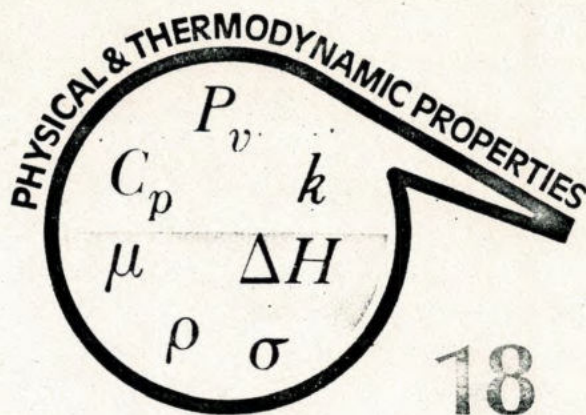# Butadiene, isoprene and chloroprene

Property data for three major diolefins
are presented in some detail
in this continuing series.

PHYSICAL & THERMODYNAMIC PROPERTIES

$$P_v \quad k$$
$$C_p \quad \mu \quad \Delta H$$
$$\rho \quad \sigma$$

18

***Carl L. Yaws**, Lamar University*

☐ Butadiene, isoprene and chloroprene have major commercial applications. Butadiene is principally used for production of SBR rubber (copolymer with styrene), for cis-1,4-polybutadiene rubber (diene polymer) and for oil-resistant rubbers such as buna N. It is also used in plastics and resins. Almost all isoprene is polymerized to *cis*-polyisoprene, *trans*-polyisoprene or butyl rubber. Chloroprene goes mainly into making synthetic elastomers such as neoprene. Smaller volumes of each of these diolefins are used in synthesizing specialty products.

Critical Properties—Table 18-1

Critical-constant values for butadiene are provided by experimental data [3,4,9,10,14,416,417,546,620,637, 639,640]. Critical-temperature data [4,620] are available for chloroprene.

Values for the remaining critical constants—isoprene (T_c, P_c, V_c) and chloroprene (P_c, V_c)—were estimated by the Lydersen and Riedel methods (Eq. 16—1, 16—2 and 16—3.† Estimated results and experimental data compared favorably. Average deviations were 0.3 to 1.2% for butadiene, and 1.8% for chloroprene.

Heat of Vaporization—Fig. 18—1

Experimental data in the temperature region around the boiling point, and Watson's correlation (Eq. 1—1), were effectively used to cover the complete saturated liquid phase for each diolefin.

Vapor Pressure—Fig. 18—2

Extensive vapor-pressure data for each diolefin were extended with the Cox-Antoine relation (Eq. 1—2) to achieve complete coverage of the saturated liquid phase. Two straight lines fitted the data. The results from the various investigators are in close agreement.

*To meet 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 of Jan. 19, 1975, issue (Part 17) lists publication dates of Parts 1 through 16.

Heat Capacity—Fig. 18—3, 18—4

Results for the heat capacity at constant pressure (1 atm) of the ideal gas cover a wide temperature range for butadiene and isoprene. Values are available only in the room-temperature range (0 and 100°C) for chloroprene. Results from the various literature sources agree, with average variations being less than 0.3%.

Ideal-gas heat capacities for chloroprene beyond room-temperature range were estimated with the group contribution method of Rihani and Doraiswamy [14]:

$$C_p = a + bT + cT^2 + dT^3 \qquad (18—1)$$

where C_p = ideal-gas heat capacity, cal/g mol °K; T = temperature, °K; and a, b, c, and d are functions of the atomic groups (—CH$_3$, =CH$_2$, —Cl, etc.) that make up the compound. Tabulated values of a, b, c, and d are given in Reid and Sherwood [14].

Application of the method to the three diolefins produced general agreement of estimated and experimental values. Average deviations were 3.9% for butadiene, 2.3% for isoprene, and 15.9% for chloroprene. The deviations were highest at low temperatures (4 to 18% in the range of 0 to 300°C) and considerably lower at higher temperatures (0.3 to 2% in 700 to 1,200°C). Thus, the estimated ideal-gas heat capacities for chloroprene are probably more accurate at the higher temperatures than at the average room-temperature deviation.

Liquid heat-capacity data for each diolefin were extended with the saturated-liquid density extrapolation relation (Eq. 1—3, $n = 1$). Predicted values deviated only slightly from experimental results. Average deviations: butadiene, 0.20%; isoprene, 0.16%; and chloroprene, 0.95%.

Density—Fig. 8—5

The Spencer and Danner correlation method (Eq. 15—1) was used to correlate and extend the saturated-liquid density data for each diolefin. Correlation and experimental values were extremely close—average deviations were only 0.20, 0.16 and 0.95% for butadiene, isoprene and chloroprene, respectively.

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.
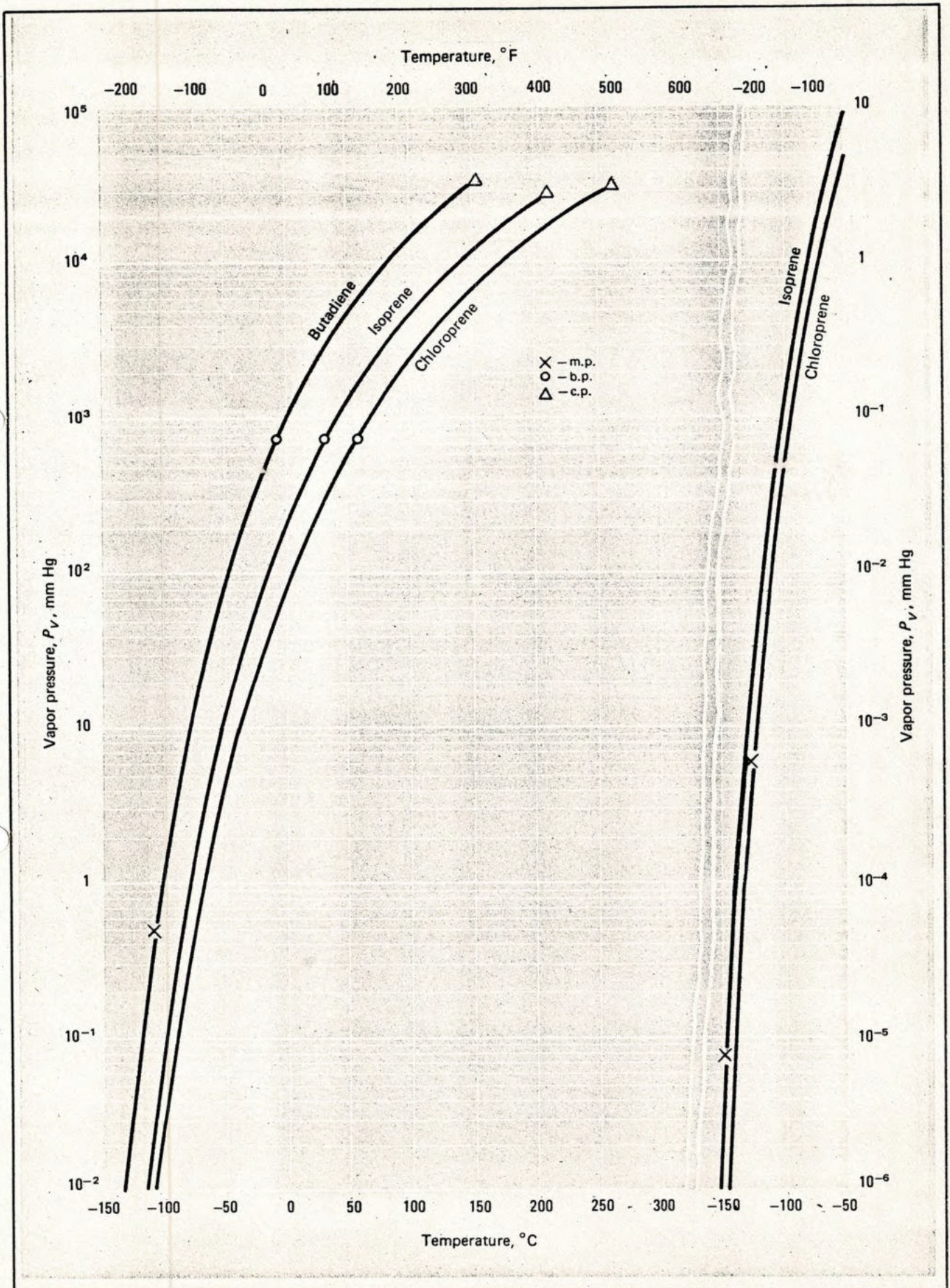
Physical properties of the diolefins — Table I

Identification	Butadiene C_4H_6	Isoprene C_5H_8	Chloroprene C_4H_5Cl
State (std. conditions)	Gas	Liquid	Liquid
Molecular weight, M	54.09	68.13	88.54
Boiling point, T_b, °C	−4.41	34.07	59.4
Melting point, T_m, °C	−108.9	−146.0	−130.0
Critical temp., T_c, °C	152.0	210.2*	261.7
Critical pressure, P_c, atm	42.7	36.9*	42.0*
Critical volume, V_c, cm³/g-mol	220.8	266.0*	260.0*
Critical compressibility factor, Z_c	0.270	0.248*	0.253*

*estimated values
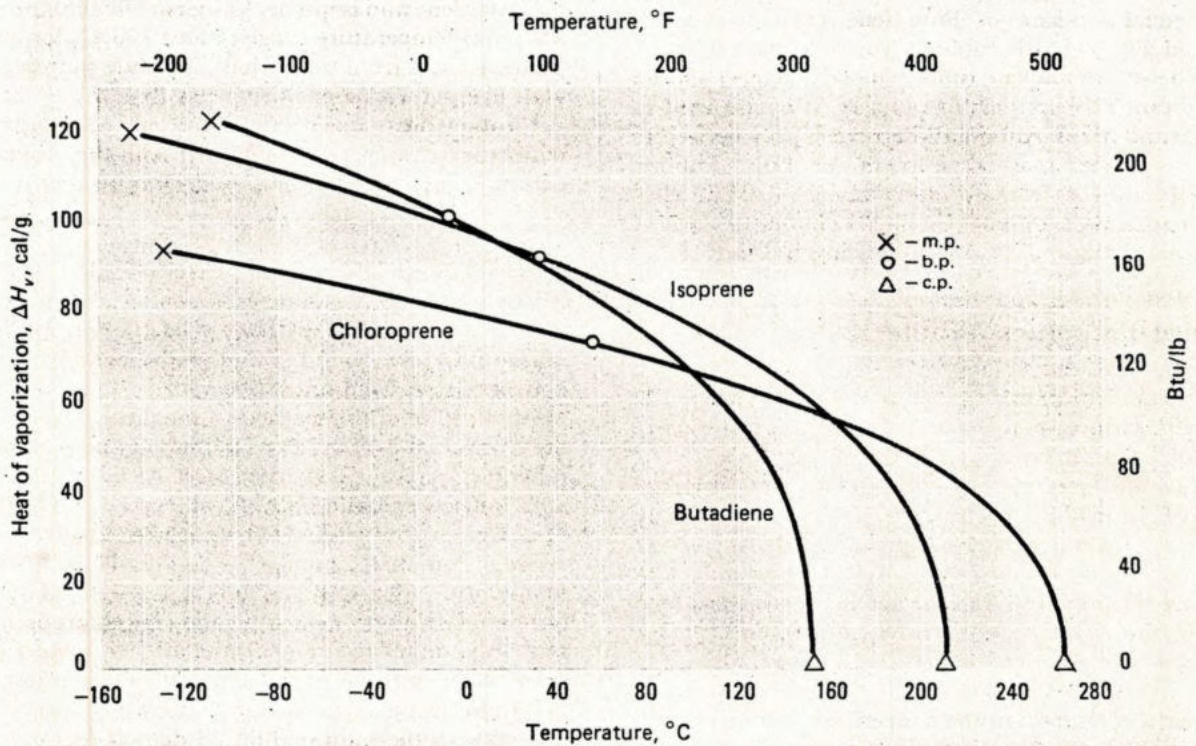
Heat of vaporization — Fig. 1

Fig. 18-1	Temperature range, °C m.p.–b.p.	b.p.–c.p.	References
Butadiene	◪	◪	10, 419, 620, 639, 640
Isoprene	◪	◪	419, 620
Chloroprene	◪	◪	4, 620

Vapor pressure — Fig. 2

Fig. 18-2	Temperature range, °C m.p.–b.p.	b.p.–c.p.	References
Butadiene	◪	■	3, 4, 10, 416, 417, 419, 529, 546, 548, 620, 633, 637, 639, 640
Isoprene	◪	◪	417, 419, 529, 548, 620, 637, 643, 645
Chloroprene	◪	◪	4, 548, 620, 637, 643

Fig. 3 — Vapor heat capacity chart. Temperature, °F (top axis: 0 to 1,800); Vapor heat-capacity, C_p, cal/(g) (°C) vs Temperature, °C (bottom axis: −100 to 1,000); Btu/(lb) (°F). Curves: Isoprene, Butadiene, Chloroprene.
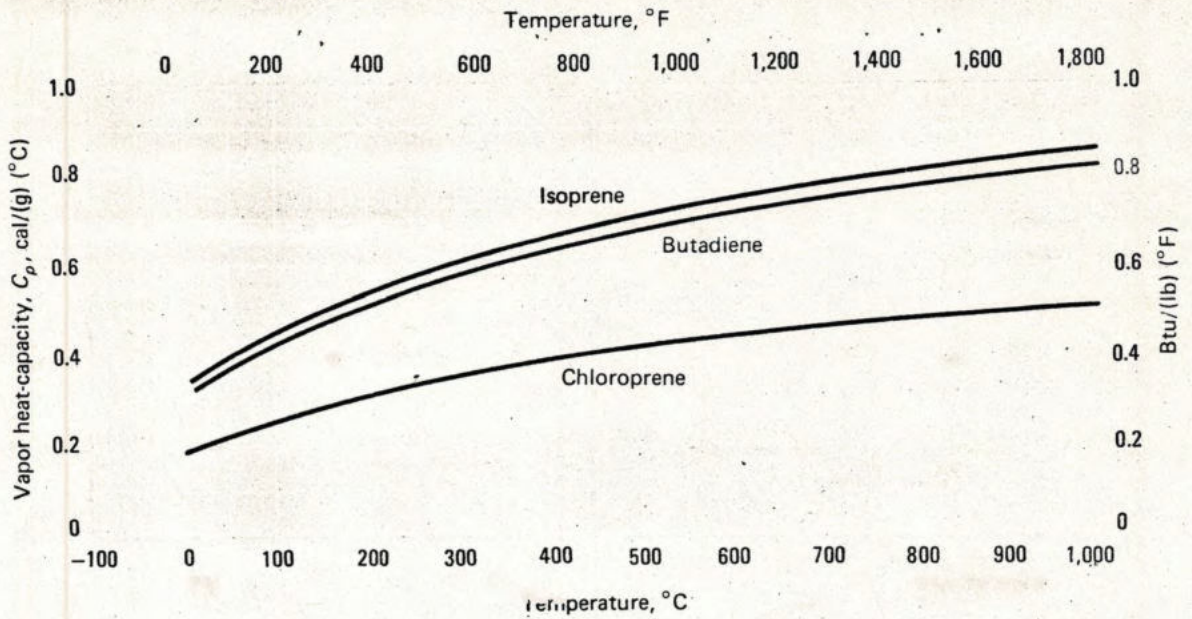
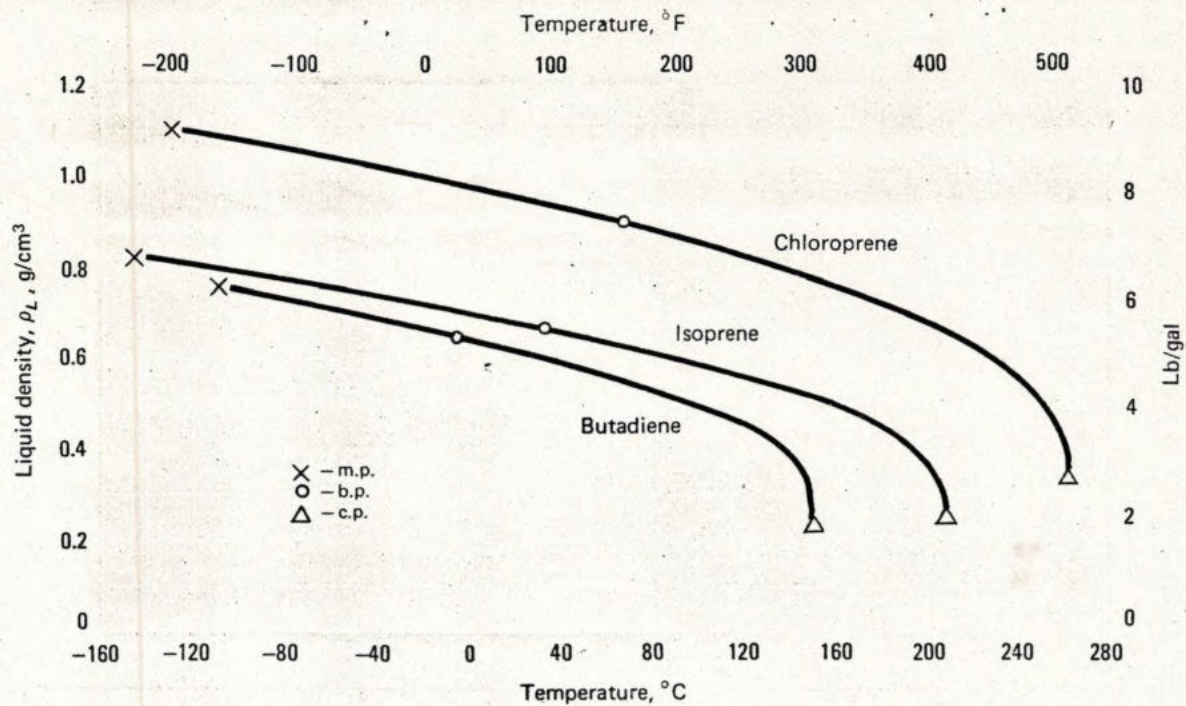**Vapor heat capacity**   **Fig. 3**

Fig. 18–3	Temperature range, °C		References
	0–500	500–1,000	
Butadiene	◩	◩	10,15,416,417,620,630,631,636,641
Isoprene	◩	◩	15,416,417,620,636
Chloroprene	◩	☐	4,14,620

Liquid heat capacity   **Fig. 4**

Fig. 18–4	Temperature range, °C		References
	m.p.–b.p.	b.p.–c.p.	
Butadiene	◩	◩	10,415,416,640,646
Isoprene	◩	☐	416,620,638,645
Chloroprene	◩	☐	4,620

Fig. 4 — Liquid heat capacity chart. Temperature, °F (top axis: −200 to 500); Liquid heat-capacity, C_p, cal/(g) (°C) vs Temperature, °C (bottom axis: −160 to 280); Btu/(lb) (°F). Legend: X − m.p., O − b.p., △ − c.p. Curves: Butadiene, Isoprene, Chloroprene.

Liquid density chart (Fig. 18-5)

Y-axis: Liquid density, ρ_L, g/cm³ (0 to 1.2)
Right axis: Lb/gal (0 to 10)
Top axis: Temperature, °F (−200 to 500)
Bottom axis: Temperature, °C (−160 to 280)

Curves: Chloroprene, Isoprene, Butadiene

Legend:
× – m.p.
○ – b.p.
△ – c.p.

Liquid density			Fig. 5

Fig. 18–5	Temperature range, °C		References
	m.p.–b.p.	b.p.–c.p.	
Butadiene	▨	▨	3,4,10,473,546,620,635,637,639,640,646
Isoprene	▨	☐	3,4,620,645
Chloroprene	▨	☐	4,620,632

Surface tension			Fig. 6

Fig. 18–6	Temperature range, °C		References
	m.p.–b.p.	b.p.–c.p.	
Butadiene	☐	☐	14
Isoprene	☐	☐	14
Chloroprene	☐	☐	14

Surface tension chart (Fig. 18-6)

Y-axis: Surface tension, σ, dynes/cm (0 to 40)
Top axis: Temperature, °F (−200 to 500)
Bottom axis: Temperature, °C (−160 to 280)

Curves: Chloroprene, Isoprene, Butadiene

Legend:
× – m.p.
○ – b.p.
△ – c.p.

Temperature, °F

Fig. 7 Vapor viscosity chart: Vapor viscosity, μ_G, micropoise vs Temperature, °C / °F for Chloroprene, Butadiene, Isoprene. Right axis: Lb-mass/(ft) (s).
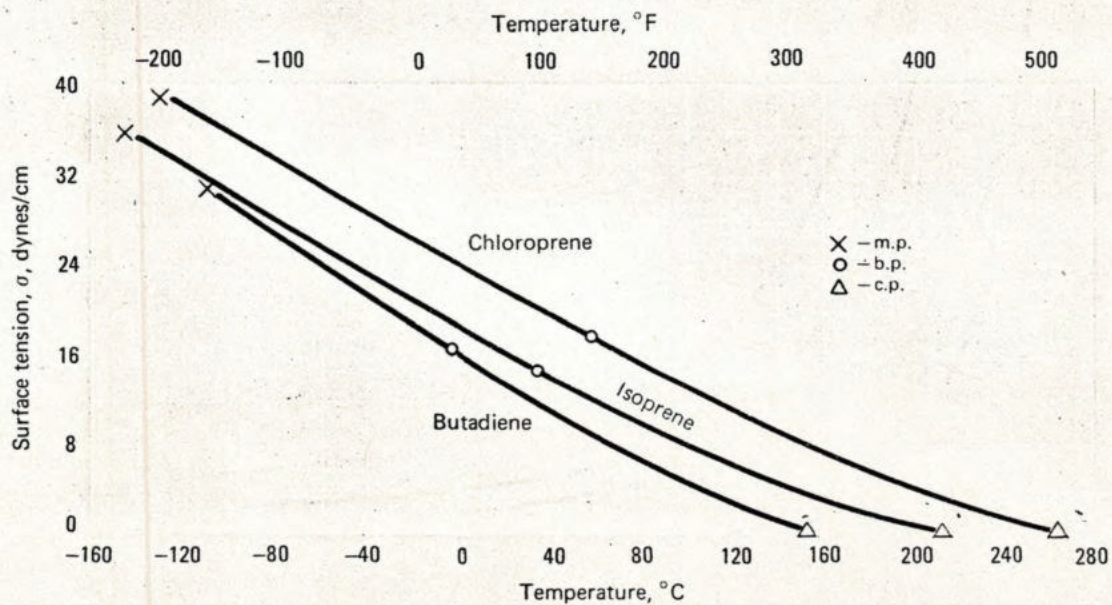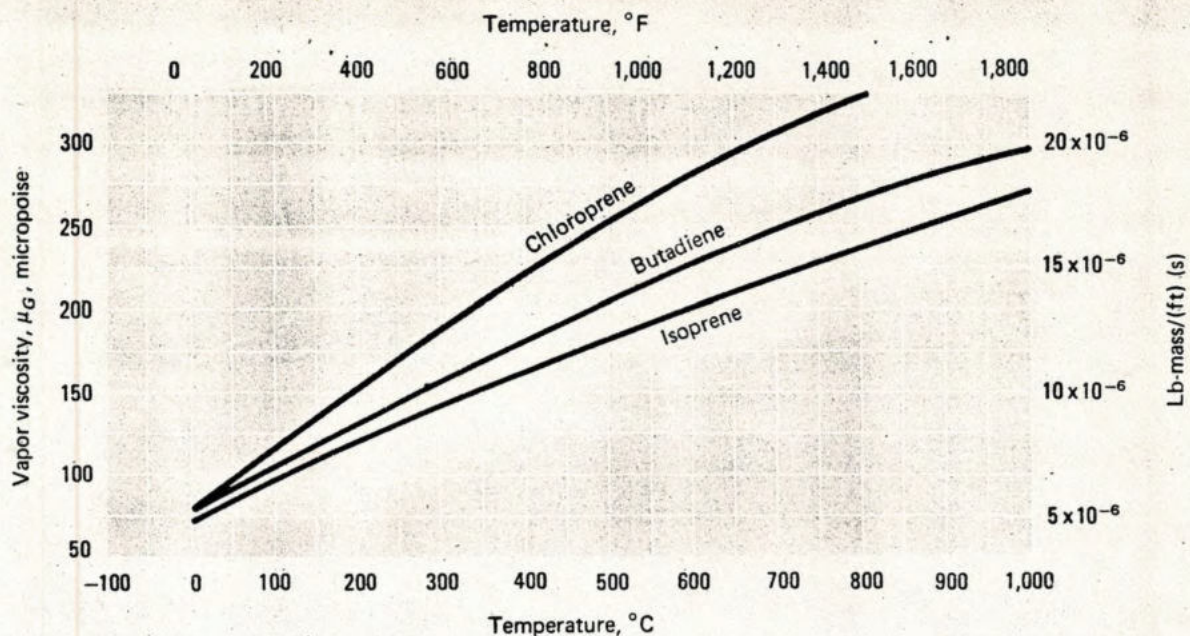
Vapor viscosity			Fig. 7

Fig. 18–7	Temperature range, °C		References
	0–500	500–1,000	
Butadiene	☑	☐	14, 546, 586, 637
Isoprene	☐	☐	14
Chloroprene	☐	☐	14

Liquid viscosity			Fig. 8

Fig. 18–8	Temperature range, °C		References
	m.p.–b.p.	b.p.–c.p.	
Butadiene	☑	☑	253, 546
Isoprene	☑	☐	9, 620, 637, 545
Chloroprene	☑	☐	4, 620, 632

Temperature, °F

Fig. 8 Liquid viscosity chart: Liquid viscosity, μ_L, centipoise vs Temperature, °C / °F for Isoprene, Chloroprene, Butadiene. X – m.p.; O – b.p.; △ – c.p.

Temperature, °F (top chart)

Temperature, °F
0 200 400 600 800 1,000 1,200 1,400 1,600 1,800

Vapor thermal-conductivity, k_G, cal/(s) (cm) (°C)

3.5 × 10⁻⁴
3.0 × 10⁻⁴
2.5 × 10⁻⁴
2.0 × 10⁻⁴
1.5 × 10⁻⁴
1.0 × 10⁻⁴
0.5 × 10⁻⁴
0

Btu/(h) (ft) (°F)
0.08
0.06
0.04
0.02
0

Butadiene
Isoprene
Chloroprene

Temperature, °C
−100 0 100 200 300 400 500 600 700 800 900 1,000

Vapor thermal conductivity			Fig. 9
Fig. 18–9	Temperature range, °C		References
	0–500	500–1,000	
Butadiene	◨	☐	586, 625, 637
Isoprene	◨	☐	637
Chloroprene	◨	☐	4, 620

Liquid thermal conductivity			Fig. 10
Fig. 18–10	Temperature range, °C		References
	m.p.–b.p.	b.p.–c.p.	
Butadiene	☐	☐	481,
Isoprene	◨	☐	445, 646
Chloroprene	☐	☐	481

Temperature, °F (bottom chart)

Temperature, °F
−200 −100 0 100 200 300 400 500

Liquid thermal conductivity, k_L, cal/(s) (cm) (°C)

4.8 × 10⁻⁴
4.0 × 10⁻⁴
3.2 × 10⁻⁴
2.4 × 10⁻⁴
1.6 × 10⁻⁴
0.8 × 10⁻⁴
0

Btu/(h) (ft) (°F)
0.12
0.10
0.08
0.06
0.04
0.02
0

Isoprene
Chloroprene
Butadiene

✕ — m.p.
○ — b.p.
△ — c.p.

Temperature, °C
−160 −120 −80 −40 0 40 80 120 160 200 240 280
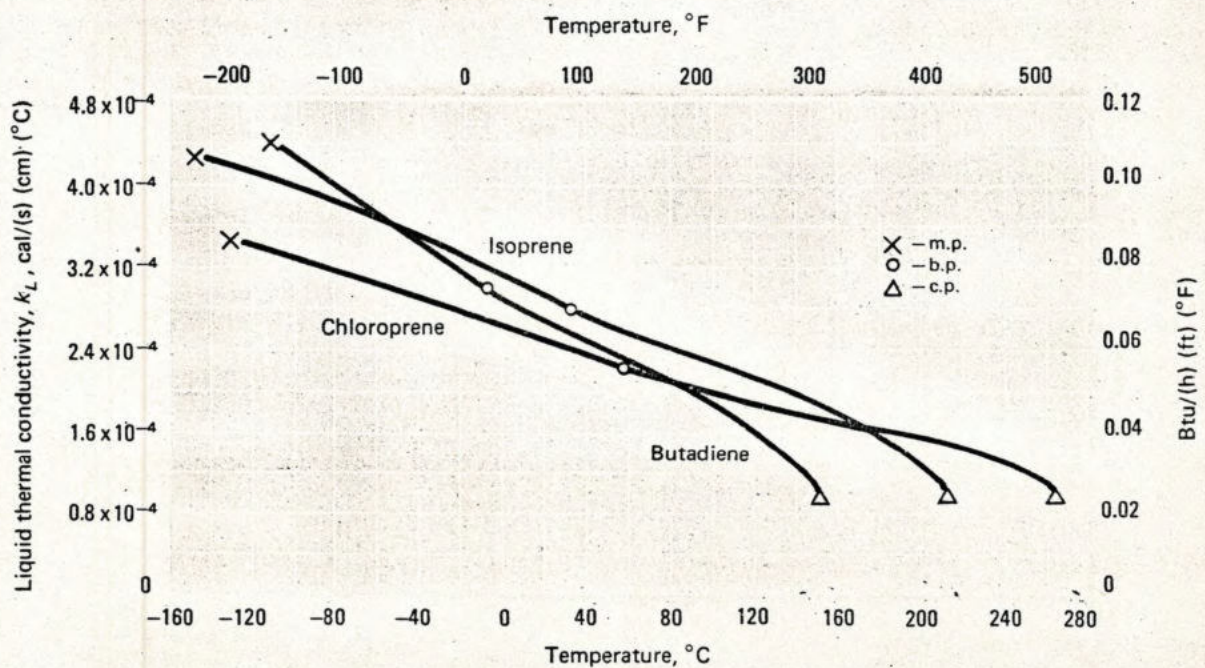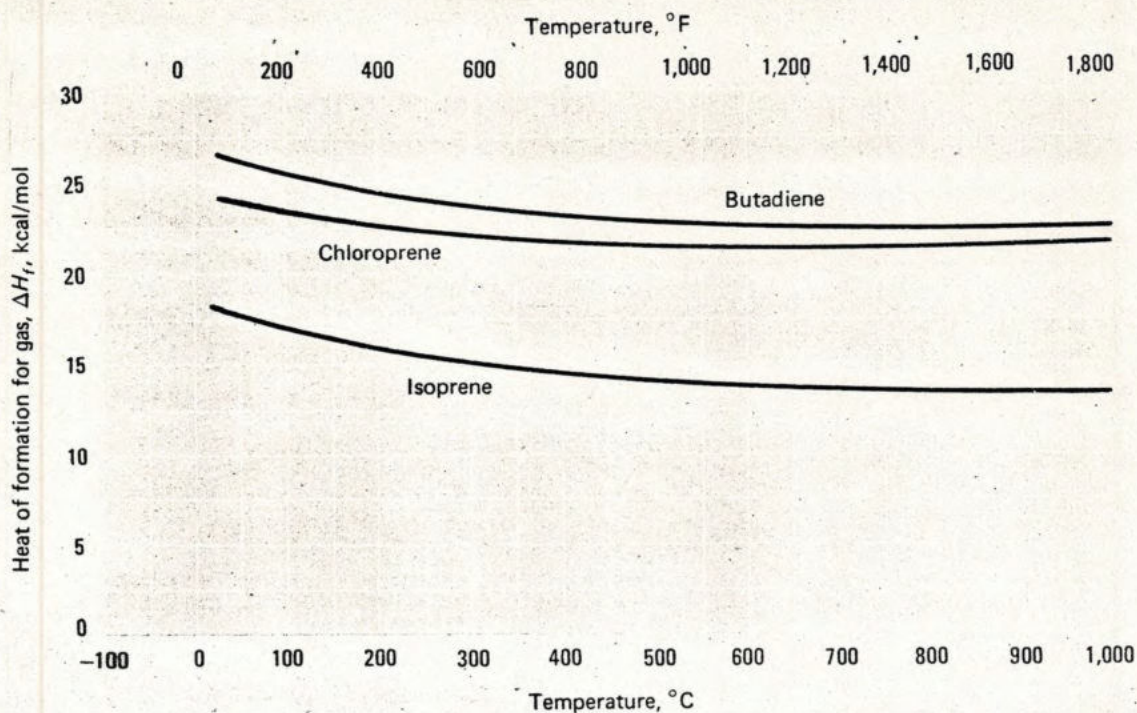
Temperature, °F

Fig. 11 — Heat of formation for gas

Fig. 18–11	Temperature range, °C		References
	0–500	500–1,000	
Butadiene	◪	◪	14, 15, 417, 630, 636
Isoprene	◪	◪	14, 15, 417, 636
Chloroprene	☐	☐	14

Fig. 18–12	Temperature range, °C		References
	0–500	500–1,000	
Butadiene	◪	◪	14, 15, 417, 630, 636
Isoprene	◪	◪	14, 15, 417, 636
Chloroprene	☐	☐	14

Heat of formation for gas — Fig. 11

Free energy of formation for gas — Fig. 12
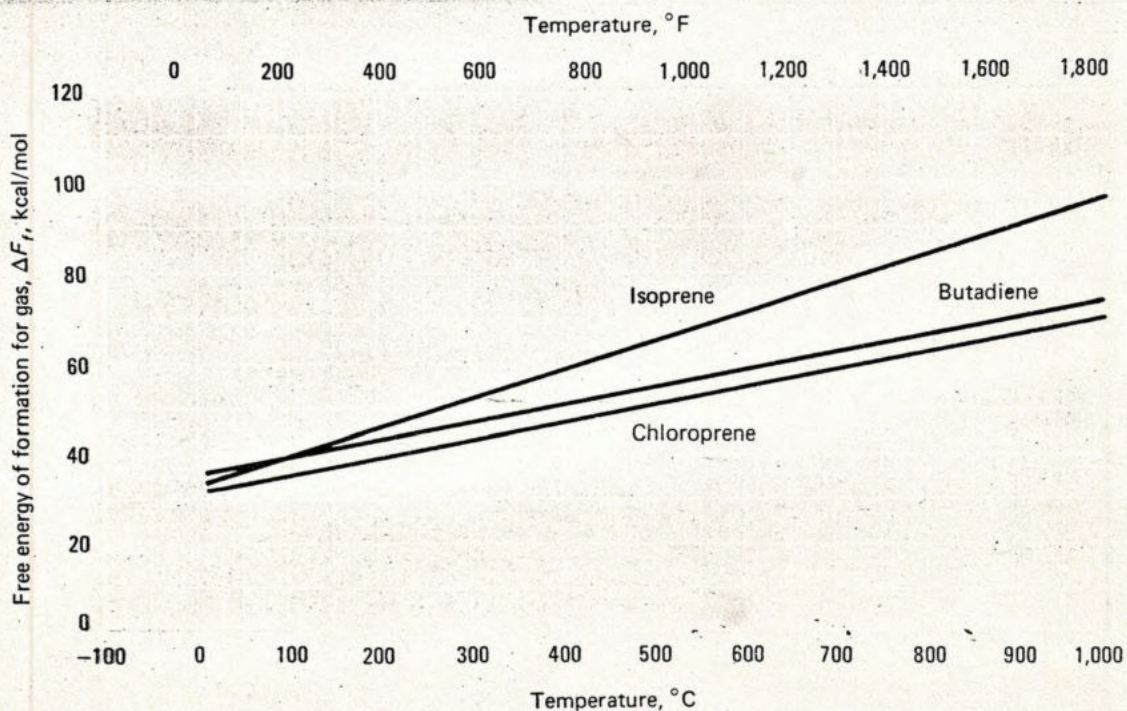
Surface Tension—Fig. 18—6

Surface tension values for each diolefin were estimated with the Bird and Brock correlation (Eq. 16—4). Unfortunately, experimental data are lacking for a direct comparison with estimated results. However, the estimated values did compare favorably with the tabulated (also calculated) values of Dreisbach [3] for butadiene and isoprene. Testing of the correlation with 84 different nonpolar organic chemicals produced an average deviation of 3% [14].

Viscosity—Fig. 18—7, 18—8

The modified Stiel and Thodos correlation (Eq. 16—5a and 16—5b) was selected to extend the limited experimental gas-viscosity data for butadiene. Testing of the modified correlation with the experimental data produced favorable results, with an average deviation of 1%.

In the absence of experimental data for the remaining diolefins, gas-viscosity values at atmospheric pressure were estimated for isoprene and chloroprene with the modified Stiel and Thodos correlation. The nonpolar form (Eq. 16—5a and 16—5b) was used for isoprene, and the polar form (Eq. 15—3) was used for chloroprene.

The Guzman-Andrade equation (Eq. 1—6) was used effectively to extrapolate liquid-viscosity data for each diolefin and for complete coverage of the saturated-liquid phase. The curve for chloroprene was approximated by going through the single data point with the same general slope as the other two olefins. Experimental and predicted values agreed. Average deviations were less than 2% for butadiene and isoprene.

Thermal Conductivity— Fig. 18—9, 18—10

Gas-phase thermal conductivity values at atmospheric pressure were extended beyond the range of the experimental data with the modified Misic and Thodos correlation (Eq. 12—2a and 12—2b). Correlation values and experimental data were reasonably close. Average deviations: butadiene, 1.1%; isoprene, 5.6%; and chloroprene, 19.2%. Greatest deviations resulted from limited data.

Liquid-phase thermal conductivity values for isoprene were correlated and extended with the modified Stiel and Thodos relation (Eq. 10—3). The relation correlated the experimental data extremely well, with an average deviation of only 2.4%.

Liquid thermal-conductivity values near the boiling point for butadiene and chloroprene were estimated with the Pachaiyappan and Naidyanathan method (Eq. 16—7). These values were then extended with the modified Stiel and Thodos relation (Eq. 10—3) to attain complete coverage of the saturated-liquid phase. Application of the estimation method to isoprene near the boiling point produced only fair agreement of calculated and experimental values (16.5% deviation). Testing of other estimation methods [14] yielded even higher deviations. The results for butadiene and chloroprene are intended to represent correct order-of-magnitude values.

Heat and Free Energy of Formation— Fig. 18—11, 18—12

The results of API-44 [417] and Stiel, Westrum and Sinke [15] were selected for heat and free energy of formation of the ideal gas for butadiene and isoprene. The agreement of these values and others from additional sources is very good; maximum respective deviations are below 0.44 and 0.02 kcal/mol.

Heat-of-formation values for chloroprene were estimated with the modified Verma and Doraiswamy method [14], which is based on group contribution:

$$\Delta H_f = A + BT \qquad (18—2)$$

where ΔH_f = ideal-gas heat of formation, kcal/mol; T = temperature, °K; and A and B are characteristic constants based on atomic groups ($-CH_3$, $=CH_2$, $-Cl$, etc.). Tabulated values of A and B are given in Reid and Sherwood [14].

Application of the modified method to butadiene and isoprene yielded agreement of estimated and experimental values; average deviations were 0.3 and 1.6%. The results for chloroprene are intended to represent correct order-of-magnitude values, with possible greater deviation.

The modified Van Krevelen method [14], which is based on atomic groups making up the compound, was selected for estimating values of free energy of formation for chloroprene:

$$\Delta F_f = A + BT \qquad (18—3)$$

where ΔF_f = ideal-gas free energy of formation, kcal/mol; T = temperature, °K. The constants A and B are evaluated from atomic group contributions; tabulated values are given in Reid and Sherwood [14].

Testing of the method with butadiene and isoprene produced favorable agreement of estimated and experimental values, with average deviations being 1.2 and 0.7%. The values for chloroprene may not be that accurate; however, the results are intended to represent correct order-of-magnitude values.

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