with their results. Myers and Fenske (*5*) reported the smoothed data for 1-methylnaphthalene between 325.45 and 516.15 K. Their values at lower ranges of investigated temperature are slightly smaller than both ours and the data of Camin and Rossini (*2*). Smoothed data of vapor pressures of 1-methylnaphthalene reported by Glaser and Ruland (*6*) at the temperature range between 515.15 and 778.15 K are in serious disagreement with our results, their data being rather higher than ours.

In Figure 3, comparison of vapor-pressure data for 2-methylnaphthalene are shown. Similarly, for 2-methylnaphthalene, good agreement with the data of Camin and Rossini (*2*) at temperature ranges between 412.34 and 514.81 K is evident, while serious discrepancies with smoothed data of Glaser and Ruland (*6*) between 515.15 and 735.15 K are noted.

For 9,10-dihydrophenanthrene, only the data of Lee-Bechtold et al. (*7*) are available, covering the temperature range from 353.15 to 418.15 K which does not overlap ours. In Figure 4 our data from higher temperatures are shown. An extrapolated line from our data to lower temperatures appears to merge with the line through their data.

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Heats of Vaporization of Five Polynuclear Aromatic Compounds at Elevated Temperatures

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Heats of vaporization of five polynuclear aromatic compounds, thianaphthene, 1-methylnaphthalene, 2-methylnaphthalene, bicyclohexyl, and diphenylmethane over a wide range of elevated temperatures have been calculated from the Clausius–Clapeyron equation by using acentric factors and vapor pressures recently measured by the authors. The values of d*p*/d*T* calculated from Chebyshev polynomials were used. Compressibility factors of saturated vapor and liquid were estimated from three-parameter corresponding-states correlation using acentric factors determined from new vapor-pressure data.

Introduction

In previous papers (*3*, *4*) the vapor pressures of polynuclear aromatic compounds over a wide range of elevated temperatures were reported. 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. In view of the importance of thermal data in coal liquefaction technology, such data are urgently needed.

In the present work we report calculated values of heats of vaporization based on our own data over a range of temperatures which were covered in the vapor-pressure measurements. The heats of vaporization were calculated by using the Clausius–Clapeyron relation and the three-parameter corresponding-states correlation of Pitzer (*1*) to evaluate the compressibility factor of saturated vapor and liquid.

Table I. Estimated Critical Parameters

		T_c, K	p_c, atm	ω
thianaphthene	C_8H_6S	752.0	38.3	0.294
1-methylnaphthalene	$C_{11}H_{10}$	772.0[a]	35.2[a]	0.340
1-methylnaphthalene	$C_{11}H_{10}$	761.0[a]	34.6[a]	0.371
bicyclohexyl	$C_{12}H_{22}$	731.4	25.3	0.394
diphenylmethane	$C_{13}H_{12}$	770.2	28.2	0.438

[a] Taken from ref *2*.

Results and Discussion

The heats of vaporization of five polynuclear aromatic compounds, thianaphthene, 1-methylnaphthalene, 2-methylnaphthalene, bicyclohexyl, and diphenylmethane, were calculated from the Clausius–Clapeyron equation:

$$\mathrm{d}p/\mathrm{d}T = \Delta Hv/(RT^2/p)\Delta Z \tag{1}$$

or

$$\frac{\mathrm{d}\ln p}{\mathrm{d}(1/T)} = -\frac{\Delta Hv}{R\Delta Z} \tag{2}$$

where

$$\Delta Z = Z_s^{\mathrm{v}} - Z_s^{\mathrm{L}}$$

Table II. Coefficients of Polynomial $Y = A_0 + A_1T_r + A_2T_r^2 + A_3T_r^3 + A_4T_r^4$ to Calculate $Z^{(0)}$ and $Z^{(1)}$ for Saturated Vapor and Liquid at Reduced Temperature Ranges between $T_r = 0.94$ and $T_r = 0.56$

	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 III. Coefficients of the Chebyshev Polynomials

$$T \log p = a_0 + \sum_{i=1}^{n} a_iE_i(x)$$

Where $x = [2T - (T_{\max} + T_{\min})]/[T_{\max} - T_{\min}]$, Used To Calculate d$p$/d$T$ for Thianaphthene, 1-Methylnaphthalene, 2-Methylnaphthalene, Bicyclohexyl, and Diphenylmethane

	thianaphthalene	1-methylnaphthalene	2-methylnaphthalene	bicyclohexyl	diphenylmethane
a_0	4259.691	2834.198	3213.125	3937.652	3991.790
a_1	1242.321	662.8349	829.1137	1167.051	1350.165
a_2	−11.818	−6.1730	−10.6894	−7.344	−16.583
a_3	−0.366	0.2501	−0.8815	6.467	8.278
a_4	−1.674	−0.4421	−1.0178	−0.953	0.543
$T_{\max}$	752.2	593.40	638.95	731.50	770.50
$T_{\min}$	424.39	424.40	424.40	424.24	424.63

and Z_s^V = compressibility factor of saturated vapor, Z_s^L = compressibility factor of saturated liquid, ΔHv = heat of vaporization, p = vapor pressure, and T = temperature.

Because we found no experimental data of critical parameters T_c and p_c and compressibility factors of vapor and liquid along the saturated curve, and chemical decomposition precluded measurement of T_c and p_c, estimated values were needed (2).

Critical parameters T_c and p_c used in these calculations are listed in Table I.

In order to evaluate the compressibility factor of saturated vapor and liquid, Pitzer's (*1*) three-parameter corresponding states correlation was used. Pitzer et al. expressed the compressibility factor as a power series in the acentric factor. In these calculations the linear form for the acentric factor was used

$$Z = Z^{(0)} + \omega Z^{(1)} \tag{3}$$

where $Z^{(0)}$ = compressibility factor for simple fluid, $Z^{(1)}$ = compressibility factor correction for deviation from simple fluid, and ω = acentric factor defined as

$$\omega = -\log P_r - 1.0 \tag{4}$$

$$T_r = 0.7$$

The values of acentric factors for the compounds investigated were calculated from the experimental vapor pressures reported previously (*3*, *4*) and estimated critical parameters whose values are listed in Table I.

Pitzer et al. (*1*) reported that tabulated values of $Z^{(0)}$ and $Z^{(1)}$, for either saturated vapor or liquid as a function of reduced temperature at temperature ranges between T_r = 0.94 and T_r = 0.56, were correlated to third- or fourth-order polynomials. The coefficients of the polynomials used are given in Table II.

In our previous papers (*3*, *4*) we reported the values of dp/dT over the range of temperatures investigated. In Table III the coefficients of Chebyshev polynomials used to calculate these values are presented. The values of dp/dT were calculated by differentiating Chebyshev polynomials using the coefficients from Table III. The advantage of using the Chebyshev polynomials to correlate experimental vapor pressure to be used to calculate dp/dT is that successive higher order terms with increasing order have little effect on the first two leading coefficients. Thus, to calculate dp/dT we used fourth-order Chebyshev polynomials.

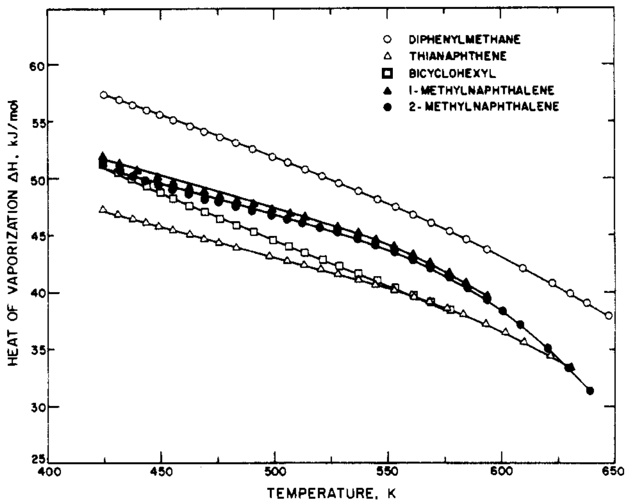

Figure 1. Calculated heats of vaporization of diphenylmethane, thianaphthene, bicyclohexyl, 1-methylnaphthalene, and 2-methylnaphthalene vs. temperature.

Table IV. Heats of Vaporization of Thianaphthene, 1-Methylnaphthalene, 2-Methylnaphthalene, Bicyclohexyl, and Diphenylmethane

T/K	thianaphthene	1-methylnaphthalene	2-methylnaphthalene	bicyclohexyl	diphenylmethane
425.15	47.2	51.8	51.2	51.1	57.3
435.15	46.6	51.0	50.4	50.1	56.6
445.15	46.0	50.3	49.7	49.1	55.8
455.15	45.4	49.6	49.0	48.2	55.1
465.15	44.9	49.0	48.4	47.3	54.4
475.15	44.4	48.5	47.9	46.5	53.6
485.15	43.8	48.0	47.4	45.7	52.9
495.15	43.3	47.5	46.9	44.9	52.1
505.15	42.8	47.0	46.4	44.1	51.4
515.15	42.3	46.5	45.9	43.3	50.6
525.15	41.8	45.9	45.3	42.5	49.8
535.15	41.2	45.3	44.7	41.8	49.0
545.15	40.6	44.6	44.0	41.0	48.1
555.15	40.0	43.8	43.3	40.2	47.3
565.15	39.4	42.9	42.4	39.4	46.4
575.15	38.6	41.9	41.5	38.6	45.5
585.15	37.9	40.7	40.4	37.7	44.5
595.15	37.0	39.4	39.1		43.6
605.15	36.1		37.6		42.6
615.15	35.1		36.0		41.5
625.15	34.1		34.2		40.5
635.15	32.9		32.2		39.3

Using calculated values of dp/dT and Z according to the procedure described above, we calculated the heats of vaporization of the compounds listed (Figure 1) at the same temperatures as our experimental vapor-pressure data.

In Table IV, the calculated heats of vaporization for even 10 K temperature intervals are reported. The accuracy of heats of vaporization calculated from experimental vapor-pressure data and estimated values of the compressibility factors for saturated vapor and liquid is estimated to be ±1.5 kJ/mol.

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Densities of Molten $K_2S_2O_7$–$KHSO_4$ and $K_2S_2O_7$–$KHSO_4$–V_2O_5

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Densities of the molten salt systems $K_2S_2O_7$–$KHSO_4$ and $K_2S_2O_7$–$KHSO_4$–V_2O_5 were measured by using the automated float method. Ten different compositions of the $K_2S_2O_7$–$KHSO_4$ system were measured. The obtained densities were fitted to equations of the form $\rho = A(X) + B(X)(t - 400)$. $A(X)$ and $B(X)$ were again fitted by polynomials of the mole fraction, X_{KHSO_4}, in each of the composition ranges $0.0000 \le X_{KHSO_4} \le 0.5000$, $0.5000 \le X_{KHSO_4} \le 1.0000$, and $0.0000 \le X_{KHSO_4} \le 1.0000$. Furthermore, all the measured data in each range were fitted to equations of the form $\rho = \sum_0^n A_n X^n + (\sum_0^m B_m X^m)(t - 400)$. It was shown that a linear relationship exists between molar volume at 400 °C and X_{KHSO_4} at all compositions. Two different compositions of the $K_2S_2O_7$–$KHSO_4$–V_2O_5 system were measured. The observed densities were at each composition fitted to a linear equation of the form $\rho = A(X_1,X_2) + B(X_1,X_2)(t - 400)$, where X_1 and X_2 are $X_{V_2O_5}$ and X_{KHSO_4}, respectively. Finally all the measured data for this system were fitted to the equation $\rho = A + BX_2 + CX_2^2 + (D + EX_2 + FX_2^2)X_1(t - 400)$.

The molten $K_2S_2O_7$–$KHSO_4$ system plays a major role as solvent for various vanadium(V) and vanadium(IV) complexes during the catalytic conversion of SO_2 to SO_3 for the manufacture of sulfuric acid. As part of a larger investigation (*1–3*) of the catalytic vanadium oxide-pyrosulfate melts, the present paper supplies density data for the $K_2S_2O_7$–$KHSO_4$ system in the whole composition range $0.0000 \le X_{KHSO_4} \le 1.0000$ and for the $K_2S_2O_7$–$KHSO_4$–V_2O_5 at compositions around $X_{KHSO_4} = 0.6$. The method employed is the previously described "automated float method" for determination of densities of molten salts (*4, 5*). This method is very well suited for the present systems, which at the employed temperatures have high vapor pressures. Especially the pure molten $KHSO_4$ is believed to exert a high vapor pressure at higher temperatures. One of the quartz cuvettes containing 100% $KHSO_4$ broke when the temperature reached 430 °C possibly due to the internal pressure. The high pressure is probably the reason that only measurements of the density of molten $KHSO_4$ at temperatures very close to the melting point have been performed (*6*). The melts containing V_2O_5 are furthermore very dark colored, thus making visual observations of floats impossible.

Experimental Section

The densities were measured by the automated float method (*4, 5*). The method is based on magnetic detection of quartz floats with iron cores, as they pass a differential transformer. The furnace and its regulation have been described in detail previously (*4*). Passage temperatures were detected by platinum resistance thermometers (from Degussa) and by chromel–alumel thermocouples (from Pyrotenax) which were calibrated at the freezing points of pure (99.99%) zinc and lead to within ±0.5 °C.

$K_2S_2O_7$ was made by thermal dissociation of $K_2S_2O_8$ (*7*) (Merck, Pro Analysi) in a stream of pure N_2 in order to avoid contamination by H_2O. The synthesized potassium pyrosulfate was sealed under vacuum into Pyrex ampules and stored in a glovebox. It is important to ensure that the hygroscopic potassium pyrosulfate is kept out of contact with atmospheric air—a commercial analytical-grade $K_2S_2O_7$ (Riedel-de Haën) was shown by Raman spectroscopy to consist of more than 60 mol % $KHSO_4$ (*1*). By weighing it was determined that $K_2S_2O_7$ did not give off any SO_3 at the employed dissociation temperature (290 °C). $KHSO_4$ (Merck, Pro Analysi) was dried at 110 °C in 3 days and stored in a glovebox. V_2O_5 (Merck, Extra Pure) was recrystallized under vacuum in a quartz ampule by quick heating to just above the melting point (658 °C), followed by slow cooling.

All handling of the solid salts was performed in a nitrogen-filled glovebox with a measured water content of ~5 ppm and continuous gas purification by forced recirculation through external molecular sieves.

Results

The experimental densities and temperatures of the $K_2S_2O_7$–$KHSO_4$ system are given in Table I. The densities of the used floats are calculated on the basis of 8–10 determinations at room temperature and corrected for the thermal expansion of quartz at the measured temperature. In Table II the results for the $K_2S_2O_7$–$KHSO_4$–V_2O_5 are given in a similar way. The standard deviations of the measured temperatures are calculated in accordance with the procedure described previously (*4*).

In Table III the measured densities for the $K_2S_2O_7$–$KHSO_4$ system are at each composition expressed by $A(X)$ and $B(X)$, where $\rho = A(X) + B(X)(t - 400)$. ρ is the density in g/cm^3, $A(X)$ is the density at the composition X_{KHSO_4} at 400 °C, $B(X)$ is the density change per degree at the composition X_{KHSO_4}, and t is the temperature in °C. As described previously (*5*) this expression gives a more satisfactory representation of the measured data than the usually employed equation $\rho = A(X) + B(X)t$. In Table IV the results for the $K_2S_2O_7$–$KHSO_4$–V_2O_5 are given analogously by $A(X_1,X_2)$ and $B(X_1,X_2)$ ($X_1 = X_{KHSO_4}$, $X_2 = X_{V_2O_5}$).

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