuracy of our experiments. There are no sufficient data available for comparison in the case of the heterocyclic aromatic compounds dibenzofuran and dibenzothiophene. The calculated heats of vaporization for even 10 K temperature intervals for fluorene and its homomorphs are tabulated in Table

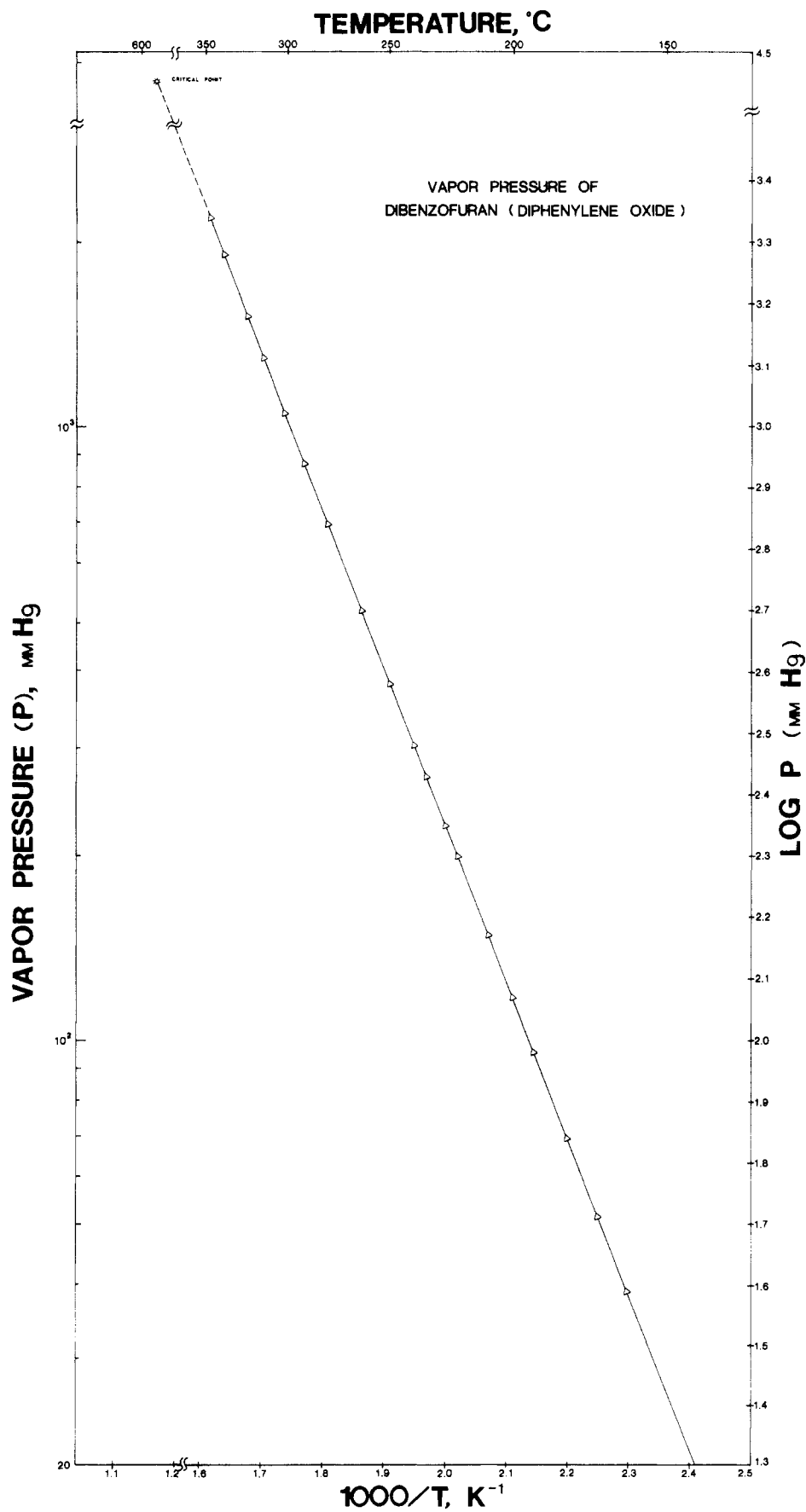


Figure 4. Vapor pressures of dibenzofuran.

VIII and are shown in Figure 5.

In all three cases ΔH_v decreases in a smooth function al-

most linearly. However, the ΔH_v value is 12% larger in the case of dibenzothiophene than that of fluorene.

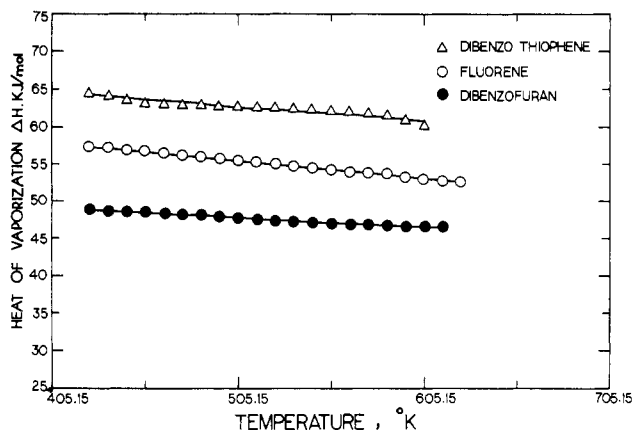


Figure 5. Heats of vaporization of fluorene, dibenzofuran, and dibenzothiophene.

In the case of dibenzofuran, the heat of vaporization has been observed to be smaller than that of fluorene.

Acknowledgment

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Thermophysical Properties of the Equimolar Mixture $\text{NaNO}_3\text{-KNO}_3$ from 300 to 600 °C

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The thermophysical properties (viscosity, surface tension, and density) of the equimolar mixture $\text{NaNO}_3\text{-KNO}_3$ have been determined over the temperature range 300–600 °C in argon and in oxygen. The surface tension is a linear function of the temperature and can be represented by the expression $\gamma(\text{dyn/cm}) = 133.12 - (6.25 \times 10^{-2})T(^\circ\text{C})$. The viscosity may be calculated from the equation $\eta(\text{cP}) = 22.714 - 0.120T + (2.281 \times 10^{-4})T^2 - (1.474 \times 10^{-7})T^3$, for T in °C. The density of the equimolar mixture is given by $\rho(\text{g/cm}^3) = 2.090 - (6.36 \times 10^{-4})T(^\circ\text{C})$. In contrast to the surface tension and the viscosity, the density is affected by the presence of nitrite, the thermal decomposition product of the nitrate anion.

The equimolar molten salt mixture $\text{NaNO}_3\text{-KNO}_3$ is being proposed as a heat-transfer fluid and a thermal-energy storage medium for various solar energy applications. In these applications the maximum operating temperature will be in the range 500–600 °C. Industrial experience and previous experimental investigations on this molten salt mixture have generally been confined to temperatures below 450 °C. In order to provide data to solve various specific design problems associated with the use of these molten nitrate salts as heat-transfer fluids, it is important that we know how the physical properties of these salts are affected by temperature and composition of the liquid and gas phases. It is the purpose of this report to present and comment on the viscosity, surface tension, and density data which we have measured for equimolar $\text{NaNO}_3\text{-KNO}_3$ over the temperature range 300–600 °C.

The implications of these data, insofar as they reflect interactions which may be taking place in the melt, will be discussed elsewhere.

Apparatus and Experimental Technique

The thermophysical-property data for the equimolar $\text{NaNO}_3\text{-KNO}_3$ mixture were taken by an instrument designed and built by the author at SNLL. This instrument is based on the principle of a damped, one-dimensional, harmonic oscillator, i.e., the motion of a body suspended from a spring and oscillating in a fluid. A description of the theoretical principles which govern the operating of this instrument, the details of construction, and its operation and response are discussed elsewhere (1, 2). Only an abbreviated description of the various modes of operating of this instrument will be given here.

The heart of the apparatus is a quartz spring oscillator, an electromagnet for remotely starting the spring oscillating, a position transducer for remote readout of the spring extension (linear variable differential transformer (LVDT)), and a gold plate suspended in a liquid whose viscosity is being measured (see Figure 1). It is the viscous drag exerted on this plate by the liquid which causes damping of the oscillatory motion of the quartz spring.

The rate of damping of the oscillations of the spring is given by the quantity δ , the logarithmic decrement, where

$$\delta = \frac{1}{n} \ln \frac{y_0}{y_n} \quad (1)$$

where y_0 and y_n are the amplitudes of the zeroth and n th