Olefins: C_2H_4, C_3H_6, 1—C_4H_8

PHYSICAL & THERMODYNAMIC PROPERTIES 10

Major physical and thermodynamic properties—based on experimental data and correlations—are presented for ethylene, propylene and 1-butene.

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Olefins are major feedstocks in the chemical process industries for the production of large-volume chemicals: *ethylene* for such important chemicals as ethyl alcohol, ethylene oxide, ethylene glycol, polystyrene and polyethylene; *propylene* for acetone, isopropyl alcohol, isopropyl benzene, isopropyl halides and polypropylene; and *1-butene* for a variety of organic compounds, such as alkyl sulfonates, aldehydes, alcohols and polymers.

Critical Properties—Table 10—1

Experimental data for the critical constants of ethylene, propylene and 1-butene are readily available [*3,4,10,14,-246,410,413,415,440*]. Critical temperatures and pressures from the various sources agree with variations of 3% and 2%, or less. Variations for critical volume are 1% or less, except for ethylene, 7.2%.

Heat of Vaporization—Fig. 10—1

Heat-of-vaporization data were extended for full liquid-phase coverage by means of Watson's correlation (Eq. **1**—1). Deviations from the mean of the results among the various data sources and correlation values are less than 2 to 3%, in most cases, for ethylene, propylene and 1-butene.

Vapor Pressure—Fig. 10—2

The considerable vapor-pressure data have been reviewed recently by Russian investigators [*440*] and API-44 researchers [*419*]. The extensive data were extended to the melting point and below, using the Cox-Antoine relation (Eq. **1**—2) with constants from API-44 [*419*]. Deviations in most cases are less than 1%.

Heat Capacity—Fig. 10—3, 10—4

Heat capacities of the ideal gas at atmospheric pressure are available for ethylene, propylene and 1-butene. The recent results of Stull, et al. [*7,15*] and Vashchenko, et al. [*440*] were selected. Results among the various investigations agreed well, with average deviations being 2 to 3%, or less, in the majority of cases.

Available heat-capacity data cover most of the liquid state, from a few degrees above the melting point to well above the boiling point. The data were extrapolated the few degrees to the melting point from the shape of the curve. For ethylene and propylene, the results of the Russian investigators, Vashchenko, et al. [*440*] were selected for temperatures above the boiling point. For 1-butene, data above the boiling point were extended with the density relation (Eq. **1**—3, $n = 1$). Tests of the relation with available data gave results having average deviations of only 1%. In general, the results from the various sources agree, with variations from the best data fittings being less than 4% in most cases for each olefin.

Density—Fig. 10—5

Lu's generalized correlation (Eq. **2**—2) was used to extend the data for full liquid-phase coverage. The correlation results and experimental values compared favorably, with average variations of 1%, 1% and 2%, respectively, for ethylene, propylene and 1-butene.

Surface Tension—Fig. 10—6

The Othmer linear relationship (Eq. **1**—4) for log σ vs. log $(T_C - T)$ was used to extend surface-tension data. A straight line was obtained for each olefin. Results from the various literature sources agree excellently.

Viscosity—Fig. 10—7, 10—8

Vapor-viscosity data at atmospheric pressure were extended with the Flynn and Thodos correlation [*142*] for hydrocarbon gases:

$$\mu_G = 10/\xi(0.291T_r - 0.058)^{3/4} \qquad (10—1)$$

(*Text continues on p. 109*)

*To meet the author, see the Feb. 17, 1975 issue.

See Part 1 of this series, Chem. Eng., June 10, 1974, for equations starting with a boldfaced numeral "**1**"; Part 2 for those with "**2**"; etc. Part 2 appeared July 8; Part 3, Aug. 9; Part 4, Sept. 30; Part 5, Oct. 28; Part 6, Nov. 25; Part 7, Dec. 23, 1974; Part 8, Jan. 20, 1975; and Part 9, Feb. 17.

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:

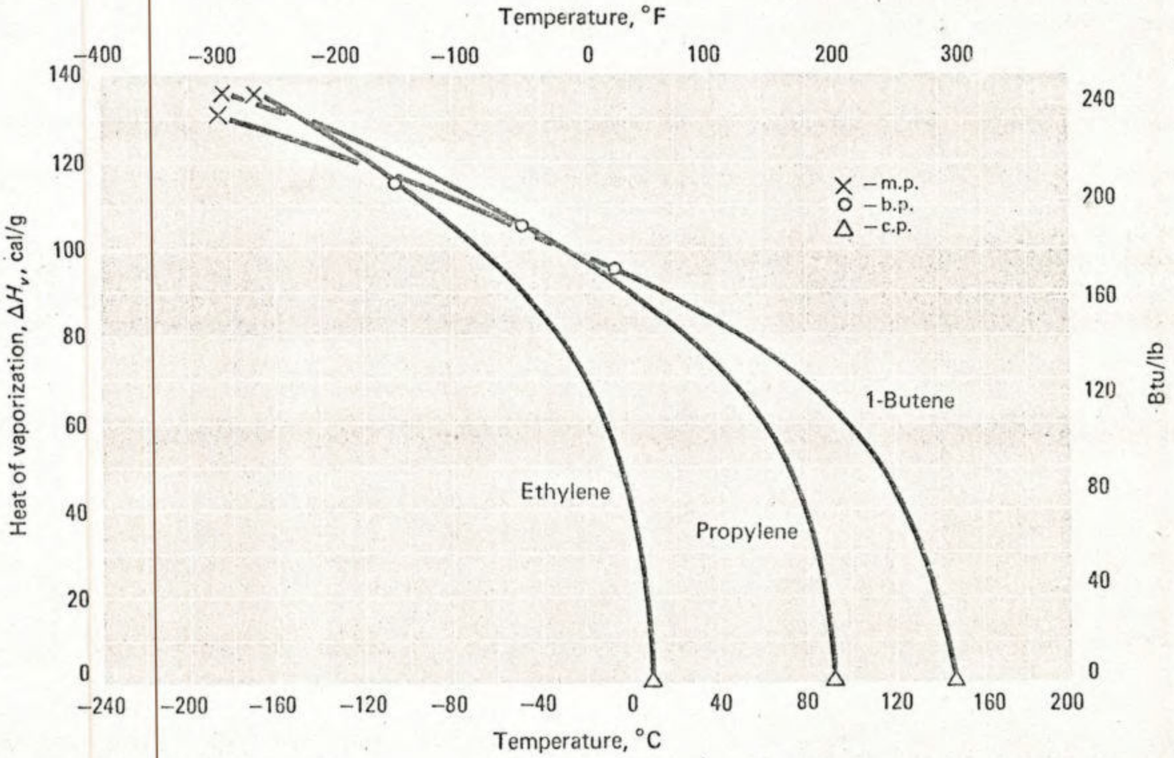
- ■ Data in this region are experimentally known.
- ◪ Experimental and correlated data used.
- □ All data in this region are correlated.

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 Major Olefins – Table 10–1

Identification	Ethylene $CH_2=CH_2$	Propylene $CH_3CH=CH_2$	1-Butene $CH_3CH_2CH=CH_2$
State (std. conditions)	Gas*	Gas*	Gas*
Molecular weight, M	28.052	42.078	56.104
Boiling point, T_b, °C	−103.7	− 47.7	− 6.3
Melting point, T_m, °C	−169.2	−185.3	−185.4
Critical temp., T_c, °C	9.9	91.9	146.2
Critical pressure, P_c, atm	50.8	45.9	39.7
Critical volume, V_c, cm^3/g-mol	132.6	181.6	240.4
Critical compressibility factor, Z_c	0.290	0.278	0.277

*Colorless.



Heat of Vaporization – Fig. 10–1

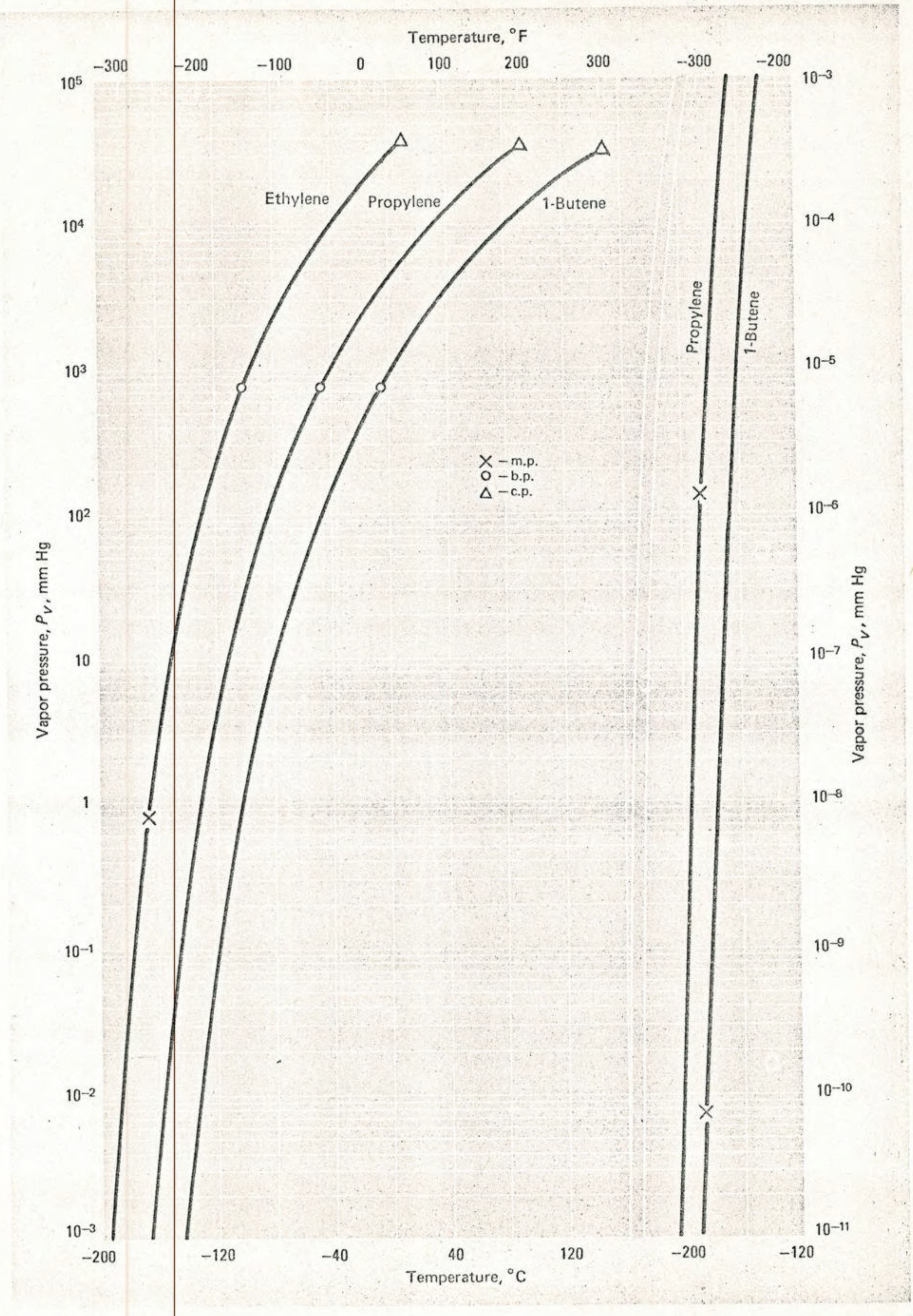
Fig. 10–1	Temperature Range		References
	m.p.–b.p.	b.p.–c.p.	
Ethylene	◪	◪	3,10,246,414,415,419,440
Propylene	◪	◪	3,10,246,414,415,419,440
1-Butene	◪	◪	3,10,246,414,415,419

■ Laboratory data ◪ Laboratory plus correlations □ All correlated data

Fig. 10–2	Temperature Range		References
	m.p.–b.p.	b.p.–c.p.	
Ethylene	■	■	3,4,10,246,310,411,413,415,416,417,419,436,440
Propylene	◪	■	3,4,10,246,410,413,415,416,417,419,437,440
1-Butene	◪	■	3,4,10,246,410,413,415,416,417,419,

■ Laboratory data ◪ Laboratory plus correlations □ All correlated data

Vapor Pressure – Fig. 10–2 ⟶



Temperature, °F
-300
-200
-100
0
100
200
300
-300
-200
Ethylene
Propylene
1-Butene
Propylene
1-Butene
× – m.p.
o – b.p.
Δ – 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^{-3}
10^{-4}
10^{-5}
10^{-6}
10^{-7}
10^{-8}
10^{-9}
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10^{-11}
-200
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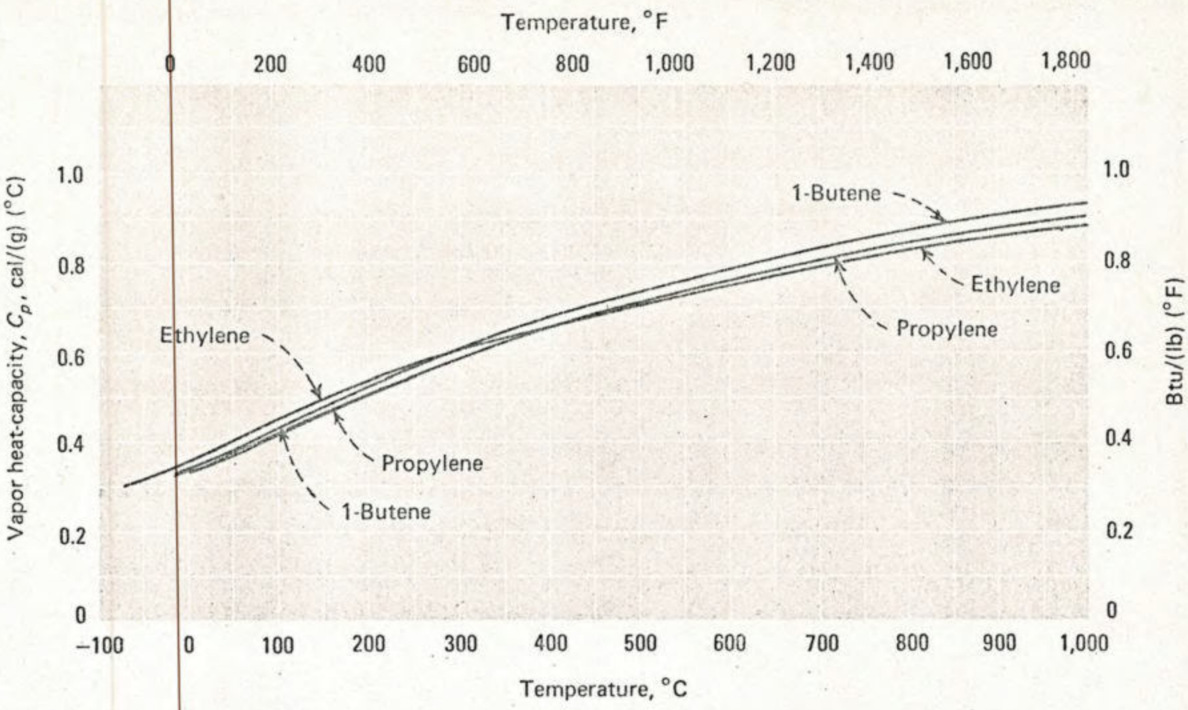
-40
40
120
-200
-120
Temperature, °C



Vapor Heat Capacity — Fig. 10–3

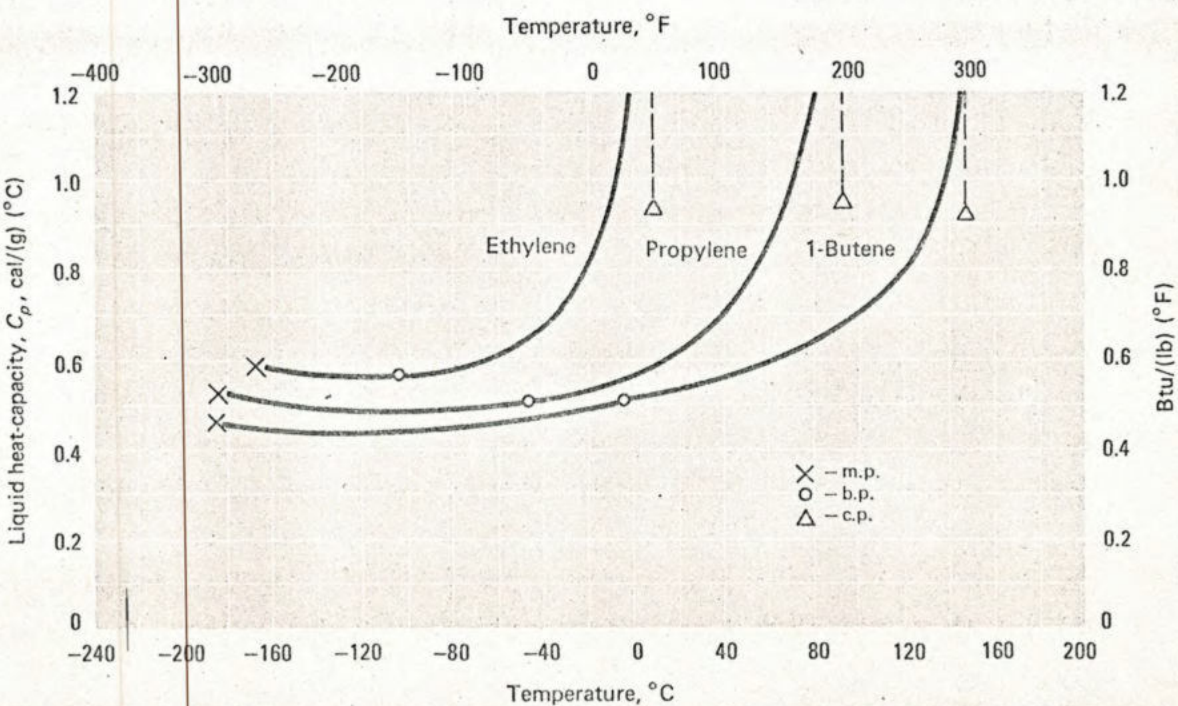
Fig. 10–3	Temperature Range		References
	m.p.–b.p.	b.p.–c.p.	
Ethylene	◪	◪	3,7,10,11,15,18,246,440
Propylene	◪	◪	3,10,15,246,440
1-Butene	◪	◪	3,10,15,246

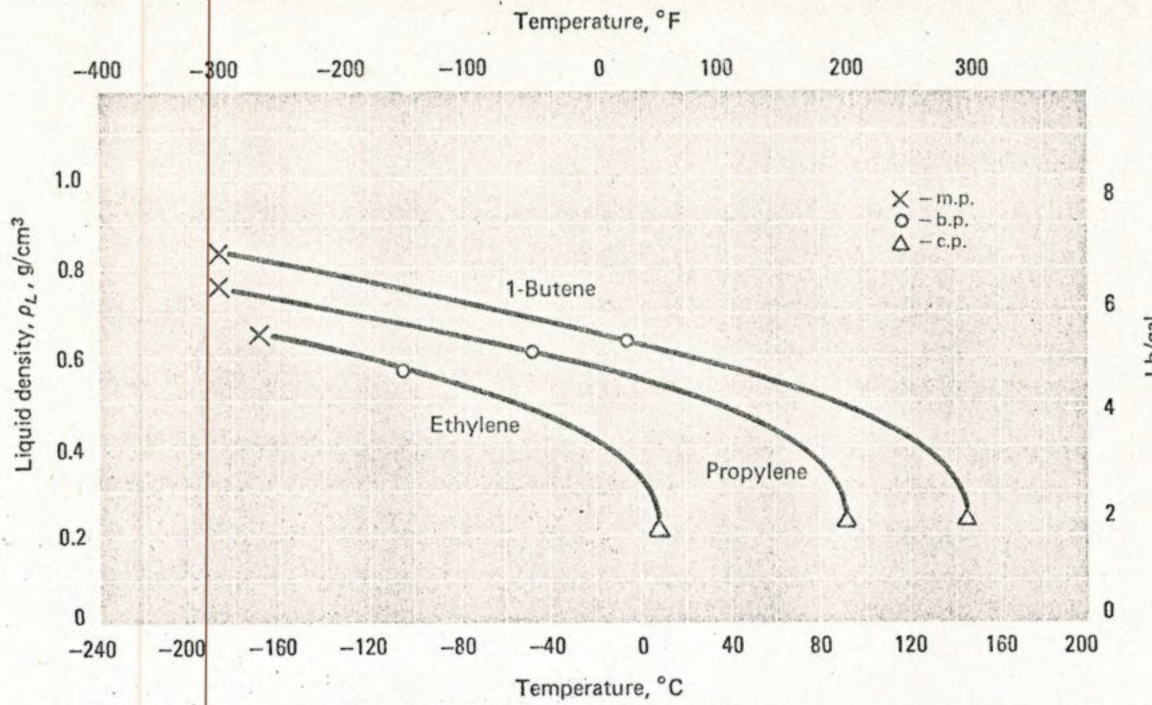
■ Laboratory data ◪ Laboratory plus correlations □ All correlated data

Fig. 10–4	Temperature Range		References
	m.p.–b.p.	b.p.–c.p.	
Ethylene	◪	◪	19,246,415,425,439,440
Propylene	◪	◪	10,246,415,425,439,440
1-Butene	◪	◪	10,246,415,425,441

■ Laboratory data ◪ Laboratory plus correlations □ All correlated data

Liquid Heat Capacity — Fig. 10–4





Liquid Density – Fig. 10–5

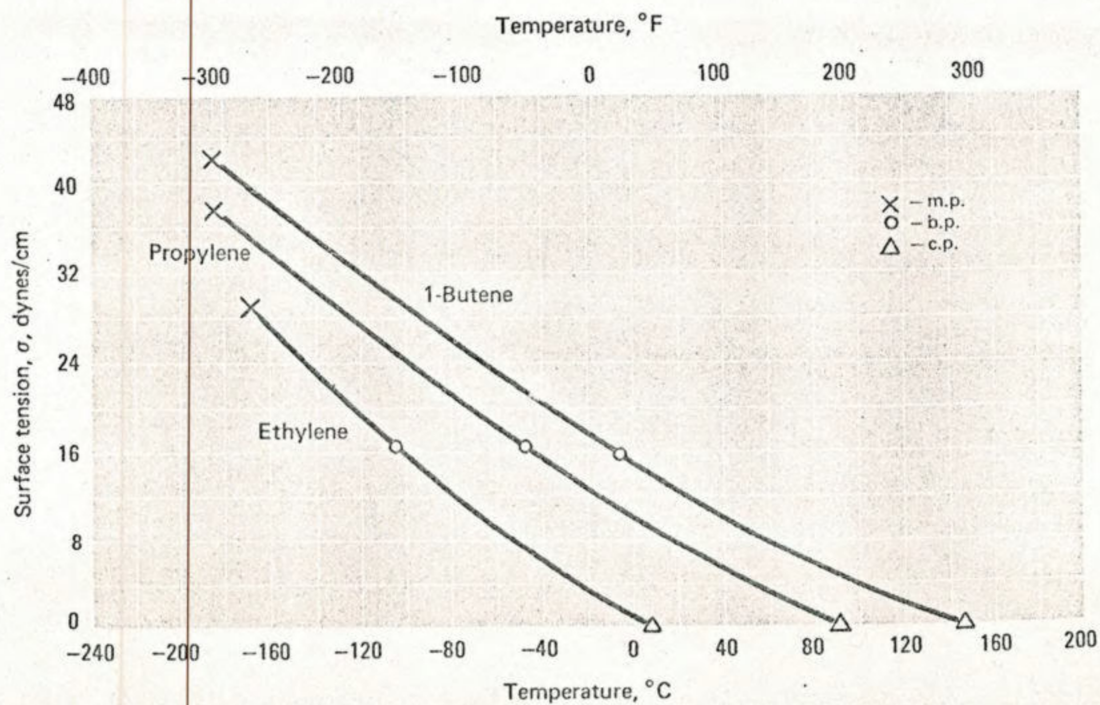
Fig. 10–5	Temperature Range: m.p.–b.p.	Temperature Range: b.p.–c.p.	References
Ethylene	Laboratory plus correlations	Laboratory data	3,9,10,246,410,413,415,420,436,440
Propylene	Laboratory plus correlations	Laboratory data	3,10,246,410,415,437,410
1-Butene	Laboratory plus correlations	Laboratory data	3,10,246,410,415

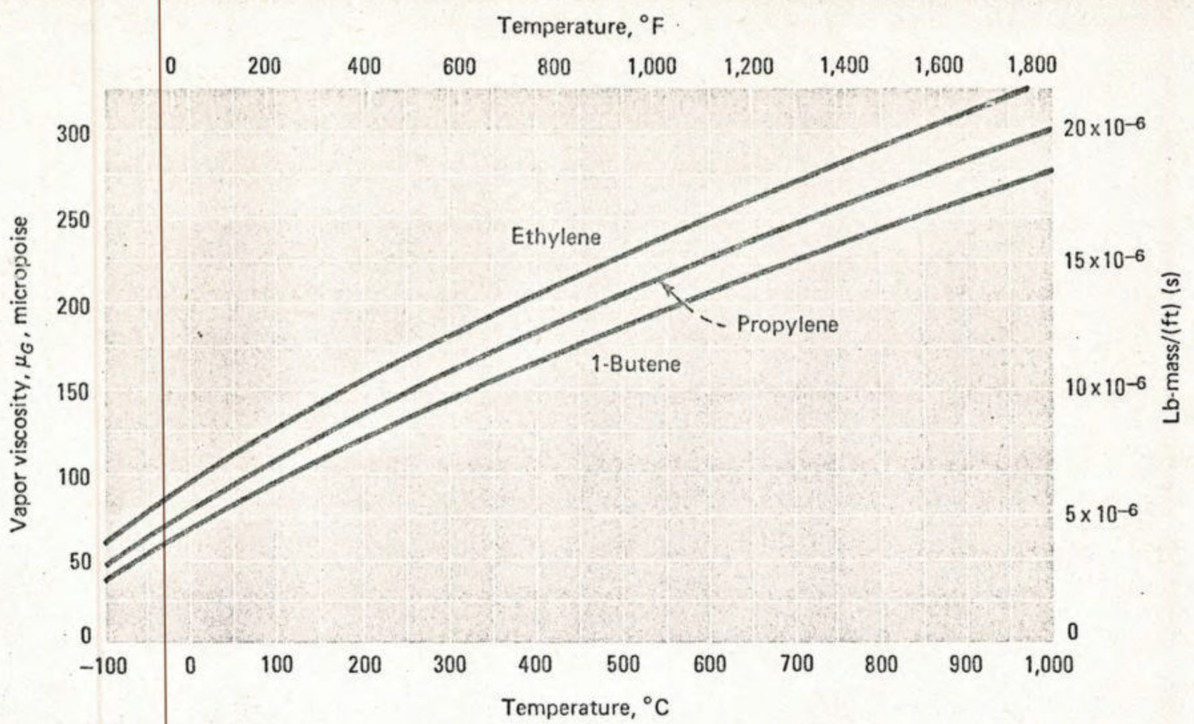
■ Laboratory data ◪ Laboratory plus correlations □ All correlated data

Fig. 10–6	Temperature Range: m.p.–b.p.	Temperature Range: b.p.–c.p.	References
Ethylene	Laboratory plus correlations	Laboratory plus correlations	4,79,246
Propylene	Laboratory plus correlations	Laboratory plus correlations	10,79,246
1-Butene	Laboratory plus correlations	Laboratory plus correlations	10,79,246

■ Laboratory data ◪ Laboratory plus correlations □ All correlated data

Surface Tension – Fig. 10–6





Vapor Viscosity – Fig. 10–7

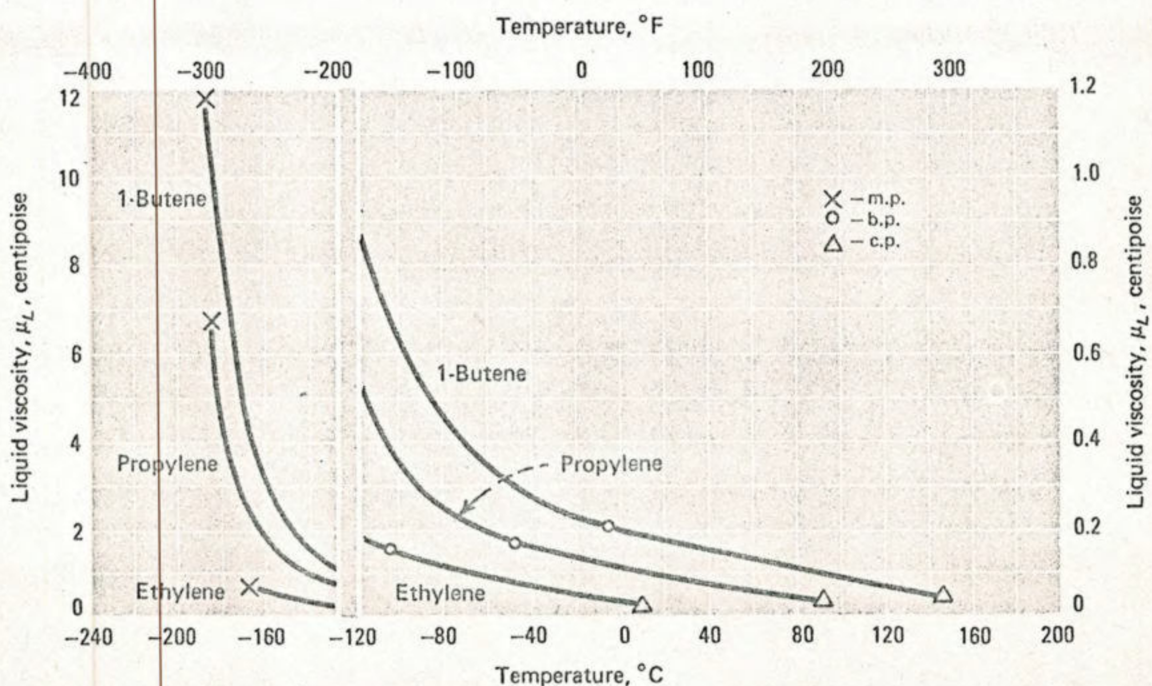
Fig. 10–7	Temperature Range		References
	m.p.–b.p.	b.p.–c.p.	
Ethylene	■	□	10,18,246,409,413,416,421,427,429,432,440,442
Propylene	■	◪	10,246,409,413,416,422,429,432,440,442
1-Butene	◪	□	10,246,413,429,433,442

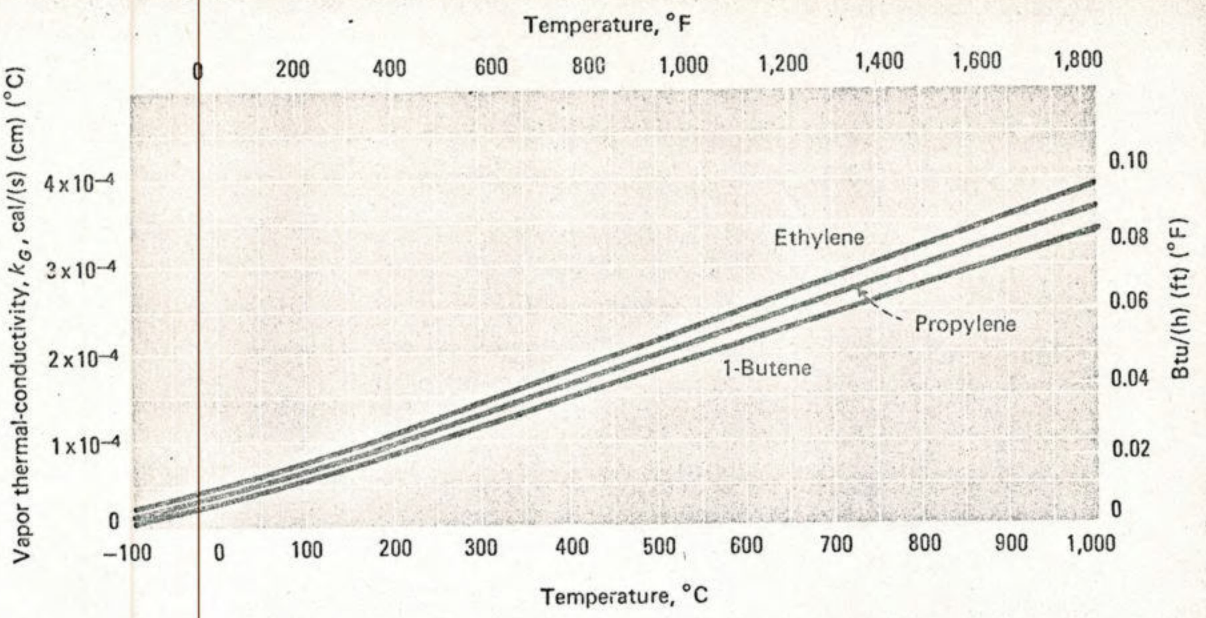
■ Laboratory data ◪ Laboratory plus correlations □ All correlated data

Fig. 10–8	Temperature Range		References
	m.p.–b.p.	b.p.–c.p.	
Ethylene	◪	■	14,246,409,415,421,440
Propylene	◪	■	246,422,434,438,440
1-Butene	◪	□	14,409

■ Laboratory data ◪ Laboratory plus correlations □ All correlated data

Liquid Viscosity – Fig. 10–8





Vapor Thermal Conductivity – Fig. 10–9

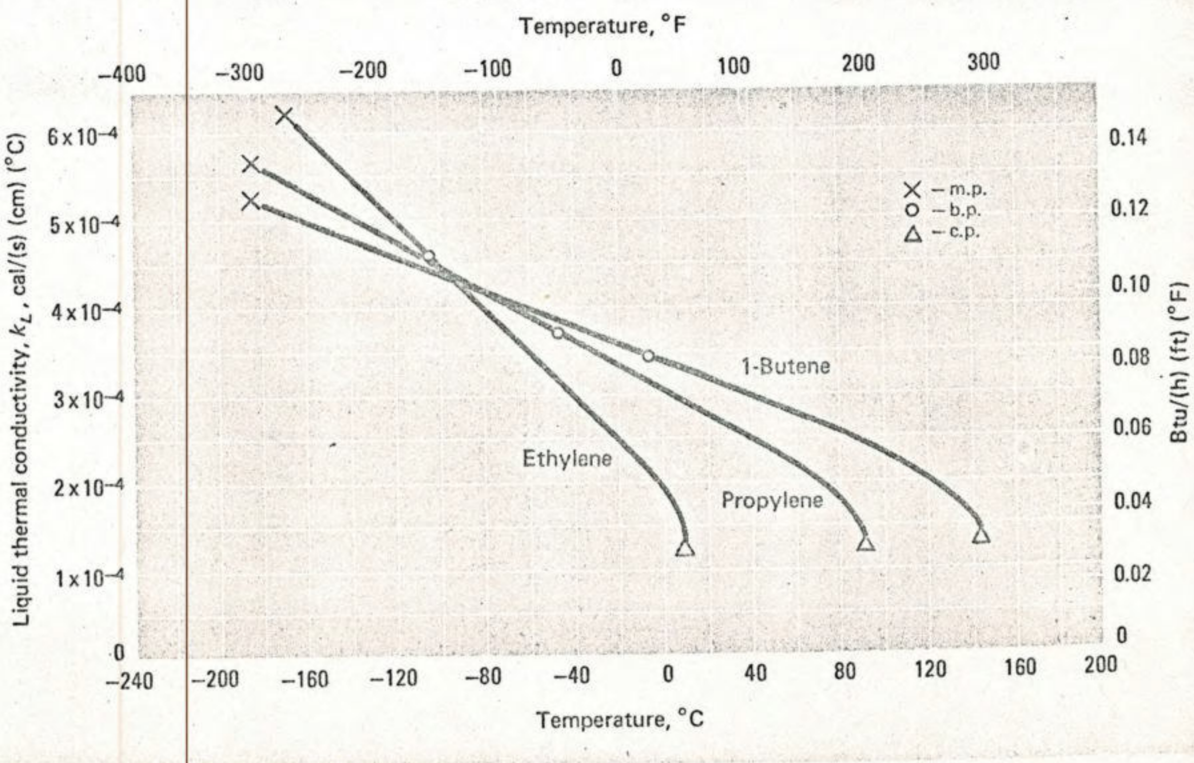
Fig. 10–9	Temperature Range		References
	m.p.–b.p.	b.p.–c.p.	
Ethylene	◪	☐	18,19,84,246,421,429,431,440,443
Propylene	◪	☐	246,422,429,430,435,440,443
1-Butene	◪	☐	246,429,433,435,443

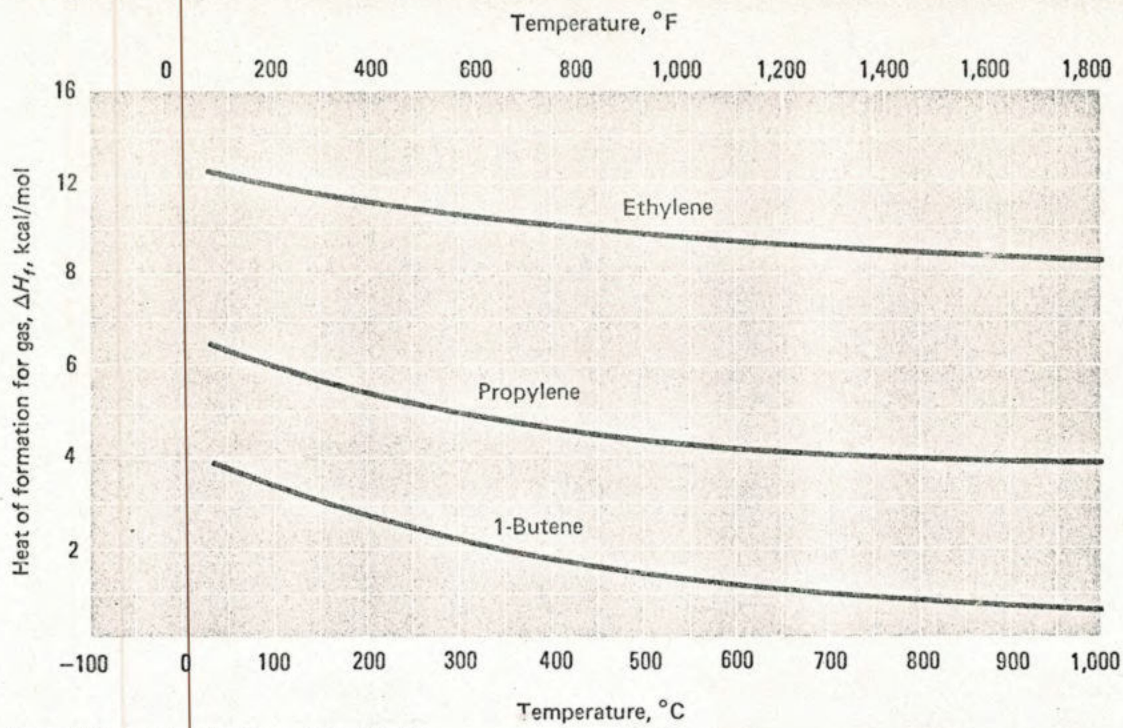
■ Laboratory data ◪ Laboratory plus correlations ☐ All correlated data

Fig. 10–10	Temperature Range		References
	m.p.–b.p.	b.p.–c.p.	
Ethylene	◪	■	14,19,84,246,421,440
Propylene	◪	■	14,246,422,426,430,440
1-Butene	☐	☐	14,246

■ Laboratory data ◪ Laboratory plus correlations ☐ All correlated data

Liquid Thermal Conductivity – Fig. 10–10





Heat of Formation for Gas – Fig. 10–11

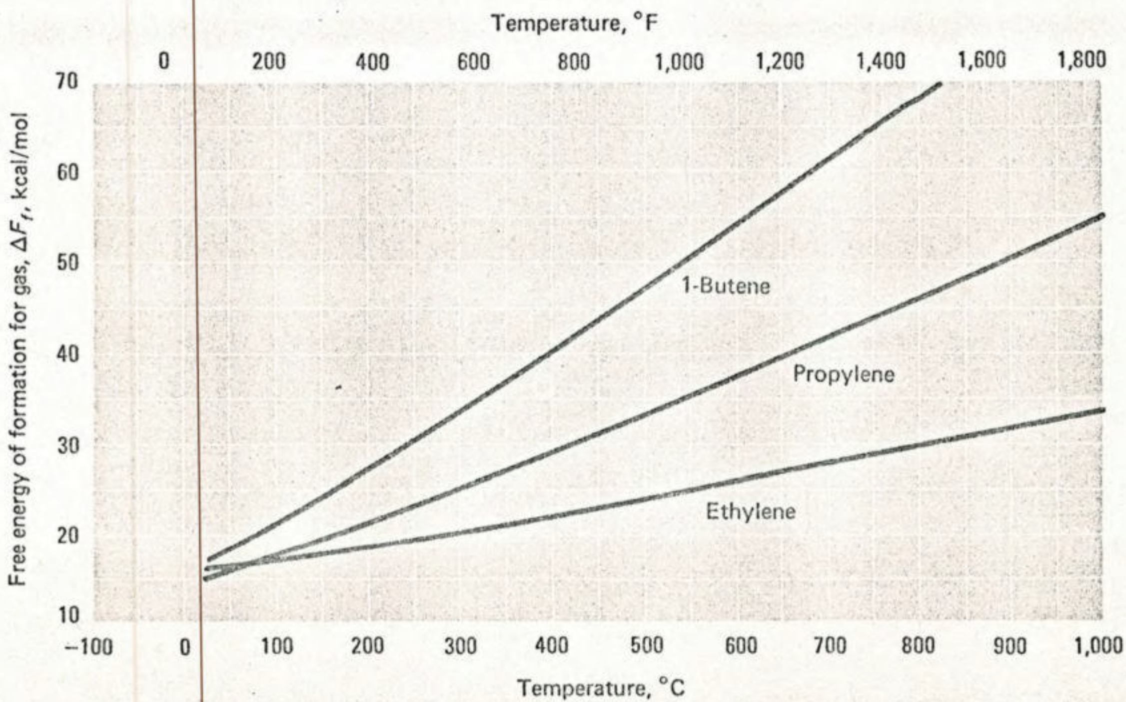
Fig. 10–11	Temperature Range		References
	m.p.–b.p.	b.p.–c.p.	
Ethylene	Laboratory plus correlations	Laboratory plus correlations	7,15
Propylene	Laboratory plus correlations	Laboratory plus correlations	15
1-Butene	Laboratory plus correlations	Laboratory plus correlations	15

Legend: Laboratory data; Laboratory plus correlations; All correlated data

Fig. 10–12	Temperature Range		References
	m.p.–b.p.	b.p.–c.p.	
Ethylene	Laboratory plus correlations	Laboratory plus correlations	7,15
Propylene	Laboratory plus correlations	Laboratory plus correlations	15
1-Butene	Laboratory plus correlations	Laboratory plus correlations	15

Legend: Laboratory data; Laboratory plus correlations; All correlated data

Free Energy of Formation for Gas – Fig. 10–12



In Eq. (10—1), μ_G = gas viscosity at low pressure (1 atm), micropoise; $\xi = T_c^{1/6}/M^{1/2}P_c^{2/3}$; and T_r = reduced temperature, T/T_c.

More recent studies by U.S. [*246,421,422*] and Russian [*433,440*] investigators, including the Chapman-Enskog relation (Eq. 4—1), have yielded identical results. The values from the correlation and experimental data agree well, with deviations of 2.2%.

Bonscher, Shipman and Yen [*421,422*] and Vashchenko, et al. [*440*] have recently analyzed liquid-viscosity data and presented results covering most of the liquid phase for ethylene and propylene. Limited data are available for 1-butene [*14,409*]. The Guzman-Andrade relation (Eq. 1—6) for log viscosity vs. reciprocal temperature was used for full liquid-phase coverage. Two straight lines, with the slope change at reduced temperature of 0.826, fitted the data for ethylene and propylene. Two straight lines were also used for 1-butene, with the slope change at the same reduced temperature. Variations between the relation and data average 4%.

Thermal Conductivity—Fig. 10—9, 10—10

Experimental data for gas-phase thermal conductivity at atmospheric pressure were extended with the Misic and Thodos correlation [*14,443*] for hydrocarbon gases:

$$k_G = (C_p/\gamma)10^{-6}(14.52T_r - 5.14)^{2/3} \qquad (10\text{—}2)$$

In Eq. (10—2), k_G = gas thermal conductivity at low pressure (1 atm), cal/(cm)(sec)(°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.

The correlation results agree well with experimental data and the recent results of U.S. [*421,422*] and Russian [*440*] investigators. Average deviations of correlation values and data were 3% or less.

Bonscher, Shipman and Yen [*421,422*] and Vashchenko, et al. [*440*] have recently reviewed liquid-thermal-conductivity data. Their results in the data range were selected for ethylene and propylene.

Liquid thermal conductivity for 1-butene was estimated with the modified Stiel and Thodos [*14*] relation:

$$k_L = f(\rho_r)/\gamma Z_c^5 + k_G \qquad (10\text{—}3)$$

In Eq. (10—3), k_L = liquid thermal conductivity, cal/(cm)(sec)(°C); k_G = gas thermal conductivity at low pressure (1 atm), cal/(cm)(sec)(°C); $\gamma = T_c^{1/6}M^{1/2}/P_c^{2/3}$; and ρ_r = reduced density, ρ/ρ_c.

The term $f(\rho_r)$ was constructed from a plot of $(k_L - k_G)\gamma Z_c^5$ vs. ρ_r, using the available liquid data for ethylene and propylene. Results from the relation agree well with data, with average deviations of 5% or less. The deviations are probably 10 to 20% for 1-butene.

Heat and Free Energy of Formation—Fig. 10—11, 10—12

The results of Stull, Westrum and Sinke [*15*] were selected for heat and free energy of formation of the ideal gas for ethylene, propylene and *1*-butene. #

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