Xylenes: Ortho, Meta, Para

Major physical, transport and thermodynamic properties—based on experimental data and correlations—are presented for ortho-, meta-, and paraxylene.

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Xylenes are major feedstocks in the chemical process industries: *o-xylene* for phthalic anhydride; *m-xylene* for isophthalic acid; and *p-xylene* for terephthalic acid and dimethyl terephthalate. These derivatives are used in various synthetic resins, fibers and films. Other intermediates find application in perfumes, pharmaceuticals, inks, adhesives and dyes. Other than as raw materials, xylenes are used as high-quality octane blending components in motor fuels, and as a solvent.

Critical Properties—Table 12—1

Experimental data provide values for the critical constants [*246,415,417,474,447,484*]. Recent results of API-44 and Russian investigators [*417,479*] were selected. Deviations for critical temperature, pressure and volume are less than 0.4%, 2.5% and 3.2%, respectively.

Vapor Pressure—Fig. 12—1

Comprehensive vapor pressure data have been extended to cover the complete liquid state with the Cox-Antoine relation (Eq. 1—2). The values from various investigators are in close agreement. Observed deviations are 3% or less.

Heat of Vaporization—Fig. 12—2

Experimental data in the boiling point region for each xylene, plus Watson's correlation (Eq. 1—1) have been used to cover the full liquid phase.

* To meet the author, see *Chem. Eng.*, May 12, 1975, p. 97.

Heat Capacity—Fig. 12—3, 12—4

Results from various literature sources agree for heat capacity at constant pressure (1 atm) of the ideal gas state. Maximum deviations are less than 1% for *o-* and *m*-xylene, and 2% for *p*-xylene.

The saturated liquid density extrapolation relationship (Eq. 1—3, $n = 5/4$) was used to extend the liquid heat capacity data for each xylene. Predicted values compared very favorably with experimental data. Average deviations were 2.75%, 2.6% and 3.3% for *o-*, *m-* and *p*-xylene.

Density—Fig. 12—5

Density data for the saturated liquid phase cover a wide temperature range for each xylene. The Rackett relation [*489*] for saturated liquid density was used to correlate the data.

$$\rho = \rho_c Z_c^{-a} \qquad (12—1)$$

In Eq. (12—1), ρ_c = critical density, g/ml; Z_c = critical compressibility factor; and $a = (1 - T_r)^{2/7}$. T_r = reduced temperature, T/T_c.

Correlation values were extremely close to experimental results. Average deviations were only 0.9%, 0.3% and 1.2% for *o-*, *m-* and *p*-xylene, respectively.

Surface Tension—Fig. 12—6

Surface tension coverage over the full liquid phase was achieved by use of the Othmer relationship (Eq. 1—4)

(*text continues on p. 122*)

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.

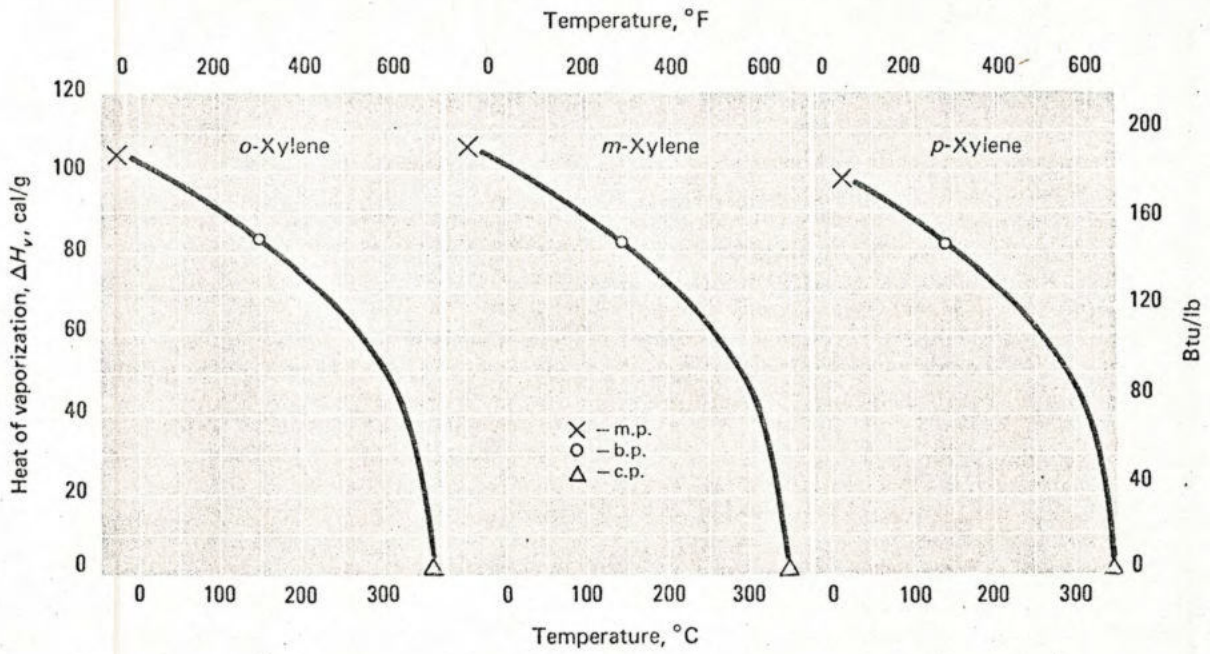
The shaded squares denote the following:

- ■ 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 Xylenes
Table 12–1

Identification	*o*-Xylene	*m*-Xylene	*p*-Xylene
State (std. conditions)	Liquid	Liquid	Liquid
Molecular weight, M	106.16	106.16	106.16
Boiling point, T_b, °C	144.4	139.1	138.4
Melting point, T_m, °C	−25.2	−47.9	13.3
Critical temp., T_c, °C	357.8	343.8	344.0
Critical pressure, P_c, atm	37.22	34.95	35.18
Critical volume, V_c, cm³/g-mol	369.0	376.0	379.0
Critical compressibility factor, Z_c	0.265	0.260	0.263



Heat of Vaporization – Fig. 12–1

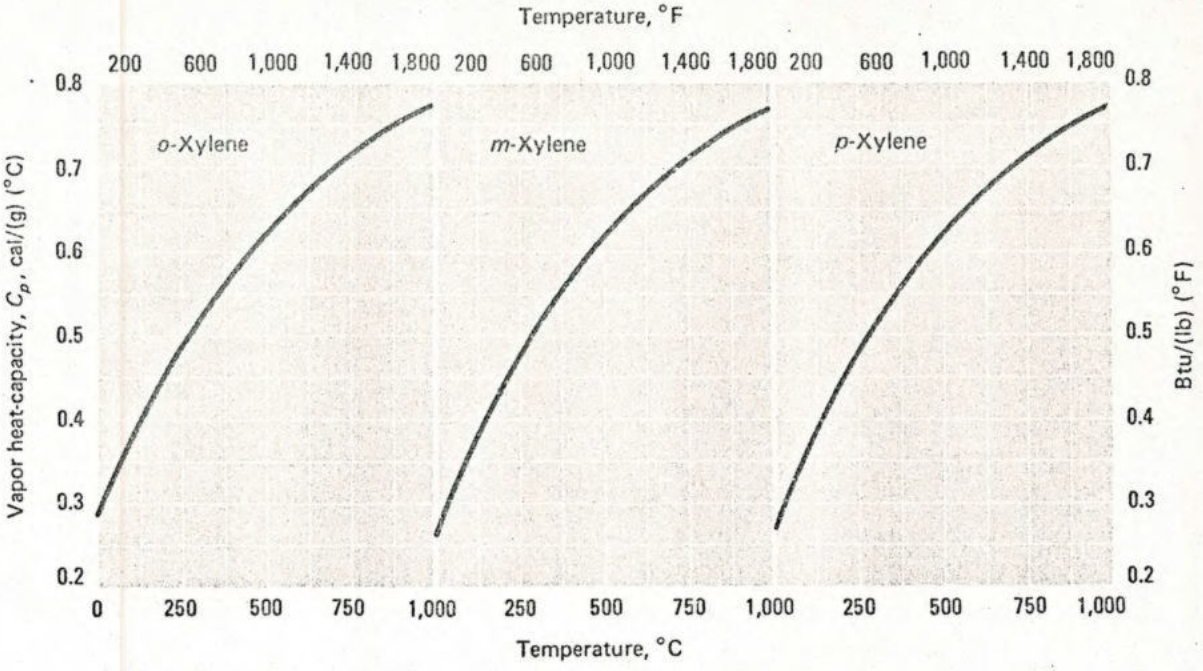
Fig. 12–1	Temperature Range, C		References
	m.p.–b.p.	b.p.–c.p.	
o-Xylene	▨	▨	2,4,9,417,419,484
m-Xylene	▨	▨	2,4,9,417,419,484
p-Xylene	▨	▨	2,4,9,417,419,472,484

■ Laboratory data ▨ Laboratory plus correlations □ All correlated data

Fig. 12–2	Temperature Range, C		References
	m.p.–b.p.	b.p.–c.p.	
o-Xylene	▨	■	4,6,13,246,415,417,419, 473,479
m-Xylene	▨	■	4,6,13,246,415,417,419, 473,478
p-Xylene	■	■	4,6,13,246,415,417,419, 473,479

■ Laboratory data ▨ Laboratory plus correlations □ All correlated data

Vapor Pressure – Fig. 12–2 ⟶



Vapor Heat Capacity — Fig. 12–3

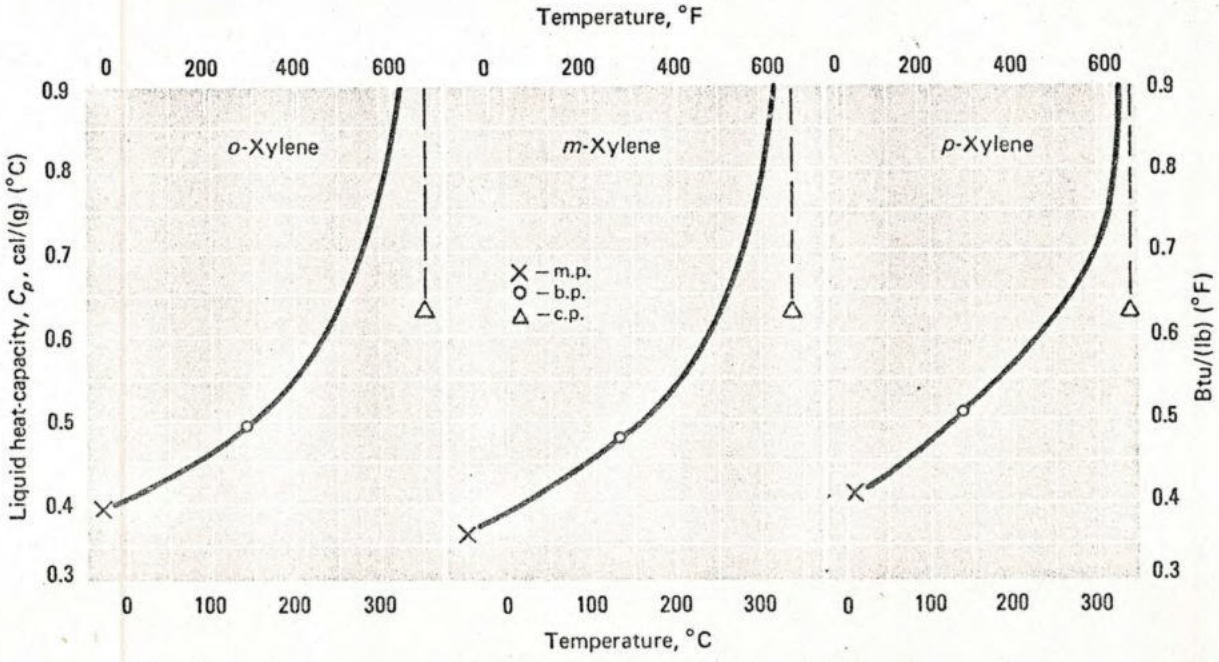
Fig. 12–3	Temperature Range, °C		References
	0–500	500–1,000	
o-Xylene	◪	◪	15,416,417
m-Xylene	◪	◪	15,416,417
p-Xylene	◪	◪	15,416, 417,472

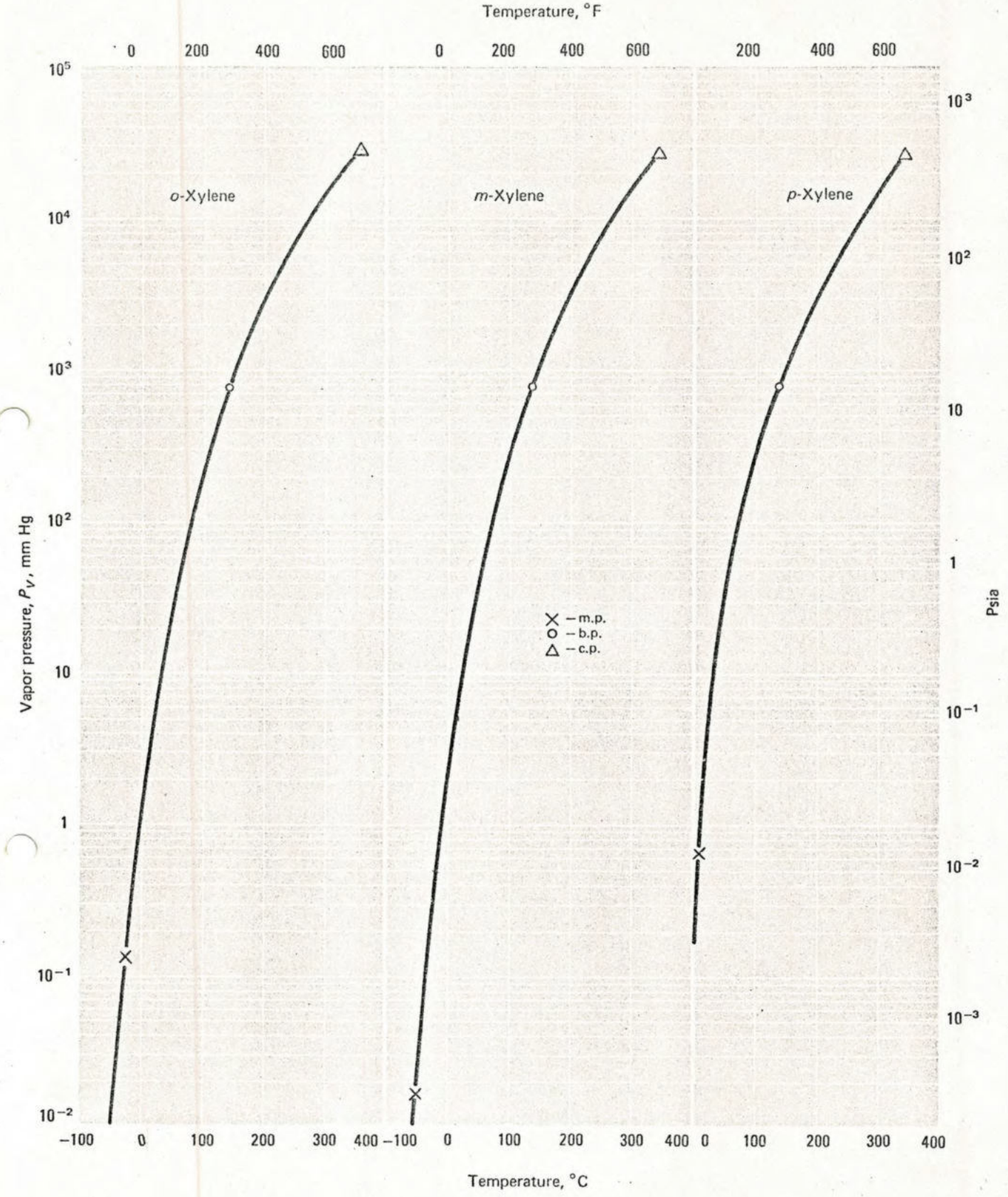
■ Laboratory data ◪ Laboratory plus correlations □ All correlated data

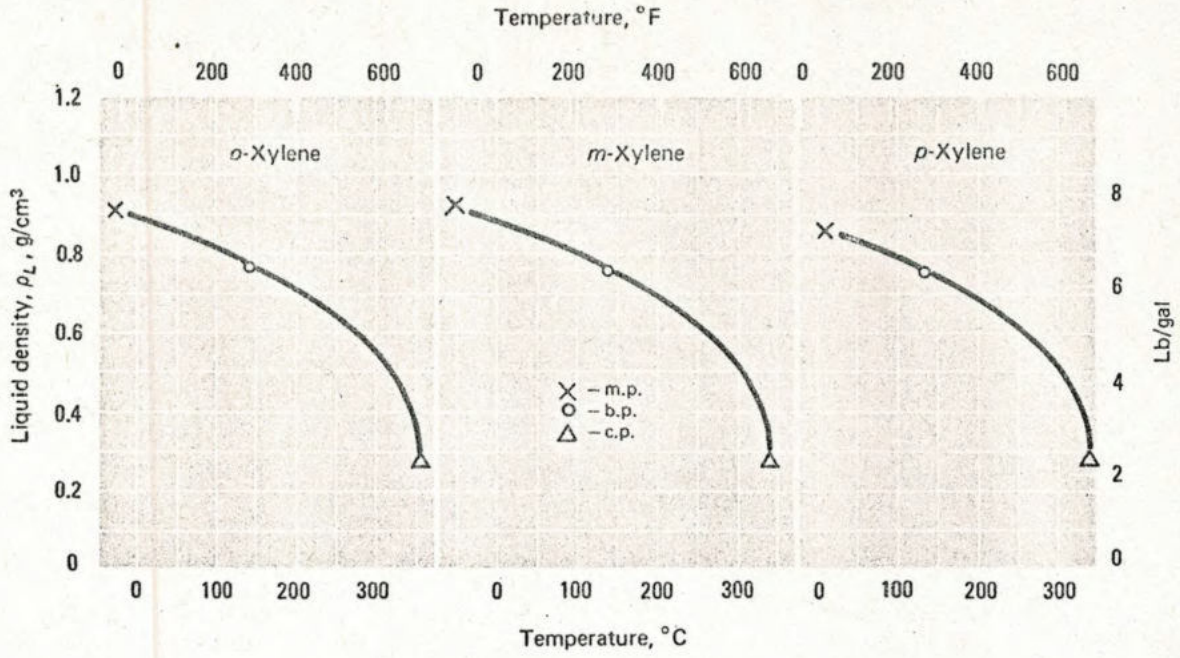
Fig. 12–4	Temperature Range, °C		References
	m.p.–b.p.	b.p.–c.p.	
o-Xylene	◪	□	9,413,488
m-Xylene	◪	□	9,413,488
p-Xylene	■	◪	9,413,415,416,487,488

■ Laboratory data ◪ Laboratory plus correlations □ All correlated data

Liquid Heat Capacity — Fig. 12–4




Temperature, °F
0
200
400
600
o-Xylene
m-Xylene
p-Xylene
× – m.p.
○ – b.p.
△ – c.p.
Vapor pressure, P_V, mm Hg
10^5
10^4
10^3
10^2
10
1
10^{-1}
10^{-2}
10^3
10^2
10
1
10^{-1}
10^{-2}
10^{-3}
Psia
–100
0
100
200
300
400
Temperature, °C



Liquid Density – Fig. 12–5

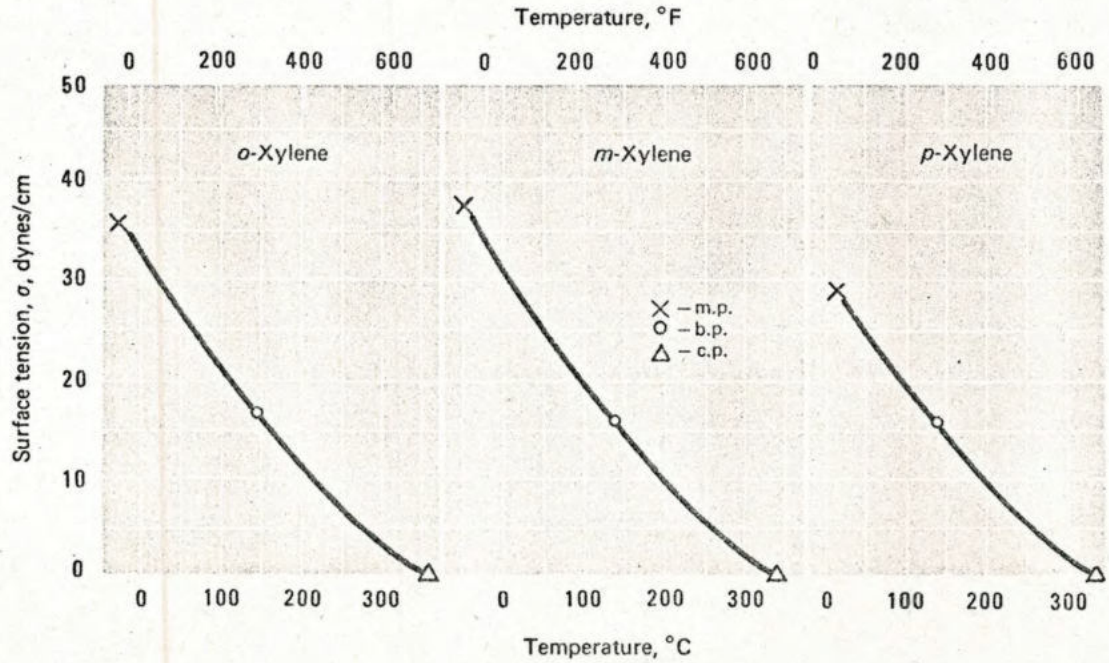
Fig. 12–5	Temperature Range, °C		References
	m.p.–b.p.	b.p.–c.p.	
o-Xylene	■	■	415,417,473,474,484,485,489
m-Xylene	■	■	415,417,473,474,477 478,484,485,489
p-Xylene	■	■	415,417,473,474,484,485,489

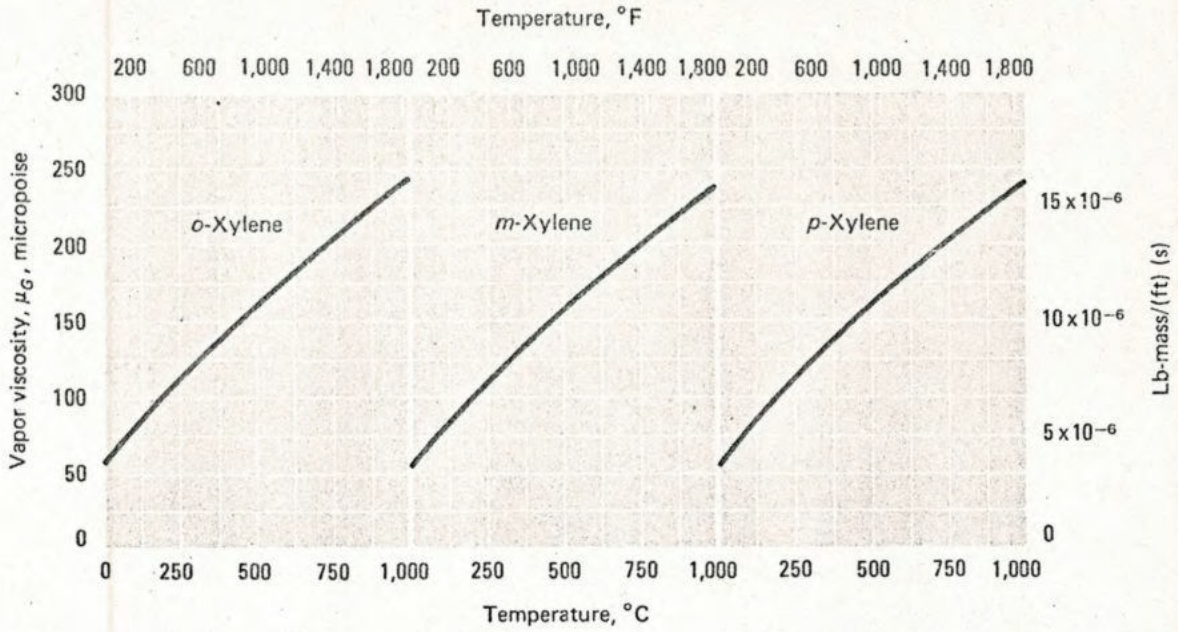
■ Laboratory data ◪ Laboratory plus correlations □ All correlated data

Fig. 12–6	Temperature Range, °C		References
	m.p.–b.p.	b.p.–c.p.	
o-Xylene	◪	□	3,6,79,415,416,417
m-Xylene	◪	□	3,6,9,79,415,416,417
p-Xylene	◪	□	3,6,9,79,415,416,417

■ Laboratory data ◪ Laboratory plus correlations □ All correlated data

Surface Tension – Fig. 12–6





Vapor Viscosity – Fig. 12–7

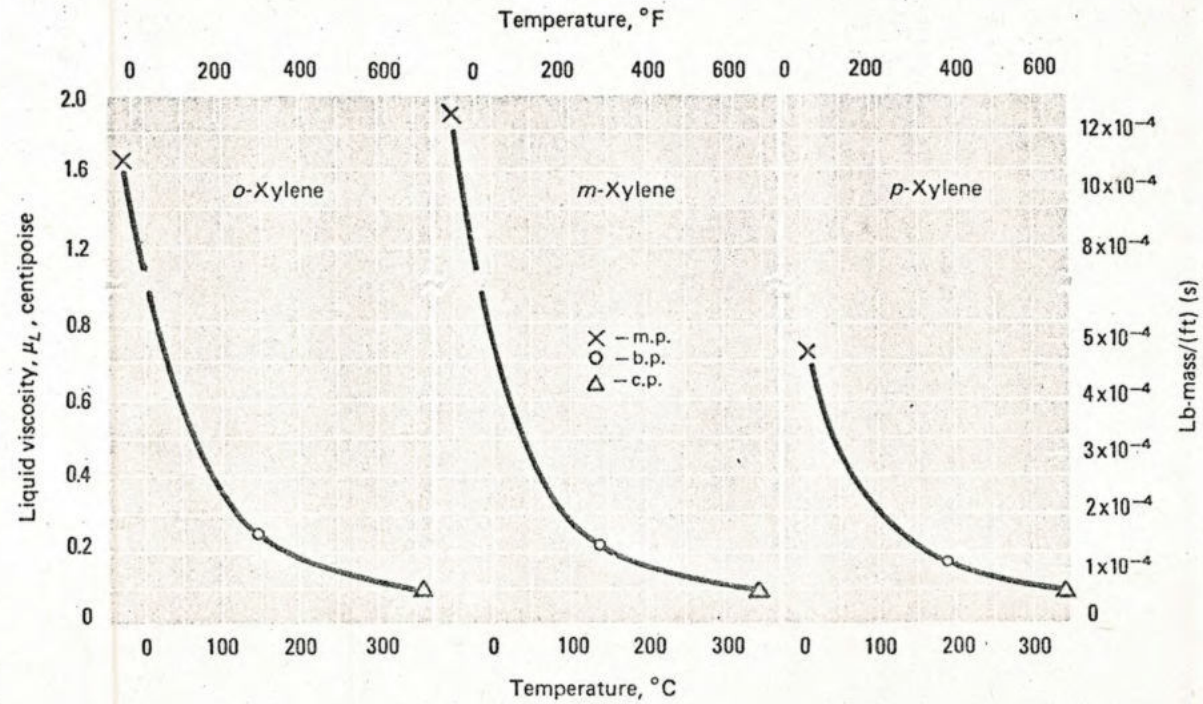
Fig. 12–7	Temperature Range, °C 0–500	500–1,000	References
o-Xylene	□	□	442
m-Xylene	□	□	442
p-Xylene	□	□	442

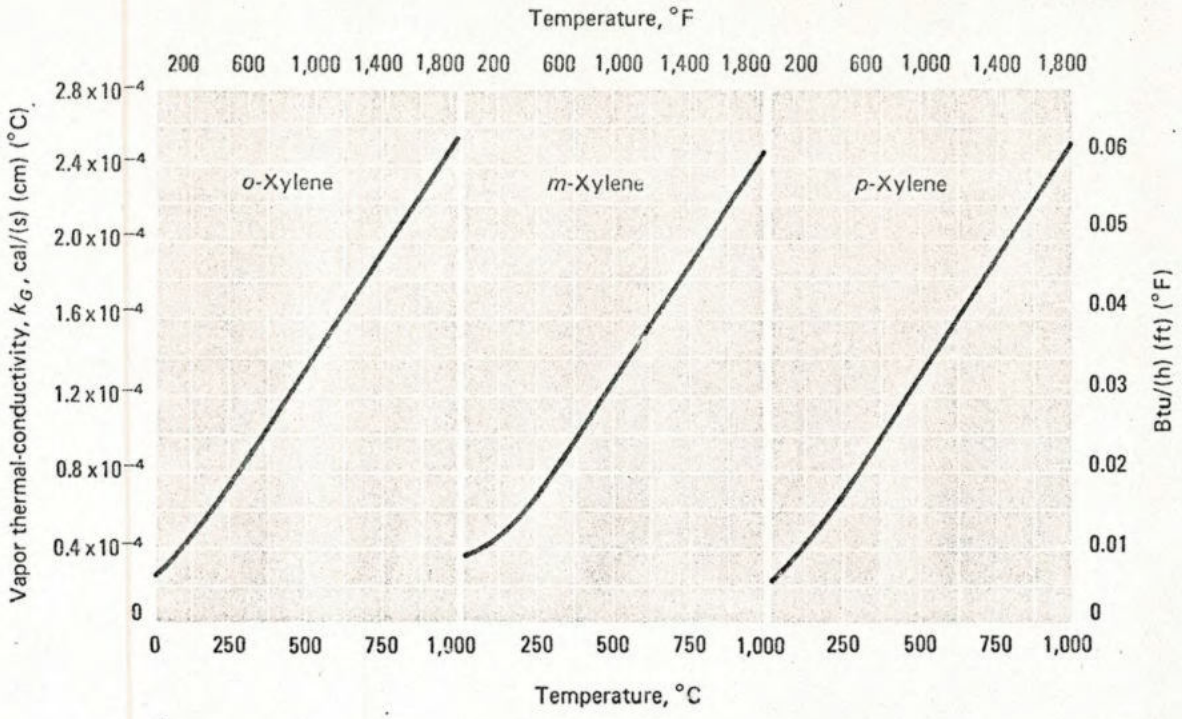
■ Laboratory data ▨ Laboratory plus correlations □ All correlated data

Fig. 12–8	Temperature Range, °C m.p.–b.p.	b.p.–c.p.	References
o-Xylene	▨	□	6,9,14,409,415,416,417,467,476,484
m-Xylene	▨	□	6,9,14,409,415,416,417,467,476,484,490
p-Xylene	▨	□	6,9,14,409,415,416,417,467,476,484,490

■ Laboratory data ▨ Laboratory plus correlations □ All correlated data

Liquid Viscosity – Fig. 12–8





Vapor Thermal Conductivity — Fig. 12–9

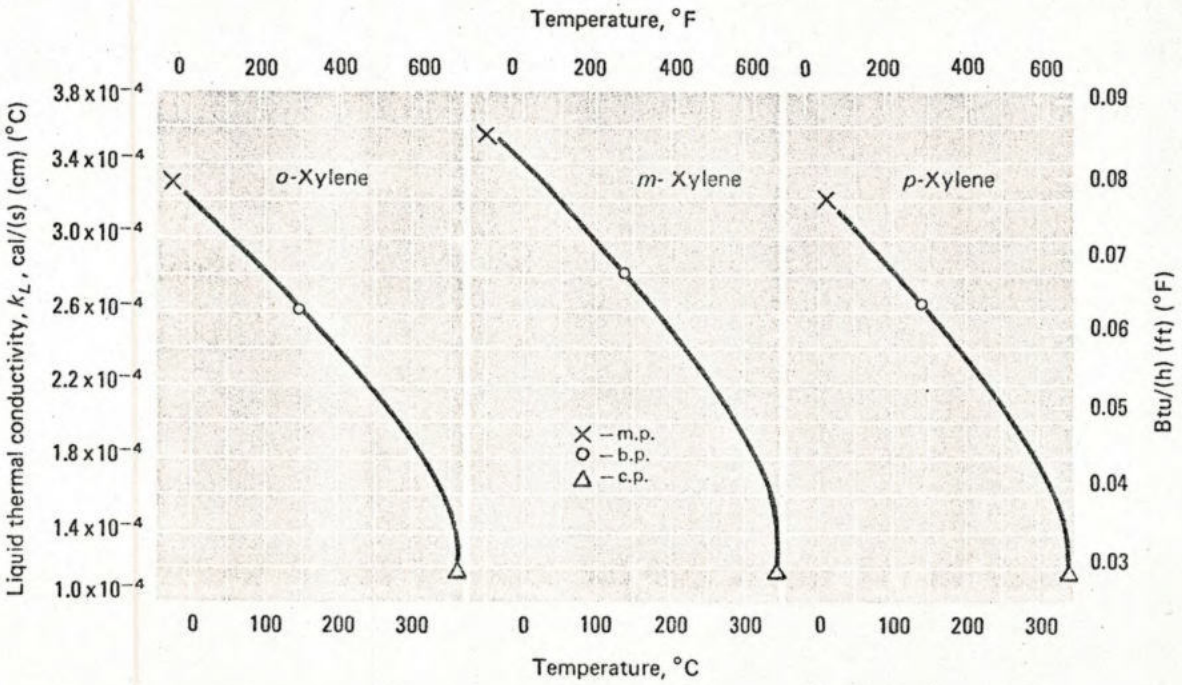
Fig. 12–9	Temperature Range, C		References
	0–500	500–1,000	
o-Xylene	□	□	14,443
m-Xylene	◪	□	14,443,470
p-Xylene	□	□	14,443

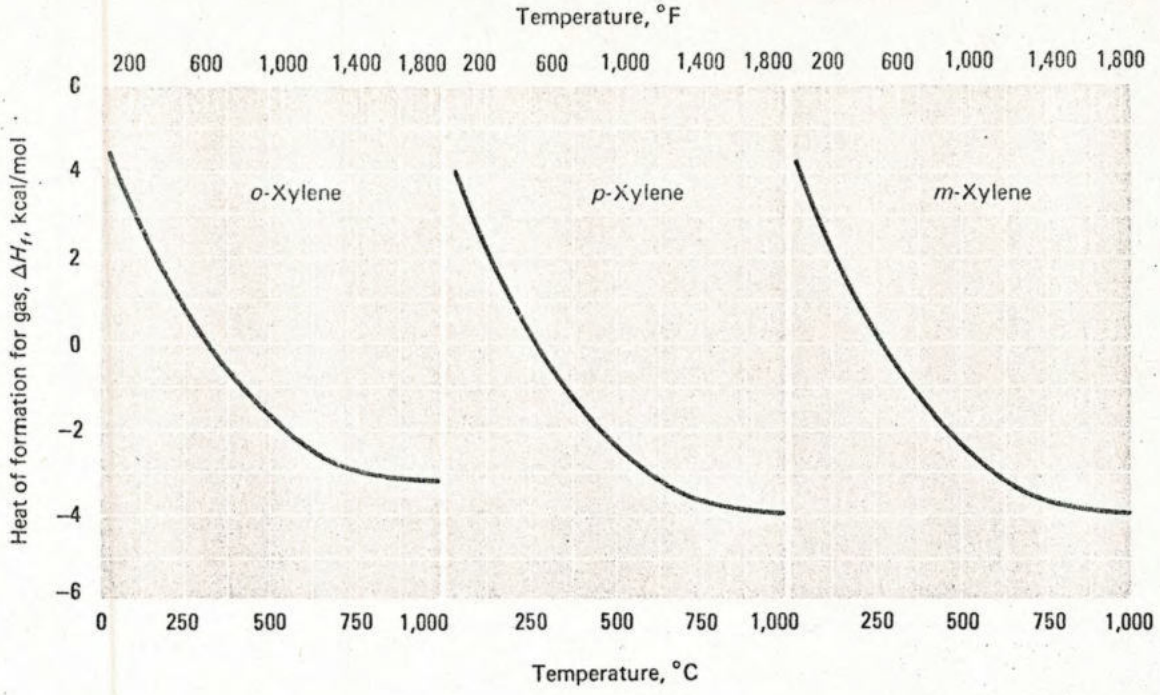
■ Laboratory data ◪ Laboratory plus correlations □ All correlated data

Fig. 12–10	Temperature Range, C		References
	m.p.–b.p.	b.p.–c.p.	
o-Xylene	◪	◪	6,9,409,413,481,486
m-Xylene	◪	◪	6,9,409,413,470,471,481,482,483,486
p-Xylene	◪	◪	475,481,483

■ Laboratory data ◪ Laboratory plus correlations □ All correlated data

Liquid Thermal Conductivity — Fig. 12–10





Heat of Formation for Gas — Fig. 12–11

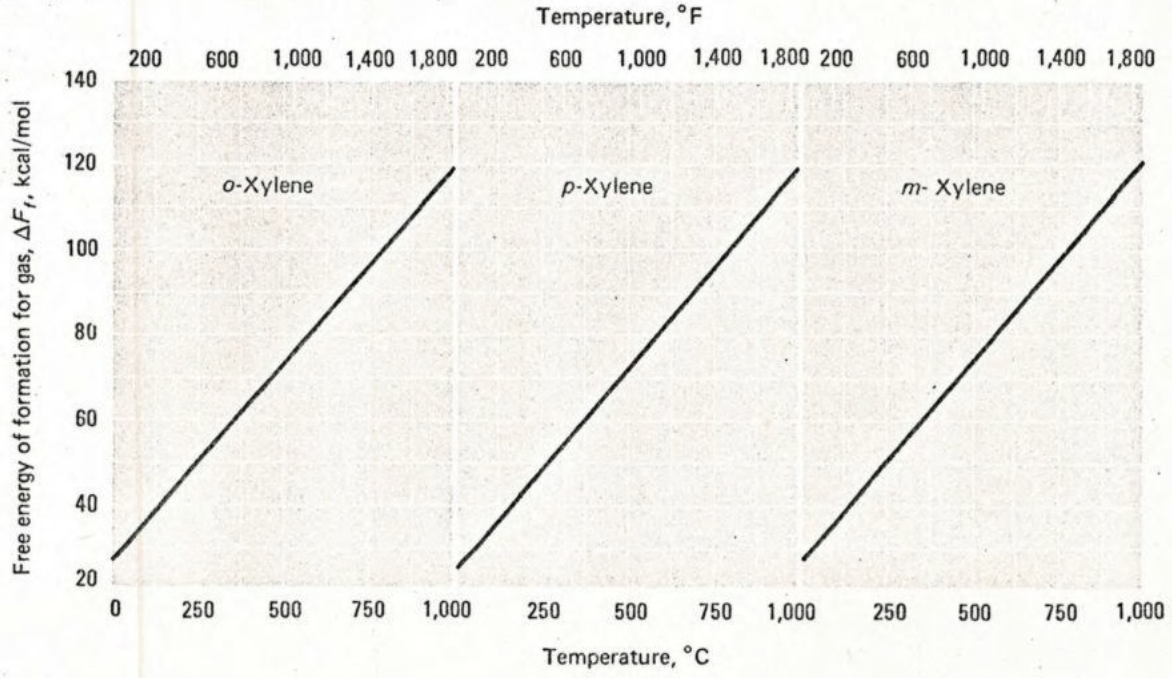
Fig. 12–11	Temperature Range, °C		References
	0–500	500–1,000	
o-Xylene	◪	◪	15,417
m-Xylene	◪	◪	15,417
p-Xylene	◪	◪	15,417

■ Laboratory data ◪ Laboratory plus correlations □ All correlated data

Fig. 12–12	Temperature Range, °C		References
	0–500	500–1,000	
o-Xylene	◪	◪	15,417
m-Xylene	◪	◪	15,417
p-Xylene	◪	◪	15,417

■ Laboratory data ◪ Laboratory plus correlations □ All correlated data

Free Energy of Formation for Gas — Fig. 12–12



for data correlation. Computed values agreed well with the experimental data.

Viscosity—Fig. 12—7, 12—8

In the absence of experimental data, the Flynn and Thodos correlation (Eq. **10**—1) was used to estimate vapor viscosity at atmospheric pressure for each xylene. Application of the correlation to a large number of hydrocarbons (25 compounds, 368 data points), including very similar aromatics such as benzene, toluene and trimethylbenzene, produced good results, with average deviations of only 2.75% [*442*]. Therefore, the estimates are considered reliable for xylenes.

Liquid viscosity data for each xylene were extended with the Guzman-Andrade equation (Eq. **1**—6) for coverage of the complete, saturated liquid phase. Comparison of experimental and predicted values yielded favorable results; deviations were 1.3%, 3.1% and 2.3% or less for *o*-, *m*- and *p*-xylene, respectively.

Thermal Conductivity—Fig. 12—9, 12—10

The correlation of Misic and Thodos [*14,443*] was applied for vapor thermal conductivity results for *m*-xylene beyond the range of experimental data:

$$k_G = [C_p/\gamma]4.45 \times 10^{-6} T_r \qquad \text{for } T_r < 1 \qquad (12\text{—}2a)$$

$$k_G = [C_p/\gamma]10^{-6}[14.52T_r - 5.14]^{2/3} \qquad \text{for } T_r > 1 \qquad (12\text{—}2b)$$

In both equations, k_G = gas thermal conductivity at low pressure (1 atm), cal/(cm)(s)(°C); $\gamma = T_c^{1/6} M^{1/2} / P_c^{2/3}$. C_p = gas heat capacity at constant pressure, cal/(g-mol)(°C); and T_r = reduced temperature, T/T_c.

In the absence of experimental data, the same correlation was also applied to *o*- and *p*-xylene. Testing of the correlation with experimental data of Abas-Zade [*470*] for *m*-xylene yielded general agreement; average deviations of 22.5% were found. Testing of other correlations [*14*] produced similar results. At temperatures of 100°C and above, average deviations were less than 11%.

The modified Stiel and Thodos relation (Eq. **10**—3) was effectively applied to each xylene to attain coverage of the complete saturated liquid phase. Results correlated extremely well with the experimental data. Deviations were 3.2%, 4.9% and 5.2% or less for *o*-, *m*- and *p*-xylene, respectively.

Heat and Free Energy of Formation—Fig. 12—11, 12—12

The results of API-44 [*417*] and Stiel, Westrum and Sinke [*15*] were adopted for heat and free energy of formation of the ideal gas for each xylene. The agreement of values is excellent. #

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Upcoming Parts of the Series

This article on the xylenes (ortho, meta, para)—12th part of the series on the physical and thermodynamic properties of industrially important chemicals—will be succeeded by the following ones, although not necessarily in the order listed below:

Cycloaromatics (benzene, naphthalene)
Alkylaromatics (toluene, ethylbenzene)
Oxygenated aromatics (furfural, cresols)
Diolefins (butadiene, isoprene)
Cyclic ethers (ethylene oxide, propylene oxide
Olefinic chlorocarbons (vinyl chloride, vinylidene chloride)
Terephthalic acid and derivatives
Chloroethanes (ethylene dichloride, ethyl chloride)
Amines (dimethylamine, methylamine)
Dibasic acids (adipic acid, sebacic acid)
Aldehydes (formaldehyde, acetaldehyde)