Olefin monomers: isobutylene and styrene

Various correlations and data provide extensive results of the physical and thermodynamic properties for the major olefin polymers, isobutylene and styrene, over a wide temperature range.

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☐ Isobutylene and styrene are of major importance to the chemical process industries, especially as primary olefin monomers for the production of sundry polymers.

Isobutylene finds effective use in organic synthesis, and in the production of high-octane aviation gasoline. However, its primary usage is as a monomer for making polymers such as butyl rubber and copolymer resins. The major application for styrene is also as a monomer for polymers. For example, such polymers are conventional polystyrene, impact polystyrene, styrene-acrylonitrile copolymer (SAN), acrylonitrile-butadiene-styrene terpolymer (ABS), and styrene-butadiene copolymer.

Critical Properties—Table 17—1

Data for the critical temperature, critical pressure and critical volume are available in the literature [*3, 4, 10, 417, 608, 613, 620*]. The reported values are in close agreement. Deviations from the selected values are 0.1%, except for critical volume, which has a 0.6% variation.

Heat of Vaporization—Fig. 17—1

The data for heats of vaporization are based on experimental data and Watson's correlation (Eq. 1-1)† for the completely saturated liquid phase.

Vapor Pressure—Fig. 17—2

Comprehensive vapor-pressure data for isobutylene and styrene were extended with the Cox-Antoine relation (Eq. 1-2) to achieve complete coverage of the saturated liquid phase. The agreement among the various data sources is close, and the deviations in most cases are less than 3%.

Heat Capacity—Fig. 17—3, 17—4

Results for the heat capacity of the ideal gas at atmospheric pressure are in substantial agreement among the various sources. Average deviations are less than 0.1% for isobutylene and styrene.

Data for the heat capacity of the saturated liquid were extended to cover the full liquid state by using the extrapolation relationship for density (Eq. 1-3) with $n = 1$ and $n = 1.5$ for isobutylene and styrene, respectively. Calculated values and experimental data compared favorably. Average deviations were 1.1% for isobutylene and 2.4% for styrene.

Density—Fig. 17—5

The modified Rackett correlation (Eq. 15-1) was selected for extending laboratory and experimental density data. The correlated values and experimental data were extremely close. Average deviations were only 0.22% for both isobutylene and styrene.

Surface Tension—Fig. 17—6

The recent results of Jasper [*79*]; Kennedy and Kirshenbaum [*620*]; and Coulter, Kehde, and Hiscock [*620*] were selected as the primary experimental data. Surface-tension data were extended for the completely saturated liquid-phase coverage with the Othmer relation (Eq. 15-2) with $n = 1.23$ for isobutylene and 0.484 for styrene. Computed values and experimental data were very close. Average deviations were 0.7% and 0.3% for isobutylene and styrene, respectively.

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*For biography of the author, *see Chem. Eng.*, May 12, 1975, p. 97.

†See Part 1 of this series for equations starting with a boldfaced numeral "1", Part 2 for those with "2", etc. Table on p. 115 lists publication dates of all previous articles in this series.

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.

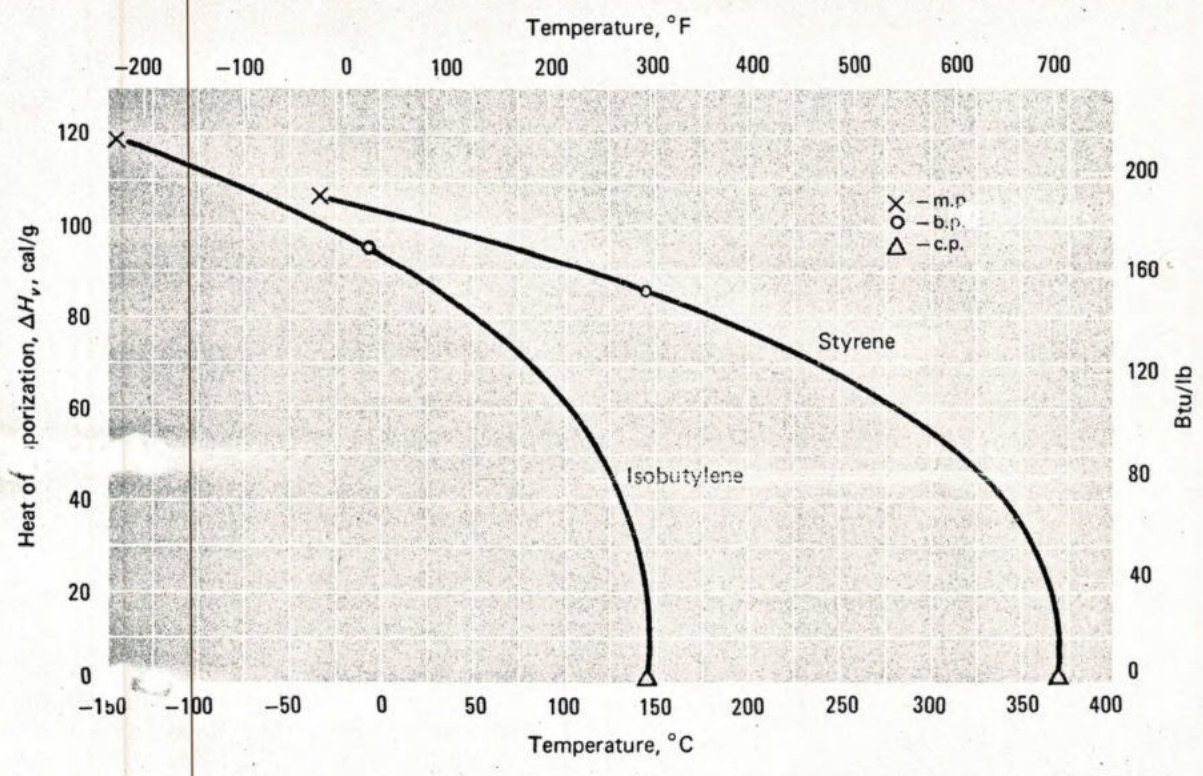
The shaded squares denote the following:

- ■ 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 two major olefin monomers — Table I

Identification	Isobutylene C_4H_8	Styrene C_8H_8
State (std. conditions)	Gas	Liquid
Molecular weight, M	56.104	104.144
Boiling point, T_b, °C	−6.9	145.0
Melting point, T_m, °C	−140.35	−30.6
Critical temp., T_c, °C	144.7	369.0
Critical pressure, P_c, atm	39.5	37.6
Critical volume, V_c, cm³/g-mol	238.7	369.7
Critical compressibility factor, Z_c	0.275	0.264

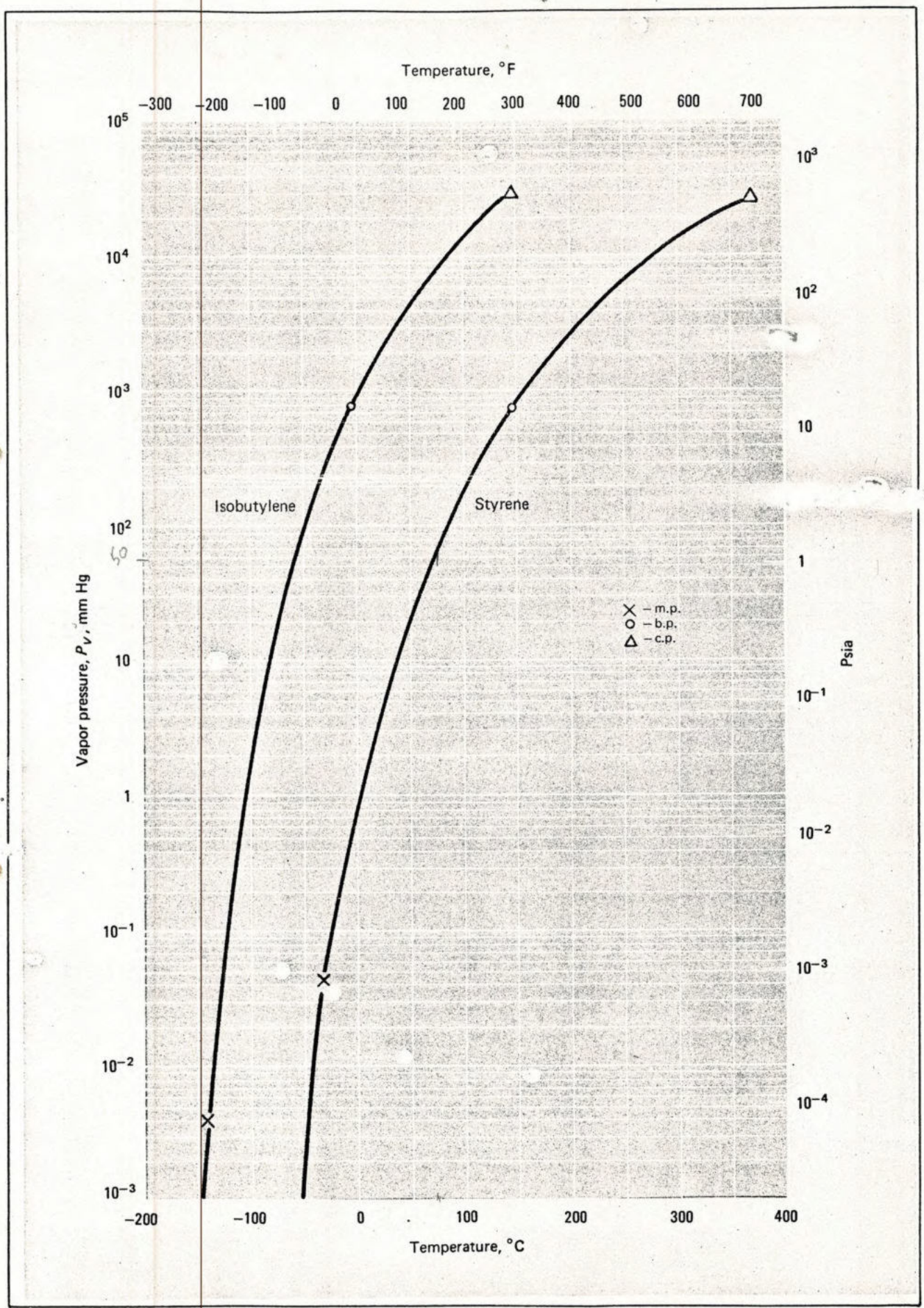


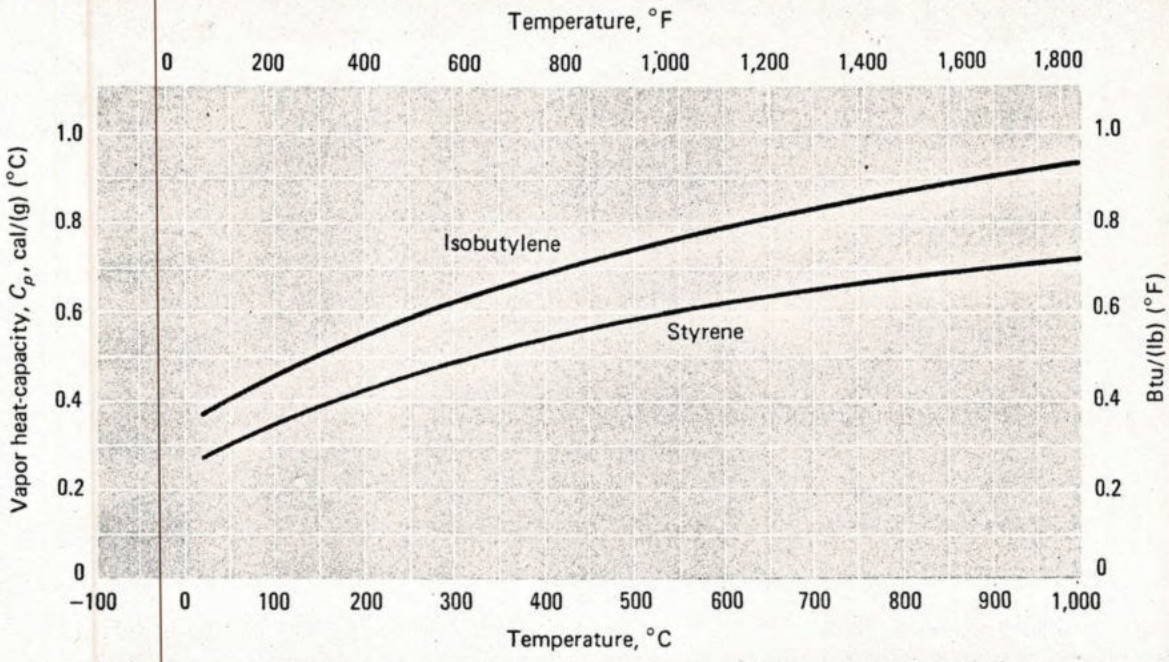
Heat of vaporization — Fig. 1

Fig. 17–1	Temperature range, C: m.p.–b.p.	Temperature range, C: b.p.–c.p.	References
Isobutylene	◪	◪	3,10,417,607,613,618,620
Styrene	◪	◪	3,611,620,622

Vapor pressure — Fig. 2

Fig. 17–2	Temperature range, C: m.p.–b.p.	Temperature range, C: b.p.–c.p.	References
Isobutylene	◪	■	3,4,10,413,415,417,419,473,529,546,548,607,609,613,619,620,624
Styrene	◪	◪	3,4,413,415,546,548,611,612,620,622


Temperature, °F
−300
−200
−100
0
100
200
300
400
500
600
700
10^5
10^4
10^3
10^2
10
1
10^{-1}
10^{-2}
10^{-3}
Vapor pressure, P_V, mm Hg
10^3
10^2
10
1
10^{-1}
10^{-2}
10^{-3}
10^{-4}
Psia
Isobutylene
Styrene
× – m.p.
○ – b.p.
△ – c.p.
−200
−100
0
100
200
300
400
Temperature, °C

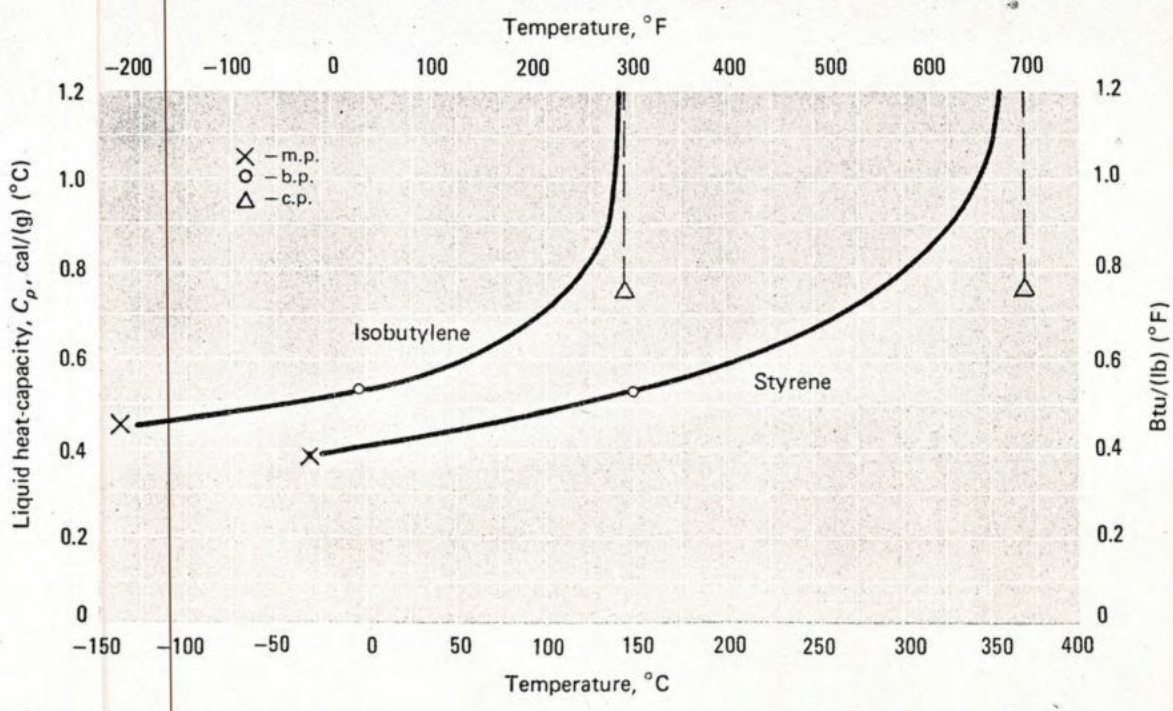


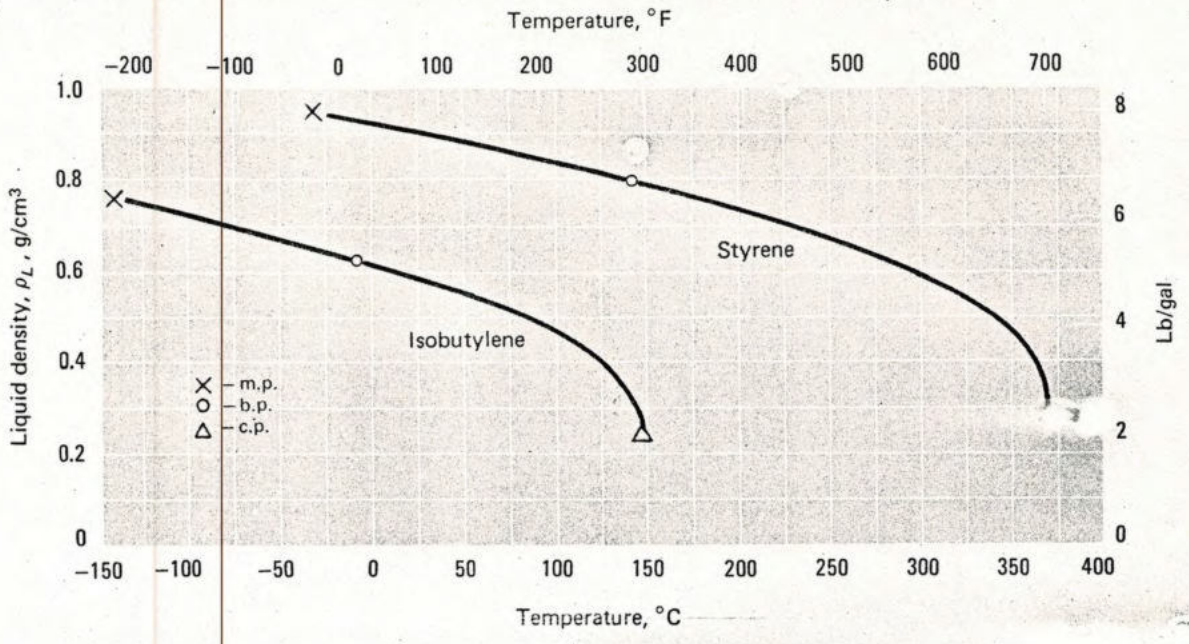
Vapor heat capacity — **Fig. 3**

Fig. 17–3	Temperature range, C		References
	0–500	500–1,000	
Isobutylene	◪	◪	15,416,417,617,624
Styrene	◪	◪	15,416,417,507,610,611

Liquid heat capacity — **Fig. 4**

Fig. 17–4	Temperature range, C		References
	m.p.–b.p.	b.p.–c.p.	
Isobutylene	◪	◪	10,415,546,607,613,619,627
Styrene	◪	□	4,620,622,626



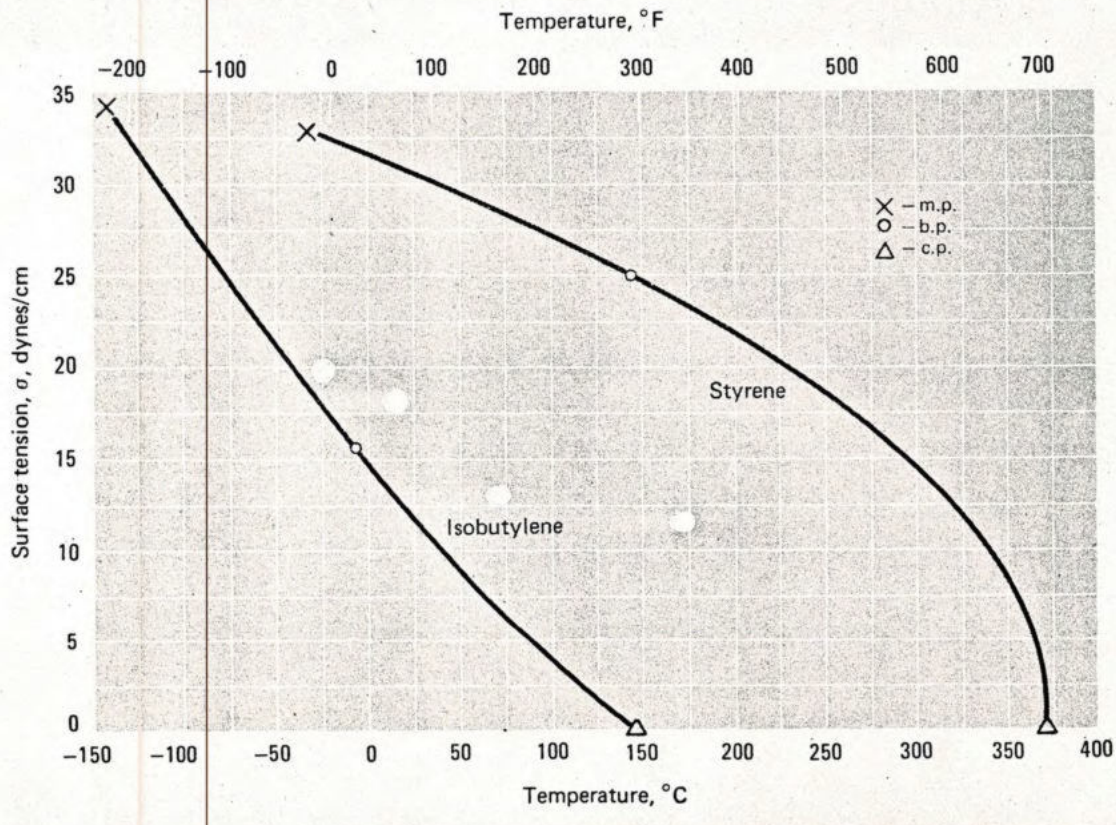


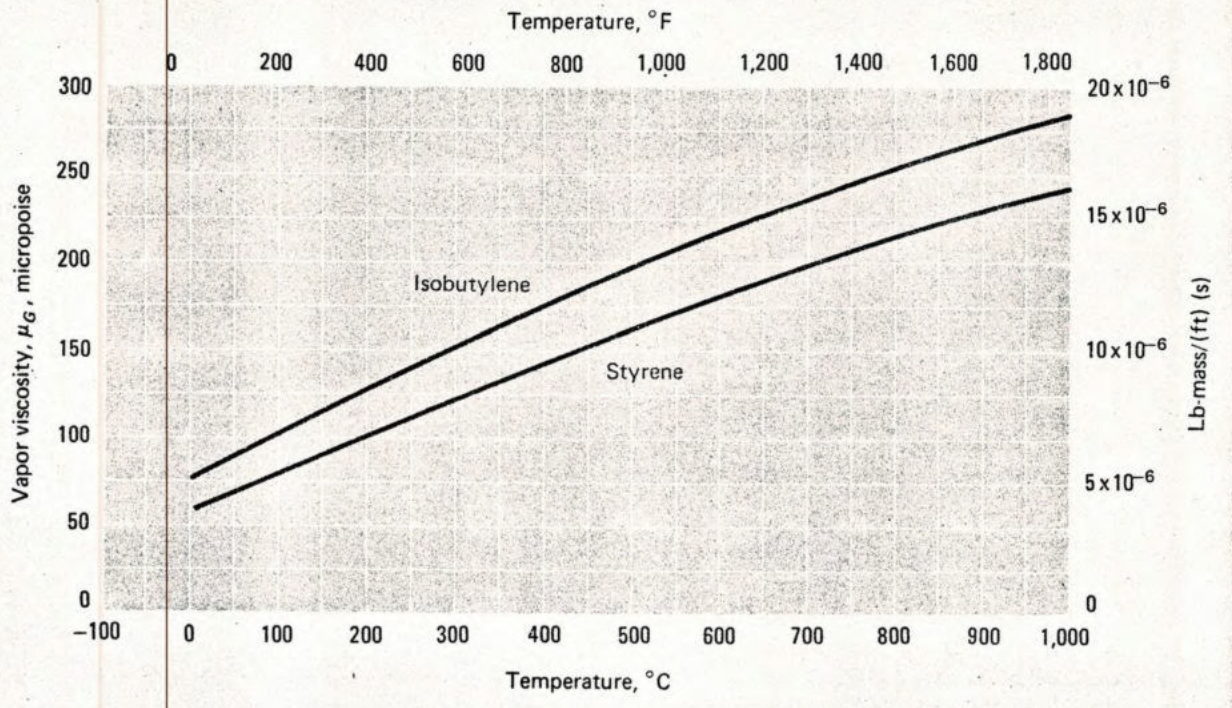
Liquid density — Fig. 5

Fig. 17–5	Temperature range, C: m.p.–b.p.	Temperature range, C: b.p.–c.p.	References
Isobutylene	◪	■	4, 10, 417, 473, 546, 607, 613, 619, 620
Styrene	◪	◪	4, 417, 611, 620, 628

Surface tension — Fig. 6

Fig. 17–6	Temperature range, C: m.p.–b.p.	Temperature range, C: b.p.–c.p.	References
Isobutylene	◪	◪	3, 4, 79, 417, 620
Styrene	◪	□	3, 4, 79, 620, 621, 628



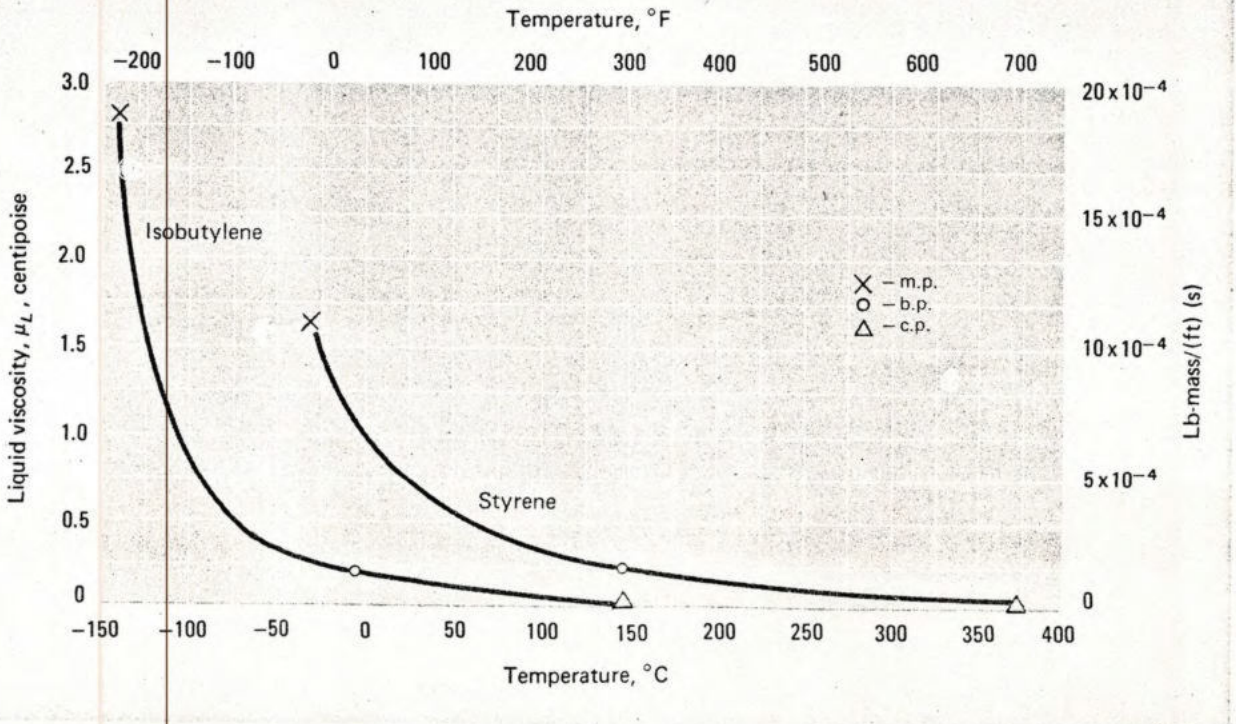


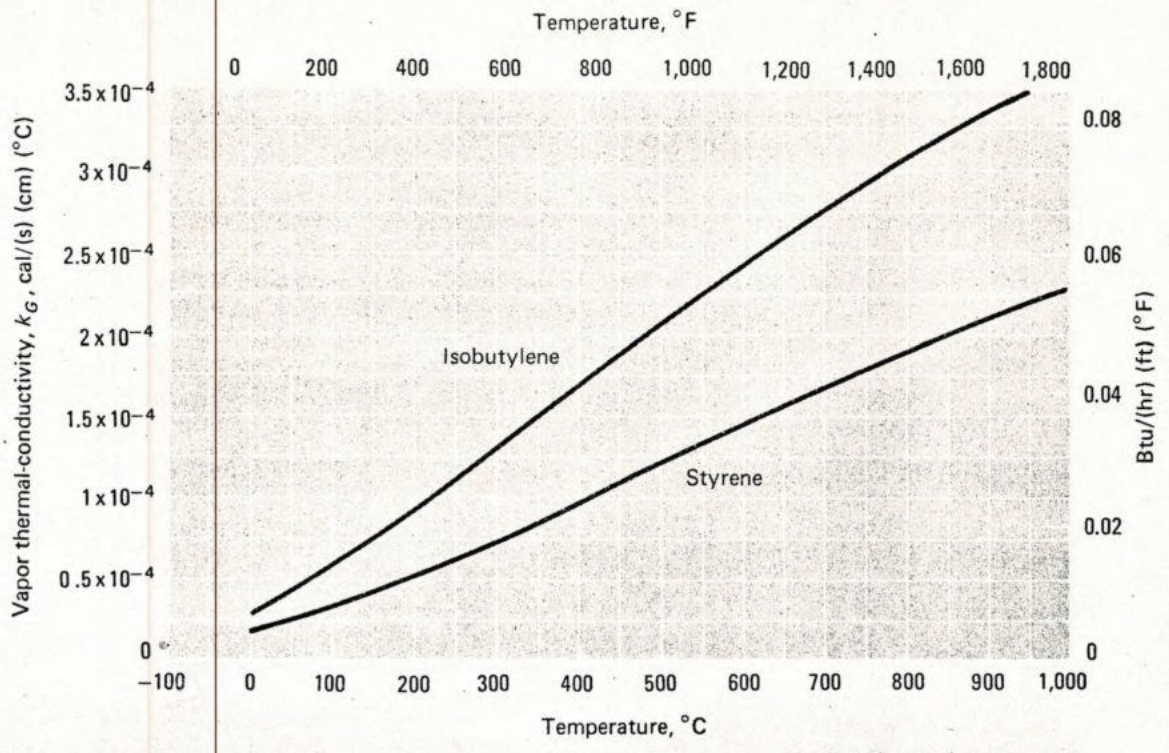
Vapor viscosity — **Fig. 7**

Fig. 17–7	Temperature range, C		References
	0–500	500–1,000	
Isobutylene	◪	□	10, 14, 467, 519, 544, 546
Styrene	□	□	14, 544

Liquid viscosity — **Fig. 8**

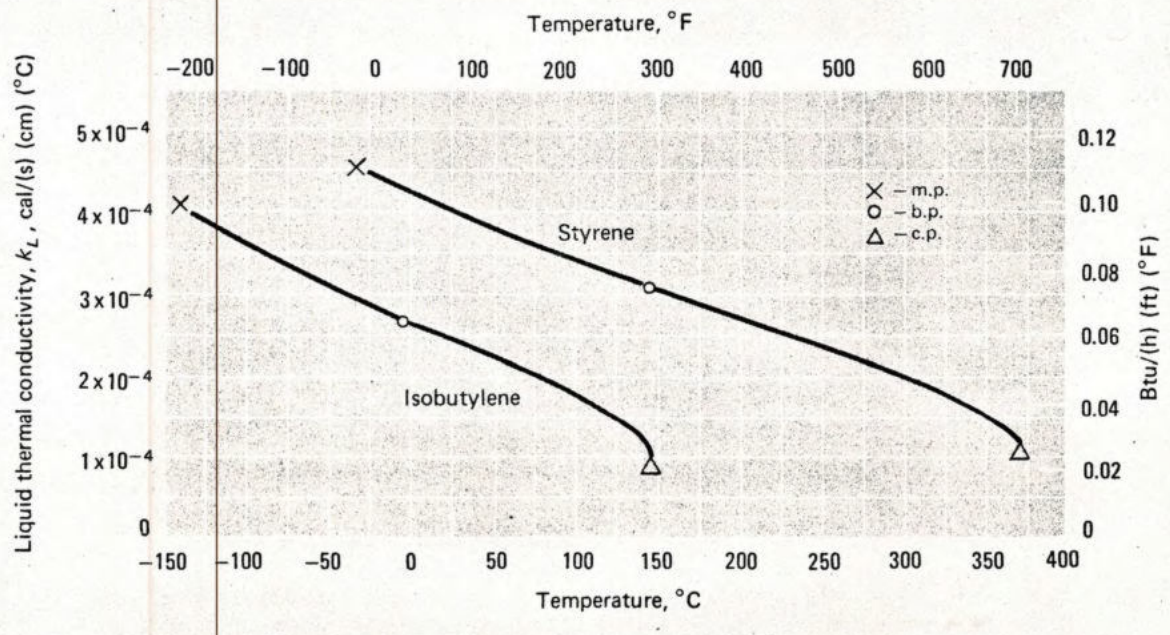
Fig. 17–8	Temperature range, C		References
	m.p.–b.p.	b.p.–c.p.	
Isobutylene	◪	◪	14, 434
Styrene	◪	□	4, 14, 467, 546, 611, 618, 620

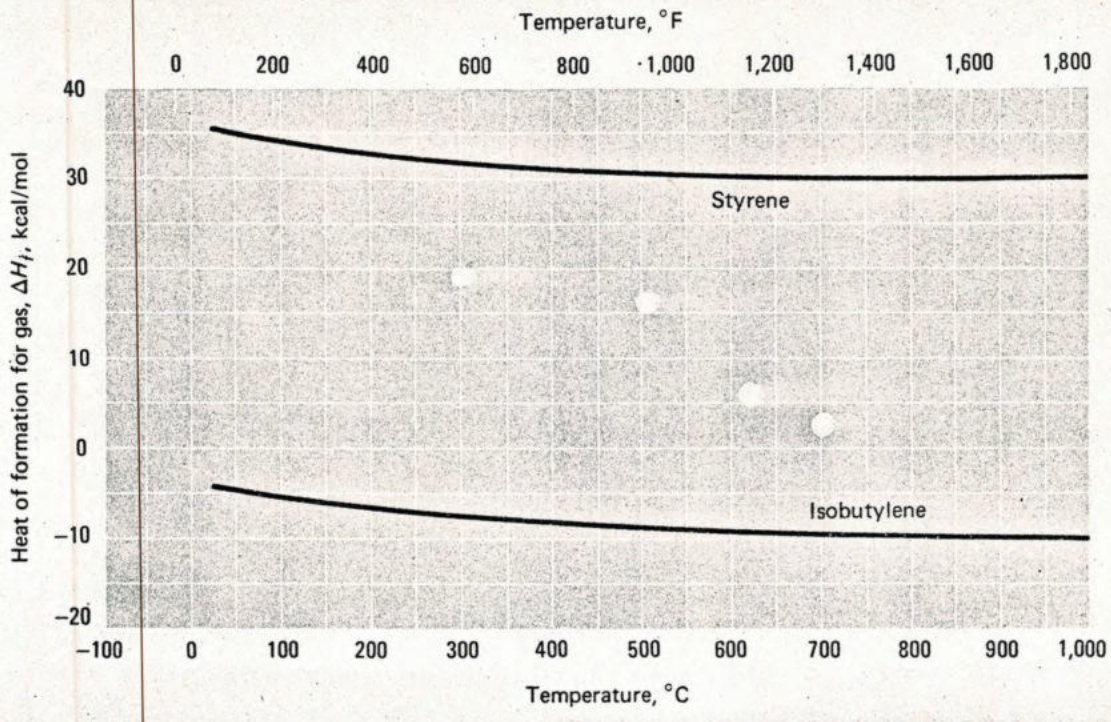




Vapor thermal conductivity			Fig. 9
Fig. 17–9	Temperature range, °C		References
	0–500	500–1,000	
Isobutylene	◪	□	14,443,614,615,616,623,625
Styrene	□	□	14,443

Liquid thermal conductivity			Fig. 10
Fig. 17–10	Temperature range, °C		References
	m.p.–b.p.	b.p.–c.p.	
Isobutylene	□	□	14,481
Styrene	□	□	14,481



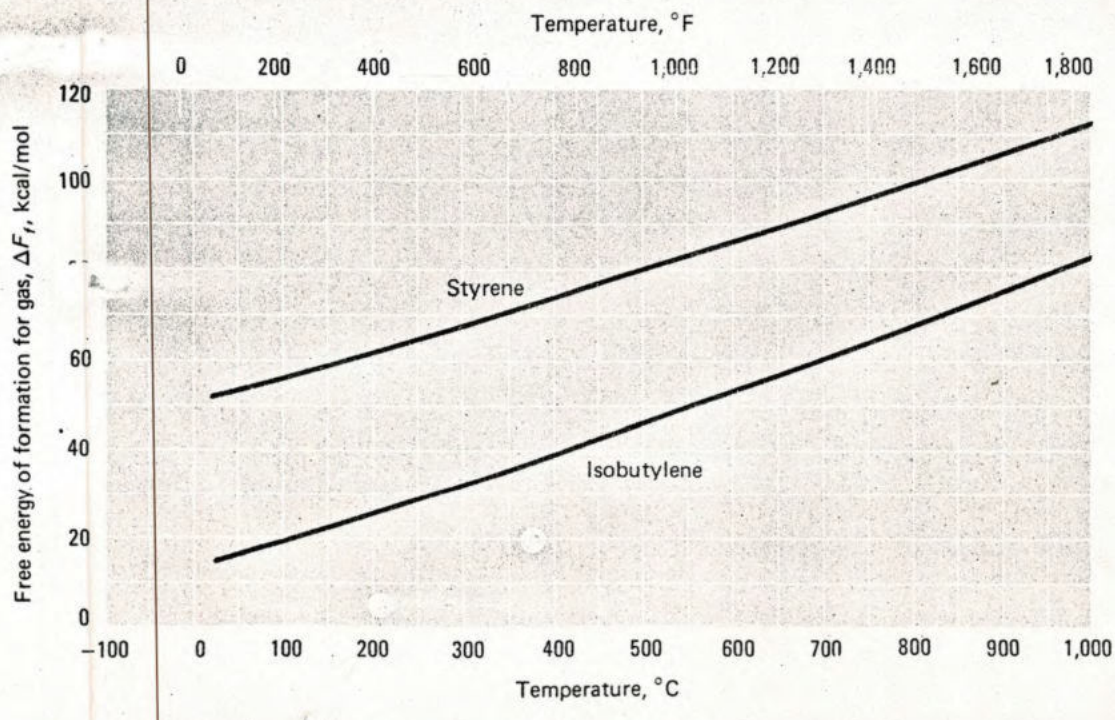


Heat of formation for gas — Fig. 11

Fig. 17–11	Temperature range, °C		References
	0–500	500–1,000	
Isobutylene	◪	◪	15,417
Styrene	◪	◪	15,417,611

Free energy of formation for gas — Fig. 12

Fig. 17–12	Temperature range, °C		References
	0–500	500–1,000	
Isobutylene	◪	◪	15,417
Styrene	◪	◪	15,417,611



Viscosity—Fig. 17—7, 17—8

The modified Stiel and Thodos correlation (Eq. 16-5a and 16-5b) was selected for extending the gas-phase viscosity data for isobutylene. The modified correlation yielded values that compared favorably with the experimental data. Average deviations were 1.4% for isobutylene.

The same correlation was adopted for estimating gas-phase viscosity of styrene. Testing the correlation [*544*] with aromatics (benzene, toluene) similar to styrene produced favorable findings. Average deviations were less than 1.6% for the similar aromatics.

Liquid-viscosity data were effectively extended with the Guzman-Andrade relation (Eq. 1-6) for obtaining full liquid-phase coverage. Two straight lines were adopted for isobutylene, while only one was required for styrene. Comparison of experimental and predicted values produced deviations of 2.1% and 2.5% for isobutylene and styrene, respectively.

Thermal Conductivity—Fig. 17—9, 17—10

Thermal conductivity data for the gas phase at atmospheric pressure are available for isobutylene. The Misic and Thodos correlation (Eq. 12-2a and 12-2b) was effectively used to extend the data and to estimate values for styrene. Correlated values and experimental data were in agreement. Average deviation was 3.83% for isobutylene.

Liquid-thermal-conductivity values for isobutylene and styrene were estimated with the Pachaiyappan and Naidyanathan correlation (Eq. 16-7) at temperatures (−30°C and 120°C, respectively) below the boiling point of isobutylene and styrene. These values were then extended with the modified Stiel and Thodos relation (Eq. 10-3). Application of this technique to similar hydrocarbon compounds (olefins and aromatics such as ethylene, propylene, toluene, and ethylbenzene) produced favorable agreement of predicted values and experimental data. Average deviations were 5 to 10%. The results for isobutylene and styrene are intended to represent correct order-of-magnitude values.

Heat and Free Energy of Formation—Fig. 17—11, 17—12

Results for heat of formation and free energy of formation for the ideal gas are available from several sources. The agreement is very good, with deviations being less than 0.03 kcal/mol.

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Subject index for series on physical and thermodynamic properties