

## Three benzene derivatives

Major physical and thermodynamic properties are presented for chlorobenzene, aniline and phenol.

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□ Benzene derivatives are of major industrial importance. Chlorobenzene is used in the production of phenol, chloronitrobenzene and DDT. Aniline is an intermediate and solvent; its applications include the manufacture of dyes (more than 160 derive from it), rubber chemicals, pharmaceuticals, and photographic chemicals. Phenol is used in the production of phenolic and epoxy resins, caprolactam, paints, and as a selective solvent for refining lube oils.

### Critical Properties—Table 15—1 (T/15—1)

Results for critical temperature, pressure and volume are available in the literature [3,4,6,413,416,484,546,574] for chlorobenzene, aniline and phenol. The reported values are in substantial agreement; deviations are less than 0.5%.

### Heat of Vaporization—Fig. 15—1 (F/15—1)

The Watson correlation (Eq. 1—1) served to extend data to cover the entire liquid range. Correlation values and experimental data were found to be in close agreement.

### Vapor Pressure—F/15—2

The Cox-Antoine method (Eq. 1—2) was used to extend data for chlorobenzene and aniline at low tem-

peratures to the melting point. Reported results for phenol span the complete, saturated liquid phase. Data from the various sources are basically in agreement.

### Heat Capacity—F/15—3, F/15—4

Various data-sources agree in their results for heat capacity of the ideal gas at atmospheric pressure. Deviations are less than 1% for chlorobenzene, aniline and phenol.

The density/heat capacity relation (Eq. 1—3,  $n = 1$ ) has been adopted for correlation and extrapolation of liquid heat-capacity data at constant pressure. Experimental data correspond closely with correlation values. Average deviations of 1.8%, 2.4% and 1.3% were encountered for chlorobenzene, aniline and phenol.

### Density—F/15—5

Liquid-density data for each derivative were correlated and extended by a modified form of the Rackett equation [489]:

$$\rho = \rho_c Z^{-(1-T_r)^{2/7}} \quad (15-1)$$

In Eq. 15—1,  $\rho_c$  = critical density, g/cm<sup>3</sup>;  $T_r$  = reduced temperature,  $T/T_c$ ; and  $Z$  = correlation parameter.

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### How To Use the Graphs

Each graph is outfitted with a key that lists references and explains just what part of the curve is determined experimentally, and what part is estimated from theoretical correlations.

The shaded squares denote the following:

- Data in this region are experimentally known.
- Experimental and correlated data used.
- All data in this region are correlated.

The "regions" referred to are the temperature ranges between the melting, boiling and critical points (m.p., b.p. and c.p., respectively), or in some cases, the specific temperatures noted in the key.

### Physical properties of the derivatives of benzene

Identification	Chlorobenzene	Aniline	Phenol
	C <sub>6</sub> H <sub>5</sub> Cl	C <sub>6</sub> H <sub>5</sub> NH <sub>2</sub>	C <sub>6</sub> H <sub>5</sub> OH
State (std. conditions)	Liquid	Liquid	Solid
Molecular weight, <i>M</i>	112.56	93.12	94.11
Boiling point, <i>T<sub>b</sub></i> , °C	131.7	184.4	181.8
Melting point, <i>T<sub>m</sub></i> , °C	-45.2	-6.15	40.75
Critical temp., <i>T<sub>c</sub></i> , °C	359.2	426.0	420.0
Critical pressure, <i>P<sub>c</sub></i> , atm	44.6	52.4	60.5
Critical volume, <i>V<sub>c</sub></i> , cm <sup>3</sup> /g-mol	308.4	273.9	229.5
Critical compressibility factor, <i>Z<sub>c</sub></i>	0.265	0.250	0.244

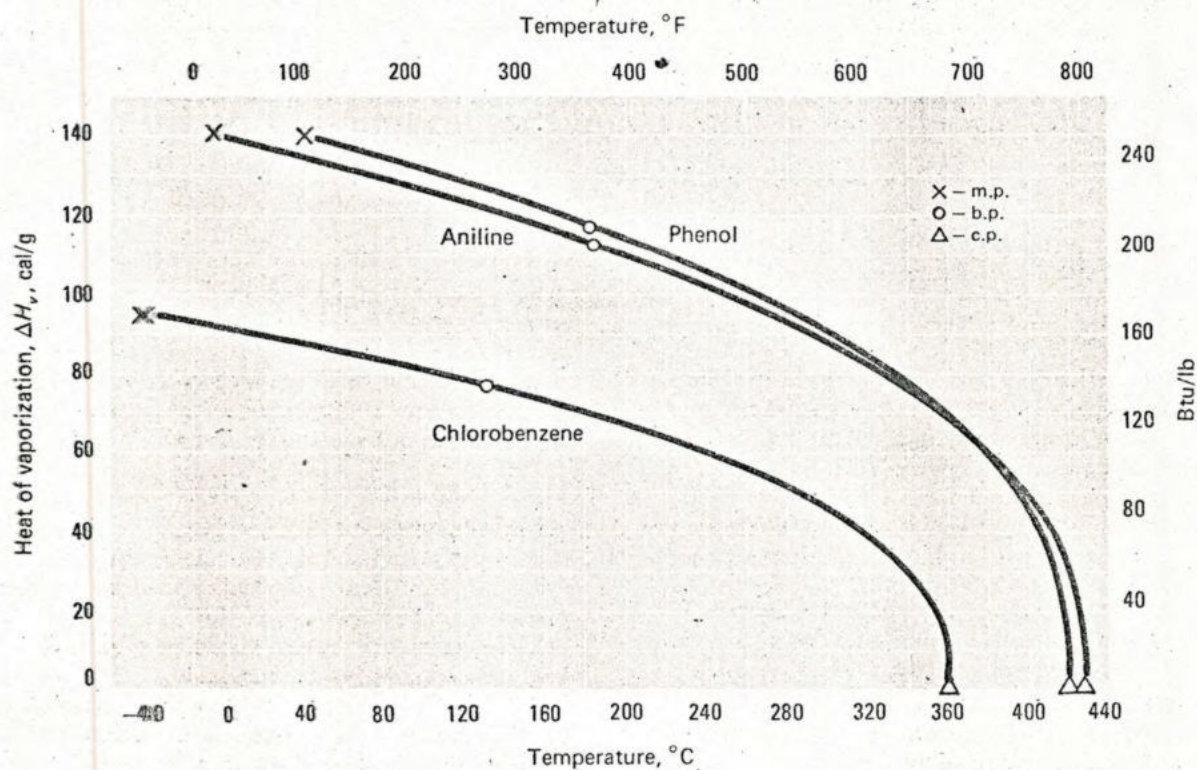
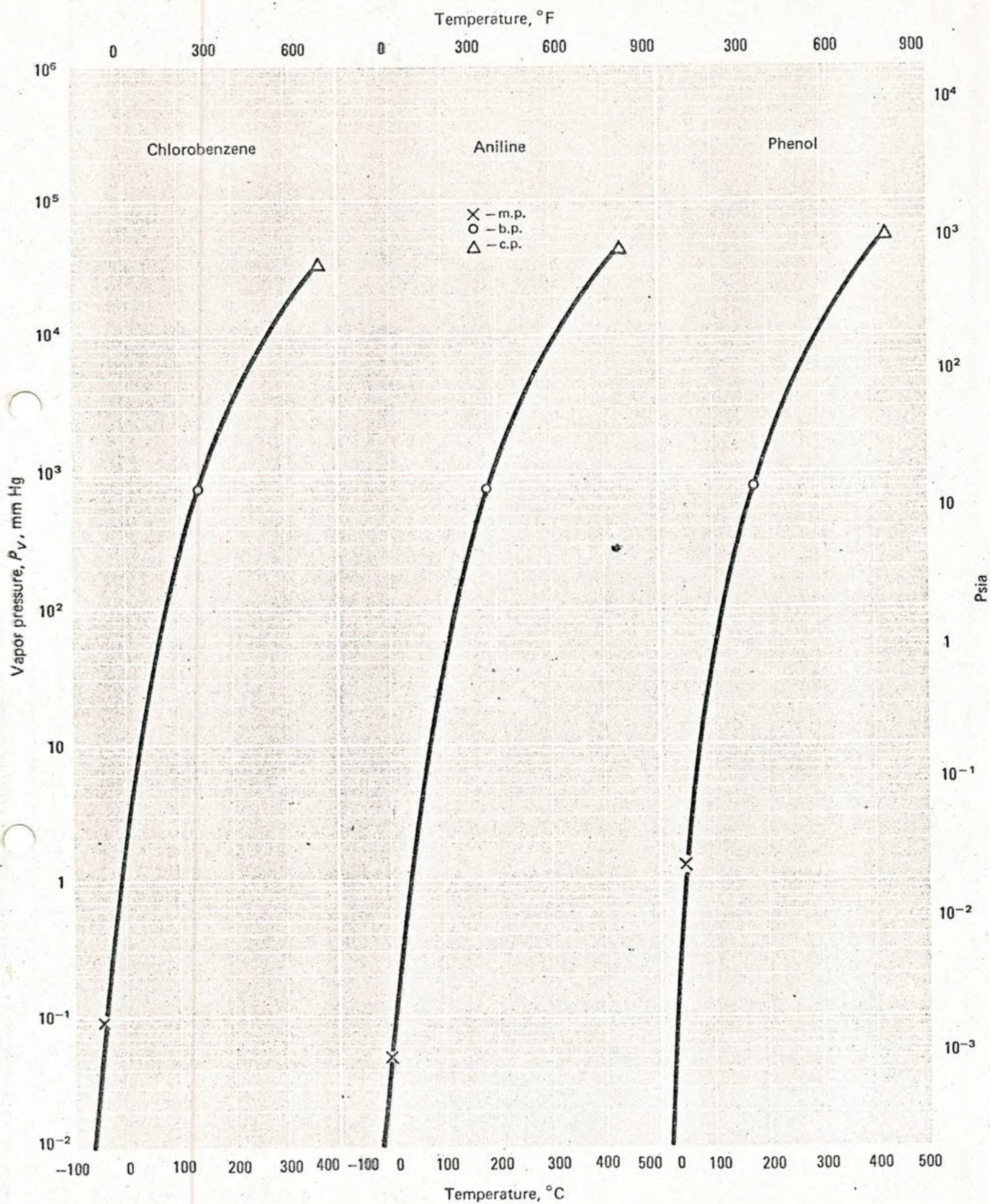
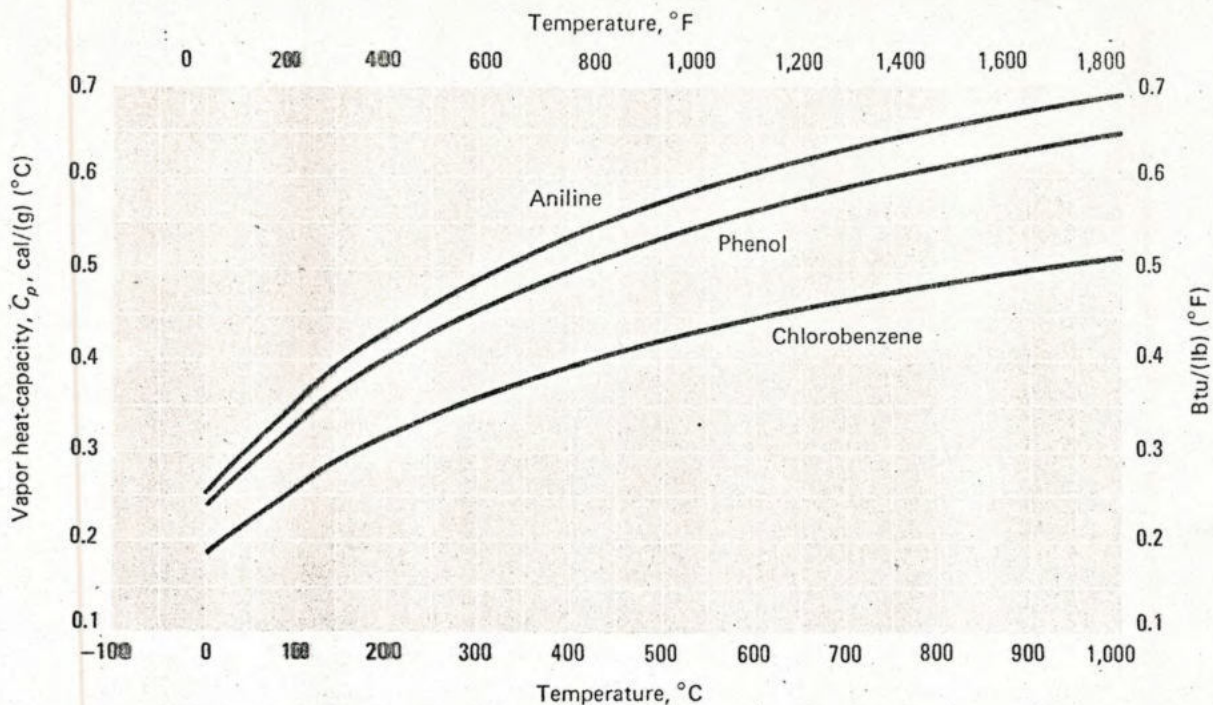


Fig. 15-1	Temperature range, °C		References
	m.p. - b.p.	b.p. - c.p.	
	Chlorobenzene	<span style="display: inline-block; width: 10px; height: 10px; background-color: #cccccc; border: 1px solid black;"></span>	
Aniline	<span style="display: inline-block; width: 10px; height: 10px; background-color: #cccccc; border: 1px solid black;"></span>	<span style="display: inline-block; width: 10px; height: 10px; border: 1px solid black;"></span>	3, 4, 413, 574
Phenol	<span style="display: inline-block; width: 10px; height: 10px; background-color: #cccccc; border: 1px solid black;"></span>	<span style="display: inline-block; width: 10px; height: 10px; border: 1px solid black;"></span>	3, 547, 563

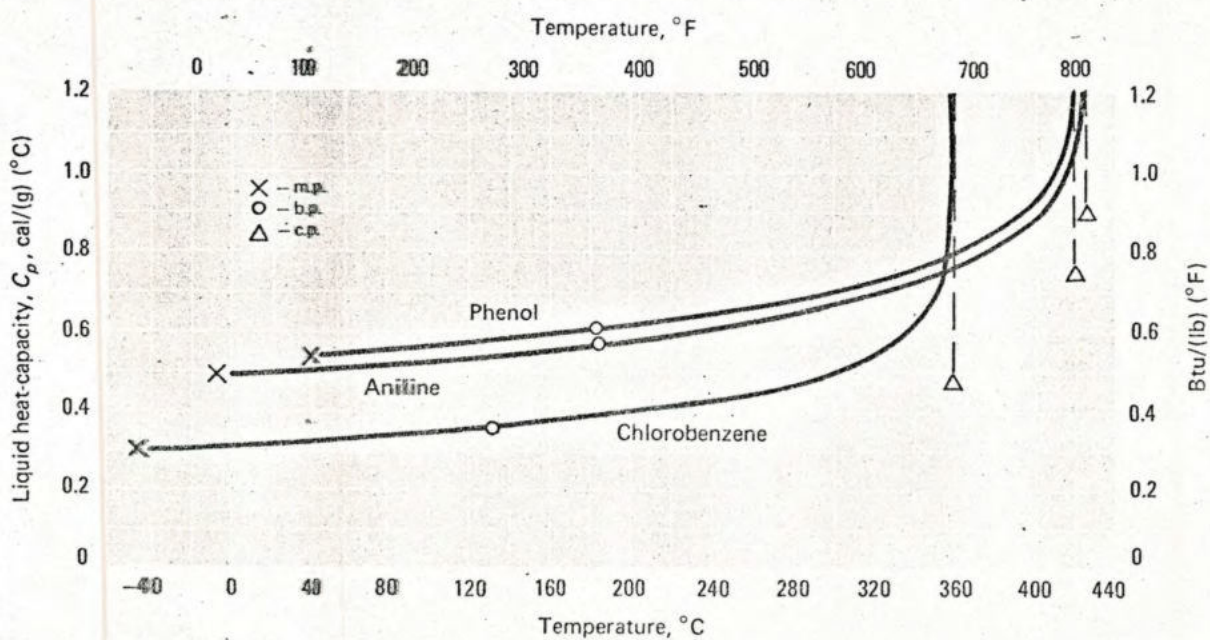
Fig. 15-2	Temperature range, °C		References
	m.p. - b.p.	b.p. - c.p.	
	Chlorobenzene	<span style="display: inline-block; width: 10px; height: 10px; background-color: #cccccc; border: 1px solid black;"></span>	
Aniline	<span style="display: inline-block; width: 10px; height: 10px; background-color: #cccccc; border: 1px solid black;"></span>	<span style="display: inline-block; width: 10px; height: 10px; background-color: #cccccc; border: 1px solid black;"></span>	3, 4, 6, 413, 415, 529, 546, 548
Phenol	<span style="display: inline-block; width: 10px; height: 10px; background-color: #cccccc; border: 1px solid black;"></span>	<span style="display: inline-block; width: 10px; height: 10px; background-color: #cccccc; border: 1px solid black;"></span>	3, 413, 415, 418, 529, 546, 563, 570

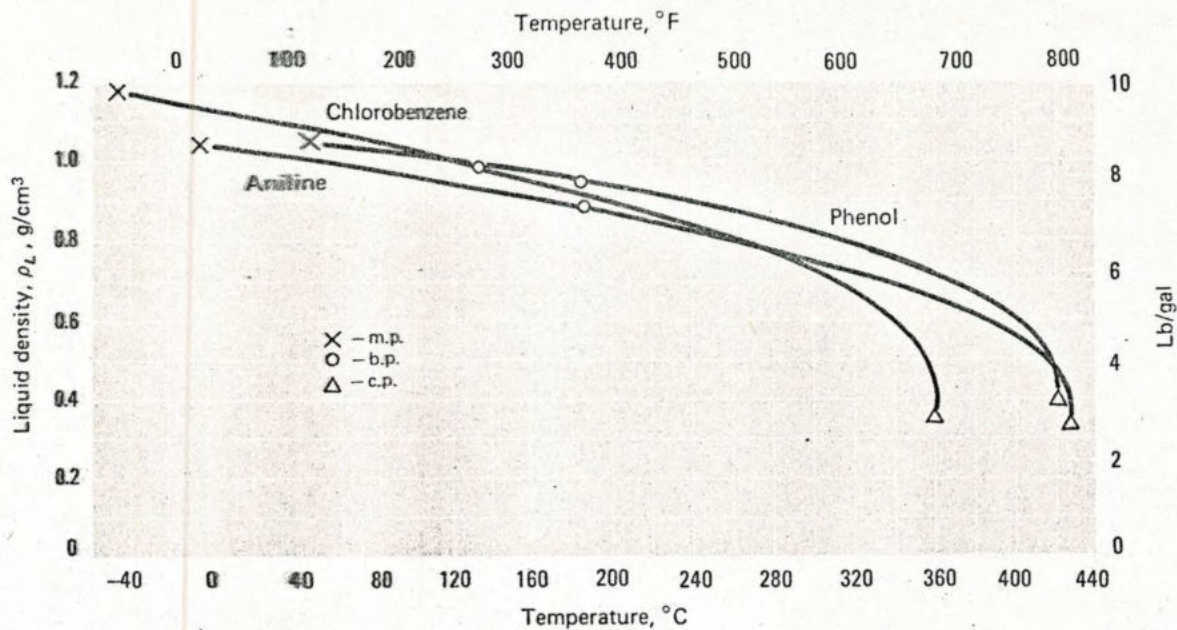




Vapor heat capacity			References
Fig. 15-3	Temperature range, °C		
	0-500	500-1,000	
Chlorobenzene	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	15,418
Aniline	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	15,418
Phenol	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	15,418

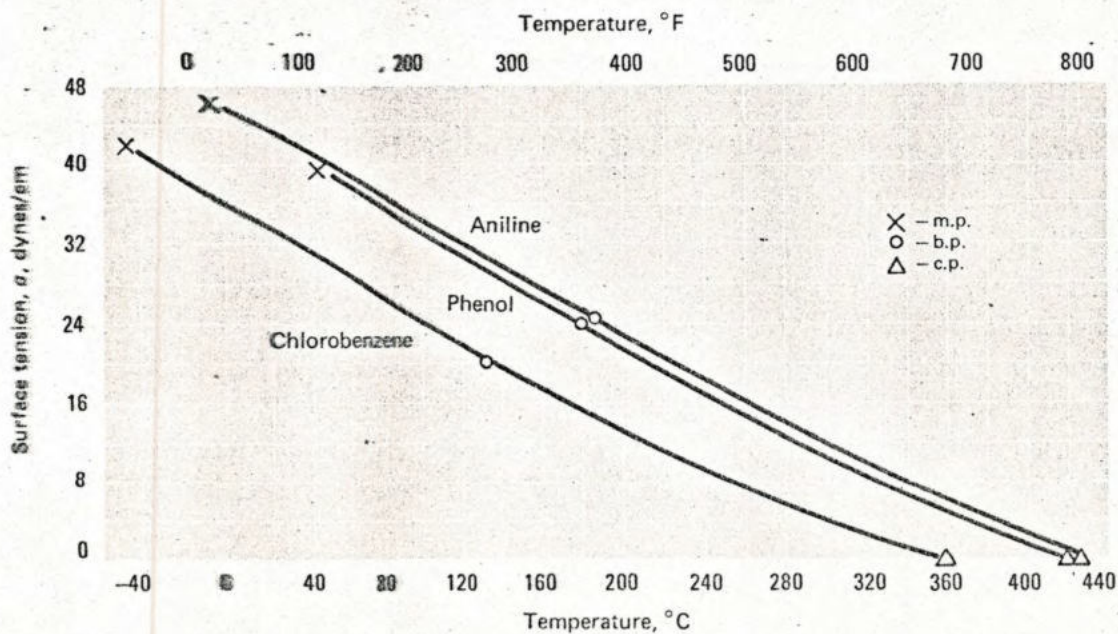
Liquid heat capacity			References
Fig. 15-4	Temperature range, °C		
	m.p.-b.p.	b.p.-c.p.	
Chlorobenzene	<input checked="" type="checkbox"/>	<input type="checkbox"/>	3,4,6,415,416,571,574
Aniline	<input checked="" type="checkbox"/>	<input type="checkbox"/>	4,415,416,556,574
Phenol	<input checked="" type="checkbox"/>	<input type="checkbox"/>	415,558,563,570,574

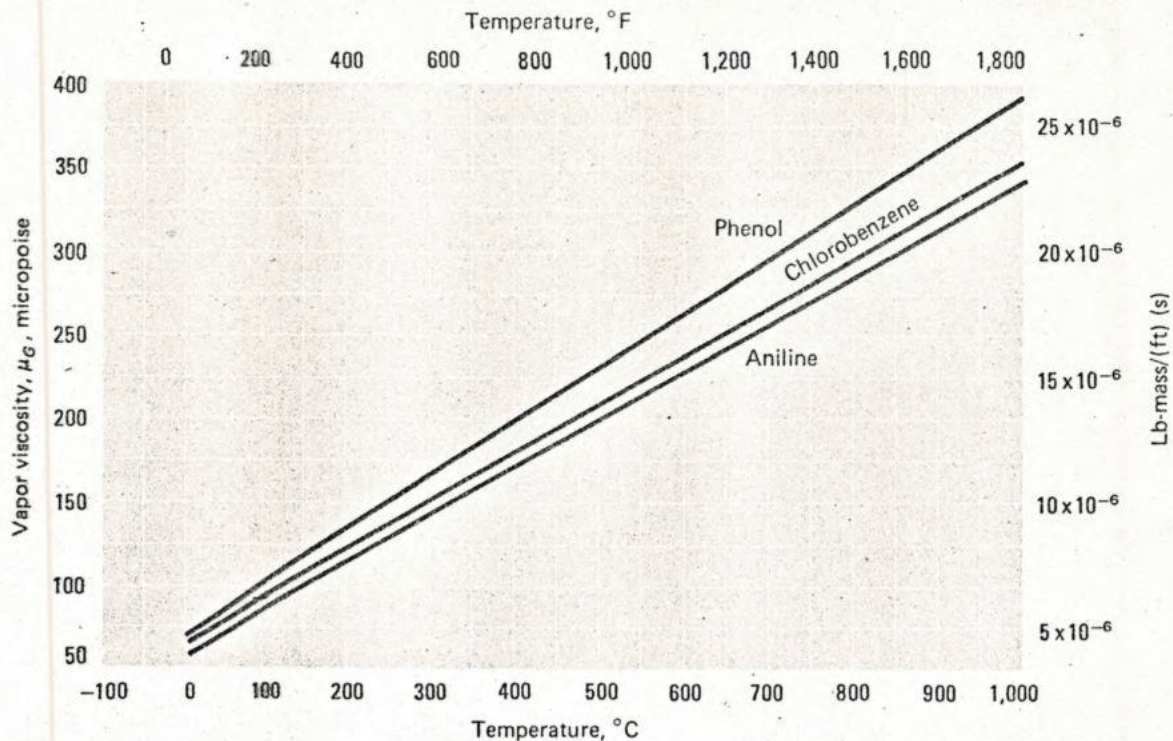




Liquid density			References
Fig. 15-5	Temperature range, °C		
	m.p. - b.p.	b.p. - c.p.	
Chlorobenzene	☑	☑	4, 6, 415, 484, 546, 558, 560, 563, 574
Aniline	☑	☑	4, 6, 415, 484, 546, 558, 561
Phenol	☑	☑	4, 6, 415, 418, 484, 574

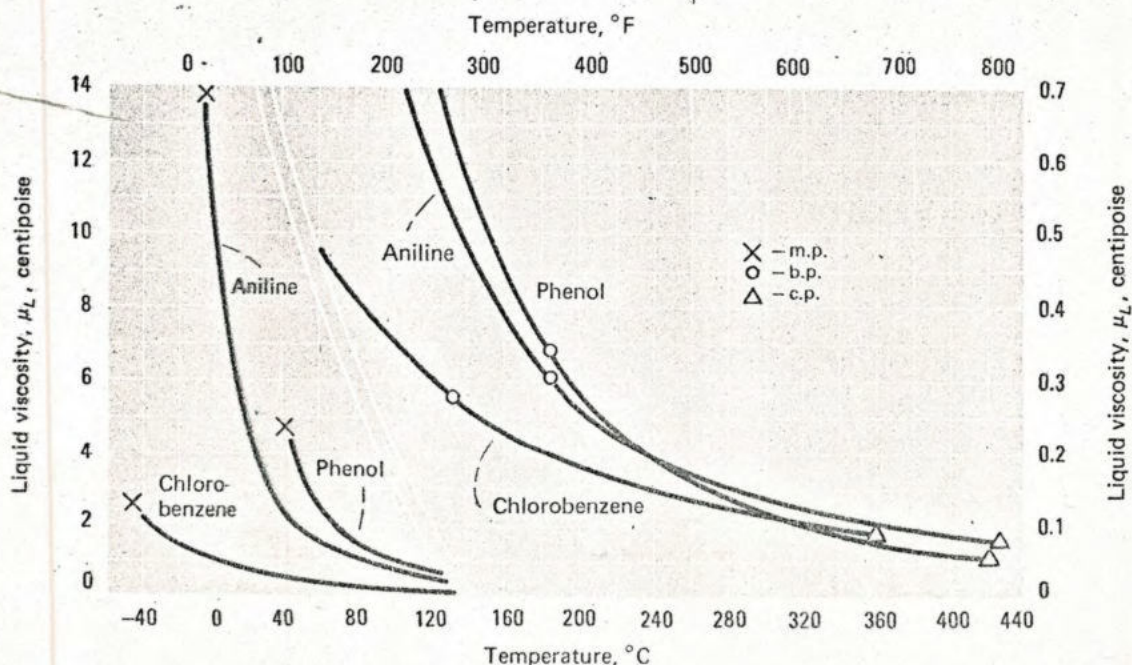
Surface tension			References
Fig. 15-6	Temperature range, °C		
	m.p. - b.p.	b.p. - c.p.	
Chlorobenzene	☑	☑	3, 4, 6, 79, 415, 546, 569
Aniline	☑	☐	3, 6, 415, 546, 569
Phenol	☑	☐	3, 6, 79, 415, 569, 570

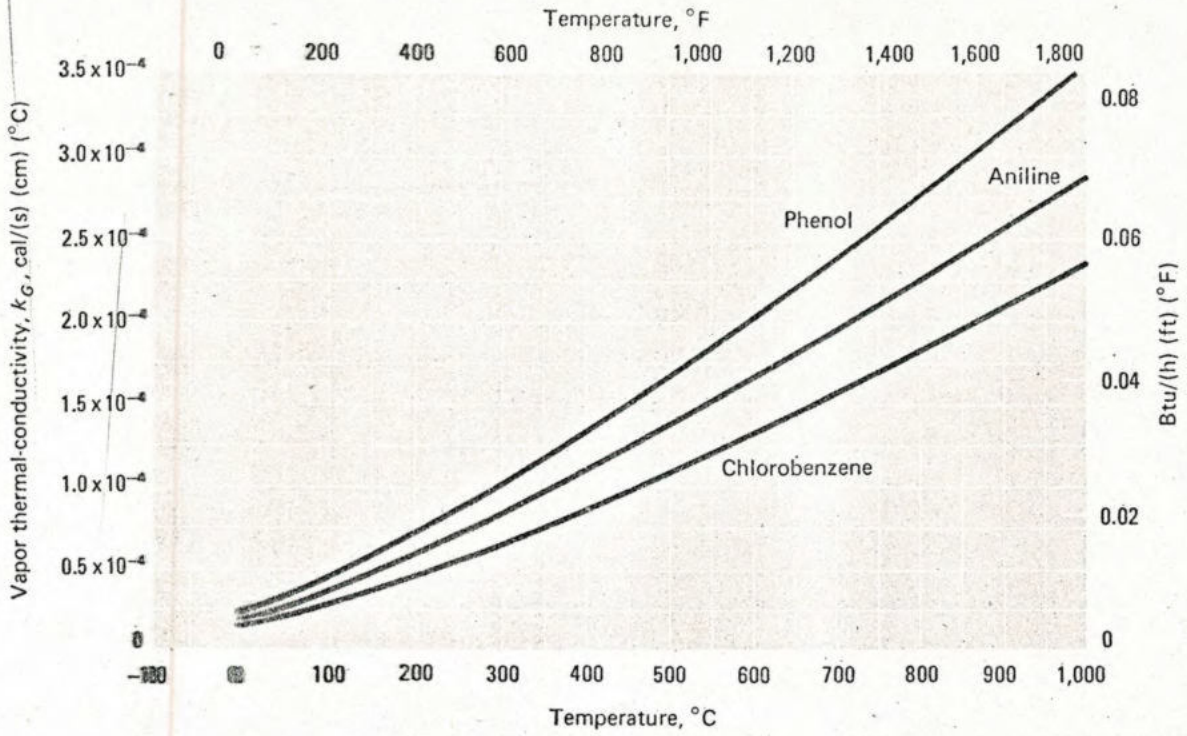




Vapor viscosity				References
Fig. 15-7	Temperature range, °C			
	0-500	500-1,000		
Chlorobenzene	<input type="checkbox"/>	<input type="checkbox"/>	14,545	
Aniline	<input type="checkbox"/>	<input type="checkbox"/>	14,545	
Phenol	<input type="checkbox"/>	<input type="checkbox"/>	14,545	

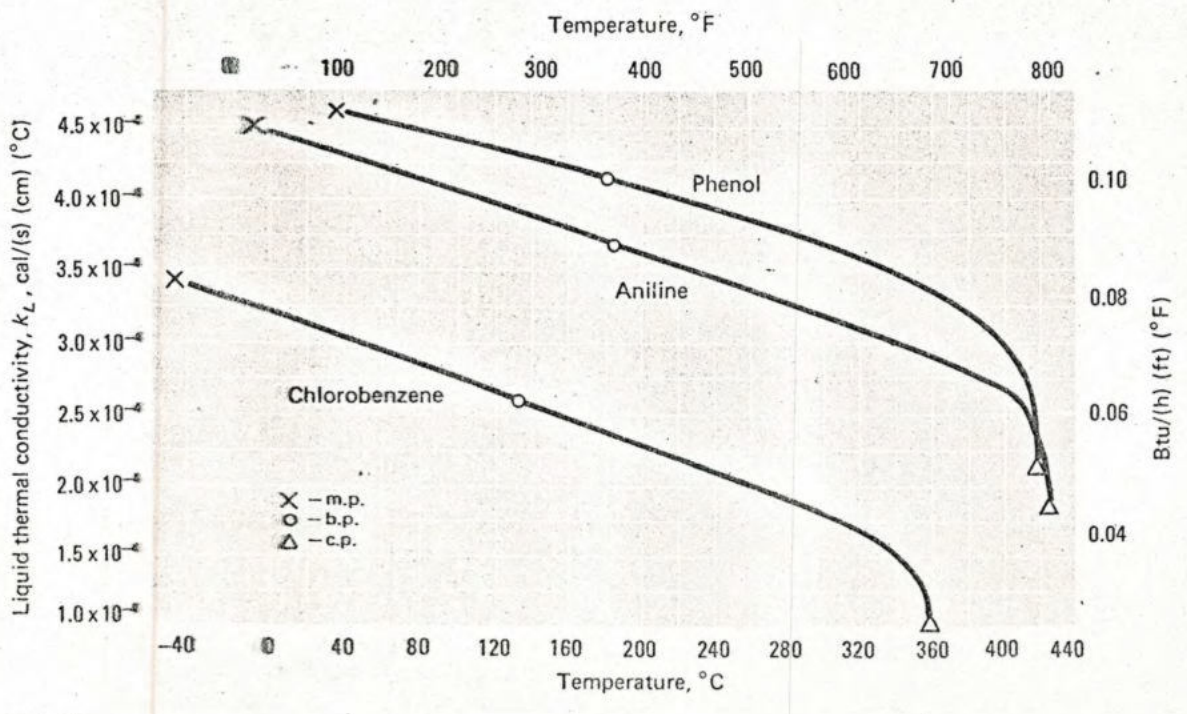
Liquid viscosity				References
Fig. 15-8	Temperature range, °C			
	m.p.-b.p.	b.p.-c.p.		
Chlorobenzene	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	3,4,6,14,415,416,467,484,546,554,555,564	
Aniline	<input checked="" type="checkbox"/>	<input type="checkbox"/>	4,6,14,409,415,416,467,484,546,557,561	
Phenol	<input checked="" type="checkbox"/>	<input type="checkbox"/>	3,6,14,415,416,467,484,564,570	

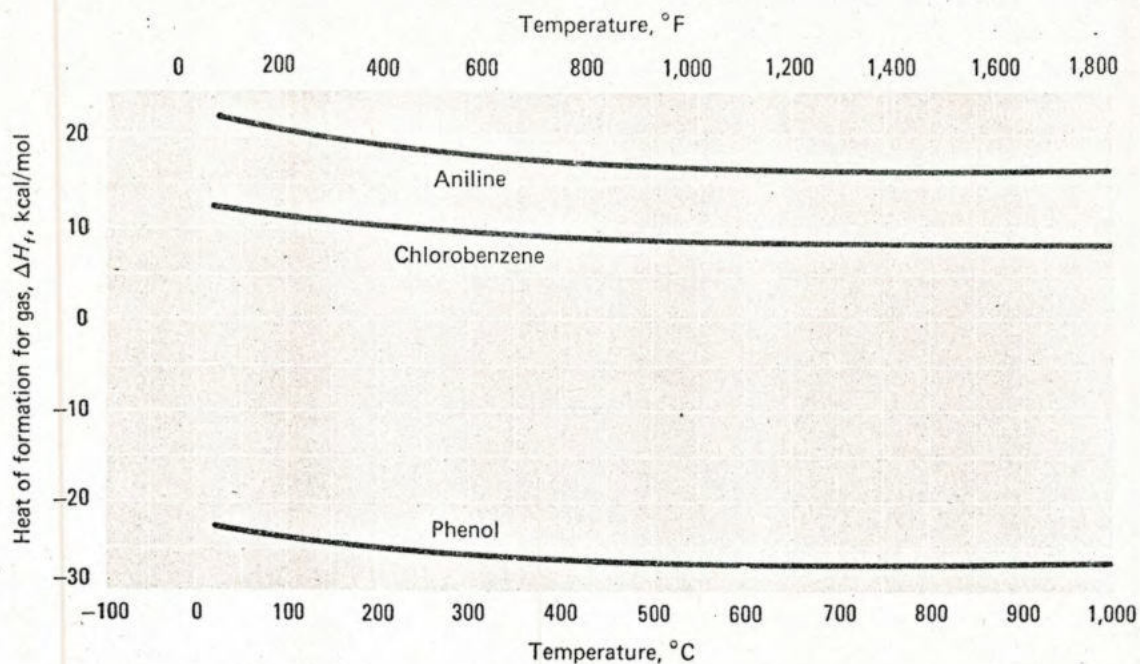




Vapor thermal conductivity			F 9
Fig. 15-9	Temperature range, °C		References
	0-500	500-1,000	
Chlorobenzene	<input type="checkbox"/>	<input type="checkbox"/>	13, 14
Aniline	<input type="checkbox"/>	<input type="checkbox"/>	13, 14
Phenol	<input type="checkbox"/>	<input type="checkbox"/>	13, 14

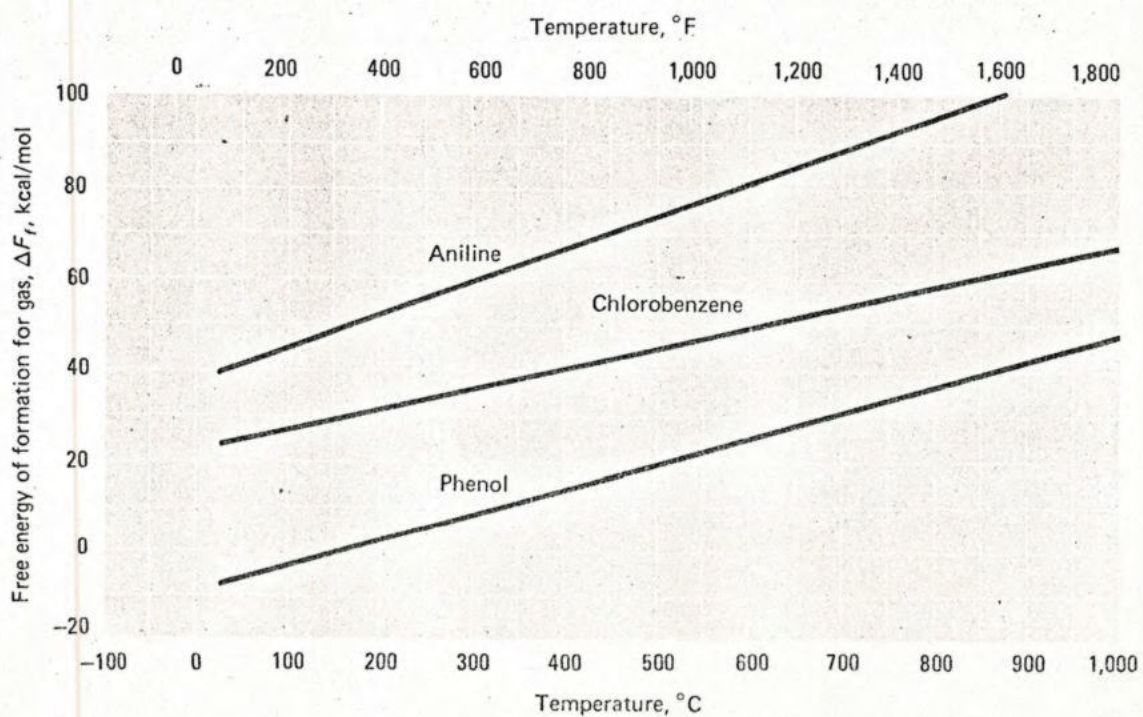
Liquid thermal conductivity			F 10
Fig. 15-10	Temperature range, °C		References
	m.p.-b.p.	b.p.-c.p.	
Chlorobenzene	<input checked="" type="checkbox"/>	<input type="checkbox"/>	14, 409, 413, 416, 481, 484, 486, 535, 539, 546, 552, 553, 559, 562, 565, 566, 567, 568, 572
Aniline	<input checked="" type="checkbox"/>	<input type="checkbox"/>	4, 14, 409, 413, 416, 481, 484, 486, 535, 539, 546, 551, 552, 559, 562, 565, 566, 568, 572
Phenol	<input type="checkbox"/>	<input type="checkbox"/>	14





Heat of formation for gas			
Fig. 15-11	Temperature range, °C		References
	0-500	500-1,000	
Chlorobenzene	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	15
Aniline	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	15
Phenol	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	15, 413, 418, 574

Free energy of formation for gas			
Fig. 15-12	Temperature range, °C		References
	0-500	500-1,000	
Chlorobenzene	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	15
Aniline	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	15
Phenol	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	15, 413, 418, 574





The parameter  $Z$  is determined from density data as suggested by Spencer and Danner [485]:

$$Z = \left( \frac{\rho_c}{\rho_1} \right)^{1/(1-T_r)^{2/7}}$$

The  $Z$  values obtained were 0.266 for chlorobenzene, 0.2765 for aniline and 0.325 for phenol.

Correlated and experimental values are in very close agreement. Average deviations are only 0.31%, 0.20% and 0.13% for chlorobenzene, aniline and phenol.

### Surface Tension—F/15—6

Experimental data were selected primarily from the recent tabulations of Jasper [79], Timmermans [415] and International Critical Tables [6]. The data were correlated and extended for full liquid-phase coverage by the Othmer relation [53]:

$$\sigma = \sigma_1 \left[ \frac{T_c - T}{T_c - T_1} \right]^n \quad (15-2)$$

Eq. 15—2,  $\sigma_1$  = surface tension at  $T_1$ , dynes/cm;  $T_c$  = critical temperature, °K;  $T$  = temperature, °K; and  $n$  = correlation parameter.

Values for  $n$  were 1.225, 1.105 and 1.075 for chlorobenzene, aniline and phenol. Correlated and data values were in close agreement; deviations were only 0.5%, 0.2% and 0.4%, respectively.

### Viscosity—F/15—7, F/15—8

In the absence of experimental data, the Stiel and Thodos correlation [14,545] was selected for estimating gas viscosity at atmospheric pressure:

$$\mu_G = \frac{Z_c^{-5/4}}{\xi} [0.755 T_r - 0.055] \quad (15-3)$$

In Eq. 15—3,  $\mu_G$  = gas viscosity at low pressure (1 atm), micropoise;  $\xi$  = correlation parameter,  $T_c^{1/6}/M^{1/2}P_c^{2/3}$ ;  $Z_c$  = critical compressibility factor; and  $T_r$  = reduced temperature,  $T/T_c$ .

Evaluation by Reid and Sherwood [14] of the correlation for a number of polar gases (including those with —Cl, —NH<sub>2</sub> and —OH groups) yielded an average error of 3.2%. The error for chlorobenzene, aniline and phenol is probably 10% or less.

The Guzman-Andrade relation (Eq. 1—6) was used to correlate and extend the liquid viscosity data. Two straight lines for each benzene derivative sufficed to correlate the data adequately. Experimental and correlated values were in close agreement; average deviations were 2% or less for chlorobenzene, aniline and phenol.

### Thermal Conductivity—F/15—9, F/15—10

Thermal conductivity of the gas phase at atmospheric pressure was estimated by Bromley's correlation (Eq. 6—3). When the correlation was tested with similar polar and slightly polar compounds (including both organics and inorganics with —Cl, —NH<sub>2</sub> and —OH groups) favorable results were obtained [14]; average errors were 7.5% or less. Errors for chlorobenzene, aniline and phenol are probably within this general range.

Liquid thermal-conductivity data for chlorobenzene and aniline were correlated and extended with the

modified Stiel and Thodos relation (Eq. 10—3) to cover the full liquid range. Average deviations were 1.1% and 4.4%, respectively.

Liquid thermal-conductivity for phenol was estimated by the Robins and Kingrea method [14,539] at low temperatures. This value was then extended to higher temperatures with the modified Stiel and Thodos relation—as used for chlorobenzene and aniline—to attain complete liquid-range coverage. Comparison of the technique with experimental data yielded maximum deviations of 5% and 4% for chlorobenzene and aniline. The results for phenol are intended to represent correct order-of-magnitude values.

### Heat and Free Energy of Formation—F/15—11, F/15—12

Ideal-gas data for chlorobenzene, aniline and phenol were selected from Stull, Westrum and Sinke [15] and the latest editions of chemistry handbooks [413,574].

### References

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Carl I. Yaws—For biography, see *Chem. Eng.*, May 12, 1975, p. 97.