Methanol, ethanol, propanol, and butanol

Data for these normal primary alcohols continues our series on physical and thermodynamic properties.

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☐ Methanol, ethanol, propanol, and butanol have widespread applications in the chemical process industries. Methanol is used to make formaldehyde, methacrylate, methylamine and methyl halide; it is also used in antifreeze and aviation fuel injection. From ethanol come intermediates and derivatives used in elastomers, drugs, beverages, dyes, detergents and cosmetics. Propanol appears in dyes, plating compounds, nail polishes and brake fluids. Butanol helps make aldehydes, esters, detergents and dehydrating agents. All are used in various solvents.

Critical Properties—Table 20—1

Critical temperatures, pressures and volumes for methanol, ethanol, propanol and butanol were taken from the literature [4, 9, 14, 574, 646, 666, 672, 692, 693, 697]. The reported experimental values are generally consistent for each alcohol.

Heat of Vaporization—Fig. 20—1

To achieve full coverage of the saturated liquid phase, heat of vaporization data were extended with the Watson correlation (Eq. 1—1, $n = 0.40$).†

*To meet the authors, see *Chem. Eng.*, May 12, 1975, p. 97 and August 19, 1974, p. 106.

†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 the Jan. 19, 1976 issue (Part 17) lists publication dates of Parts 1 through 16. Parts 18 and 19 appeared in the March 1 and April 12 issues.

Vapor Pressure—Fig. 20—2

Vapor pressure information abounds for each alcohol. The data were correlated and extended with the Cox-Antoine relation (Eq. 1—2). Several straight lines were needed for the saturated liquid. Results reported from the various sources are largely in agreement.

Heat Capacity—Fig. 20—3, 20—4

Several sources offer heat capacities for the ideal gases at low pressure. These values agree substantially, and deviations range from 2.5 to 10.0%. The widest deviations occur at low temperatures. For saturated vapor near the boiling point, the results of Stromsoe et al. [*688*] are recommended.

Liquid heat capacity data were correlated and extrapolated with the density-heat capacity relation (Eq. 1—3 with $n = 2$ for methanol and $n = 3$ for the other alcohols). Correlation values are reasonably close to experimental ones. The average deviations for methanol, ethanol, propanol, and butanol are 3.4, 4.4, 3.2 and 3.3%.

Density—Fig. 20—5

Available liquid-density information covers the entire temperature range from boiling point to critical point. For temperatures below the boiling point, the data were correlated and extended with the modified Rackett

Text continues on p. 127

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.

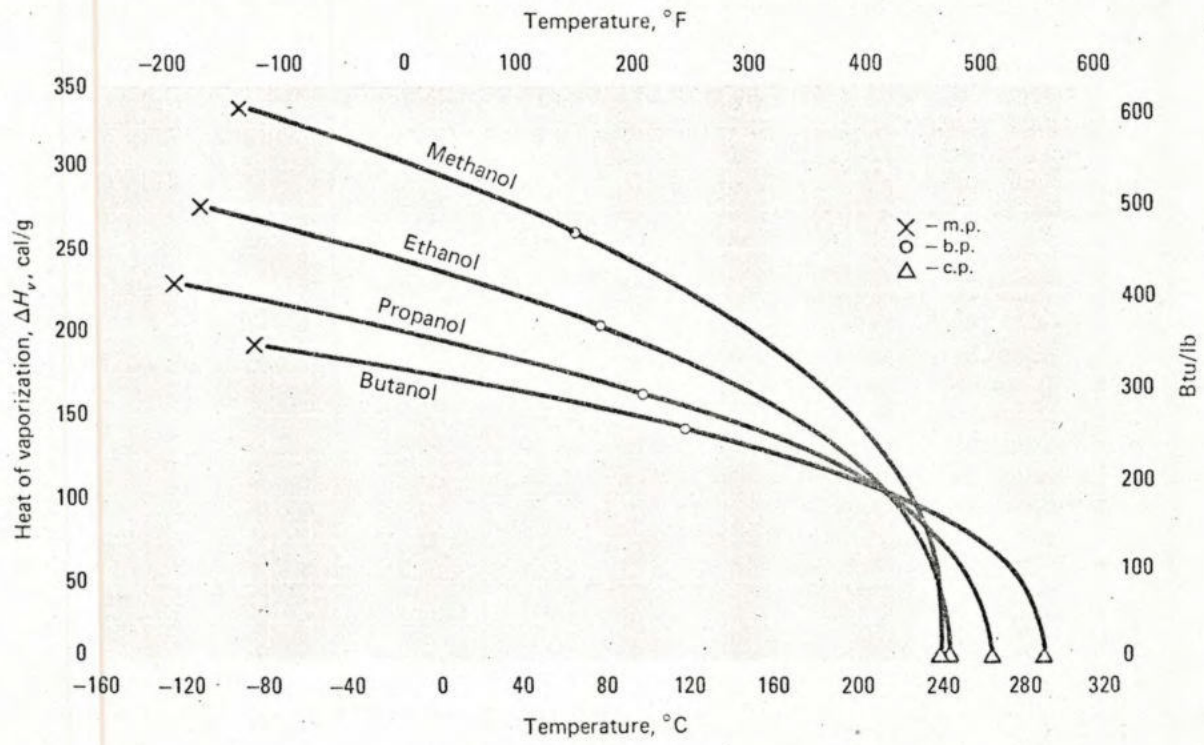
The shaded squares denote the following:

- 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 alcohols — Table I

Identification	Methanol CH_3OH	Ethanol C_2H_5OH	*n*-Propanol C_3H_7OH	*n*-Butanol C_4H_9OH
State (std. conditions)	Liquid	Liquid	Liquid	Liquid
Molecular weight, M	32.04	46.07	60.09	74.12
Boiling point, T_b, °C	64.7	78.3	97.2	117.7
Melting point, T_m, °C	−97.6	−114.1	−126.2	−89.3
Critical temp., T_c, °C	239.4	243.1	263.6	289.8
Critical pressure, P_c, atm	79.9	63.0	51.0	43.6
Critical volume, V_c, $cm^3/g\text{-}mol$	117.8	166.9	218.5	274.5
Critical compressibility factor, Z_c	0.224	0.248	0.253	0.259

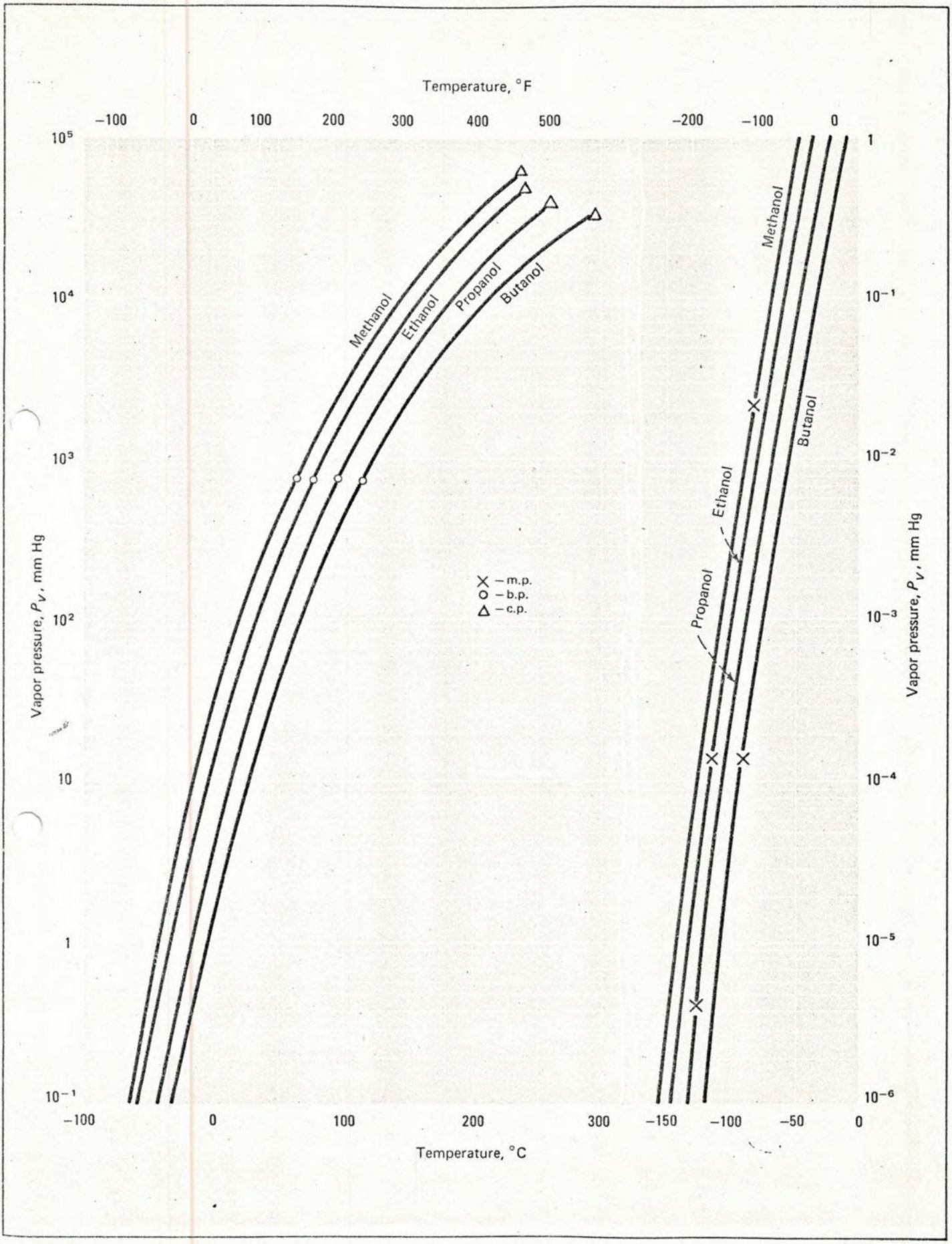


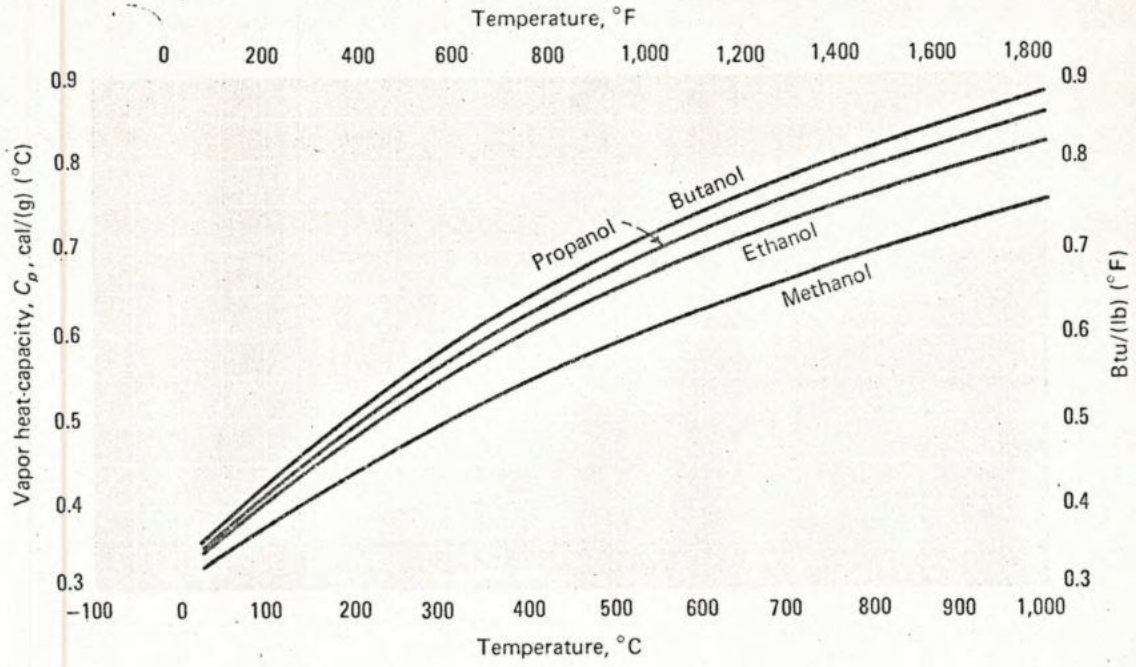
Heat of vaporization — Fig. 1

Fig. 20–1	Temperature range, °C		Reference
	m.p.–b.p.	b.p.–c.p.	
Methanol	◪	◪	4,9,15,413,646,692
Ethanol	◪	◪	4,9,15,413,646,692
Propanol	◪	◪	4,9,15,413,646,670,672,678,691,692
Butanol	◪	◪	4,9,15,413,646,692

Vapor pressure — Fig. 2

Fig. 20–2	Temperature range, °C		Reference
	m.p.–b.p.	b.p.–c.p.	
Methanol	◪	■	4,9,413,415,527,548,646,673,692
Ethanol	◪	■	4,9,413,415,527,548,646,692
Propanol	◪	■	4,9,413,415,527,548,646,666,675,678,692
Butanol	◪	■	4,413,415,527,548,646,666,675,692


Temperature, °F
−100
0
100
200
300
400
500
−200
−100
0
10^5
10^4
10^3
10^2
10
1
10^{-1}
1
10^{-1}
10^{-2}
10^{-3}
10^{-4}
10^{-5}
10^{-6}
Vapor pressure, P_v, mm Hg
Methanol
Ethanol
Propanol
Butanol
× − m.p.
○ − b.p.
△ − c.p.
−100
0
100
200
300
−150
−100
−50
0
Temperature, °C

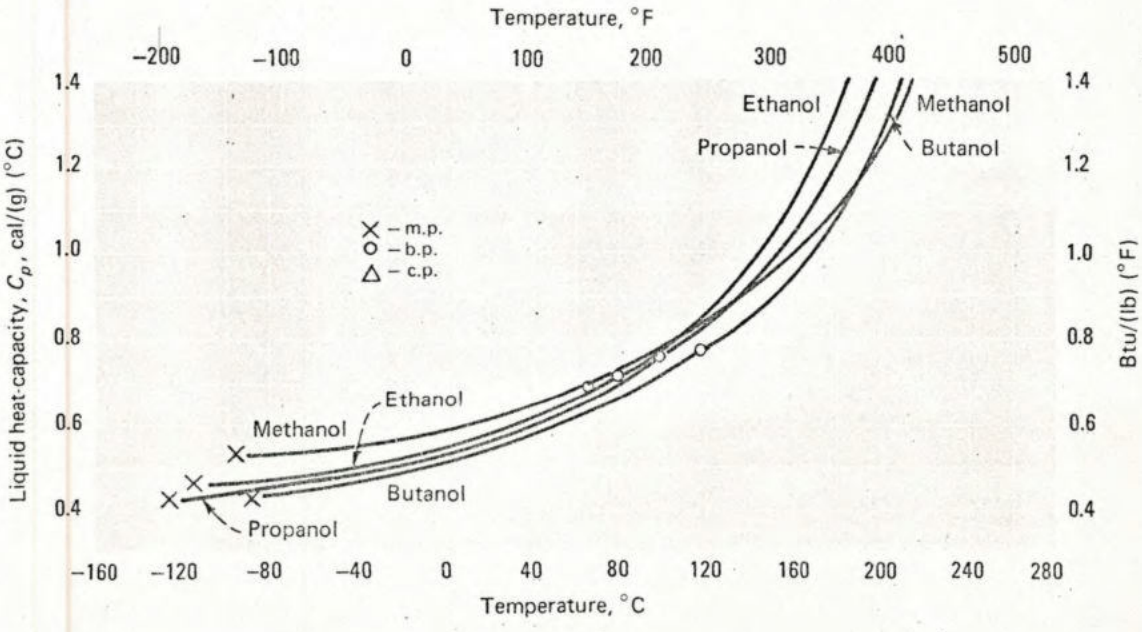


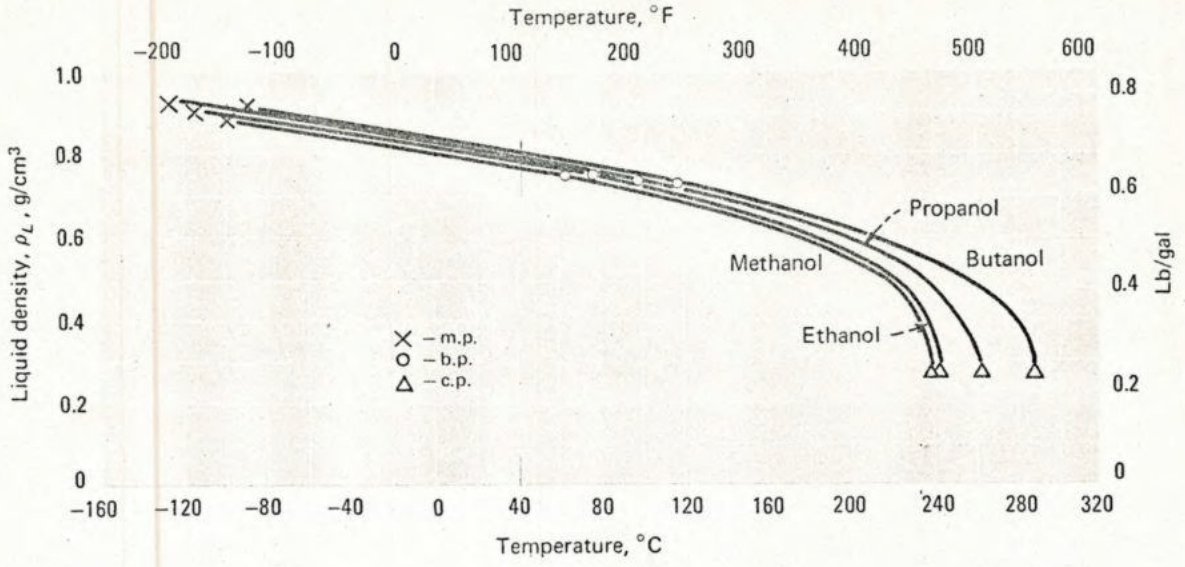
Vapor heat capacity — Fig. 3

Fig. 20–3	Temperature range, °C		Reference
	0–500	500–1,000	
Methanol	◪	◪	15,19,646,637,652,688,692
Ethanol	◪	◪	15,19,646,637,652,688,692
Propanol	◪	◪	15,646,676,688,692
Butanol	◪	◪	15,646,688,692

Liquid heat capacity — Fig. 4

Fig. 20–4	Temperature range, °C		Reference
	m.p.–b.p.	b.p.–c.p.	
Methanol	◪	◪	4,6,19,415,416,646,689,692,699,700,701
Ethanol	◪	◪	4,6,19,415,416,646,692,698,700
Propanol	◪	□	4,6,415,416,692,698
Butanol	◪	□	4,6,415,692,697,700



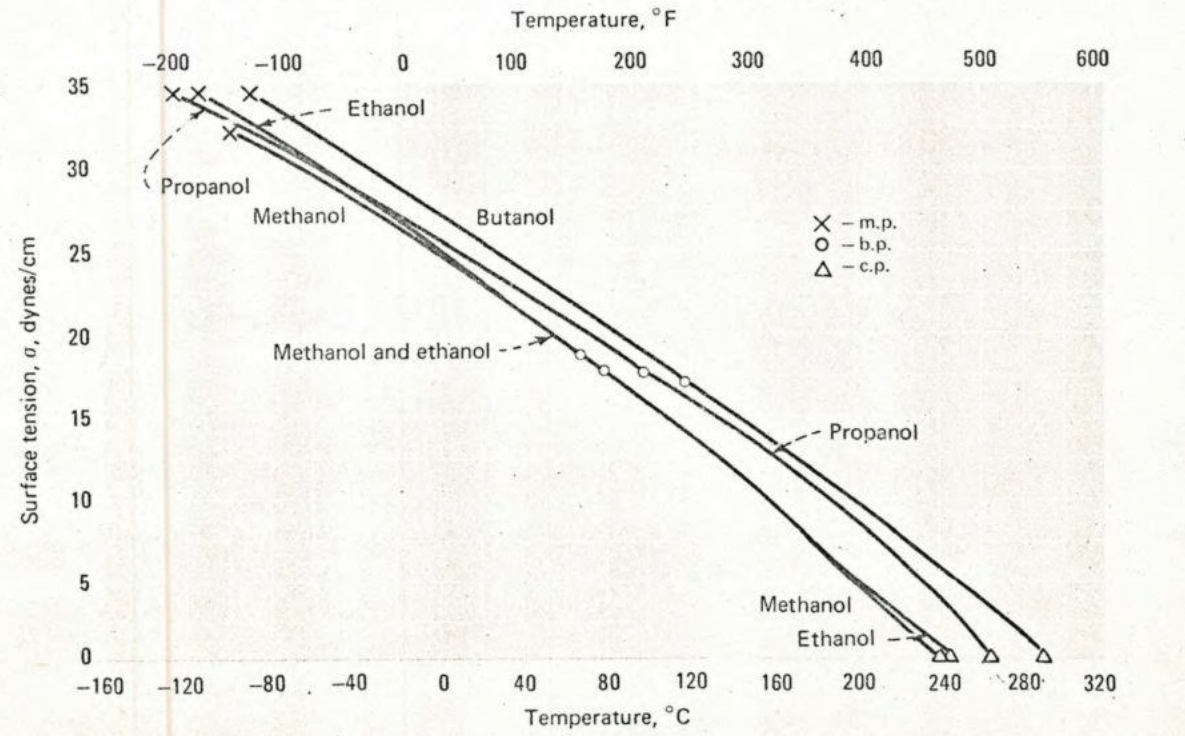


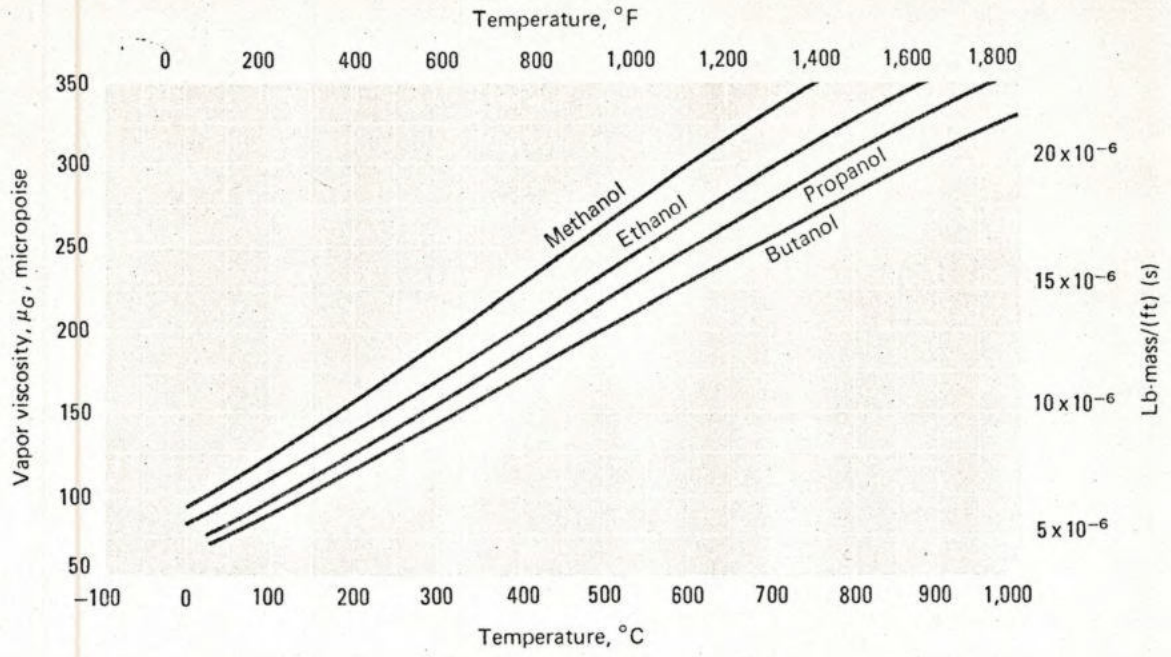
Liquid density — Fig. 5

Fig. 20–5	Temperature range, °C		Reference
	m.p.–b.p.	b.p.–c.p.	
Methanol	◪	■	4,9,415,484,637,646,692
Ethanol	◪	■	4,9,415,484,637,692
Propanol	◪	■	4,9,415,484,646,666,670,672,692
Butanol	◪	■	4,9,415,484,646,666,670,672,692

Surface tension — Fig. 6

Fig. 20–6	Temperature range, °C		Reference
	m.p.–b.p.	b.p.–c.p.	
Methanol	◪	◪	4,6,9,79,415,416,574,637,642,646
Ethanol	◪	◪	4,6,9,79,415,416,574,637,646
Propanol	◪	□	4,6,9,79,415,416,574,637
Butanol	◪	◪	6,9,79,415,416,495,574,637



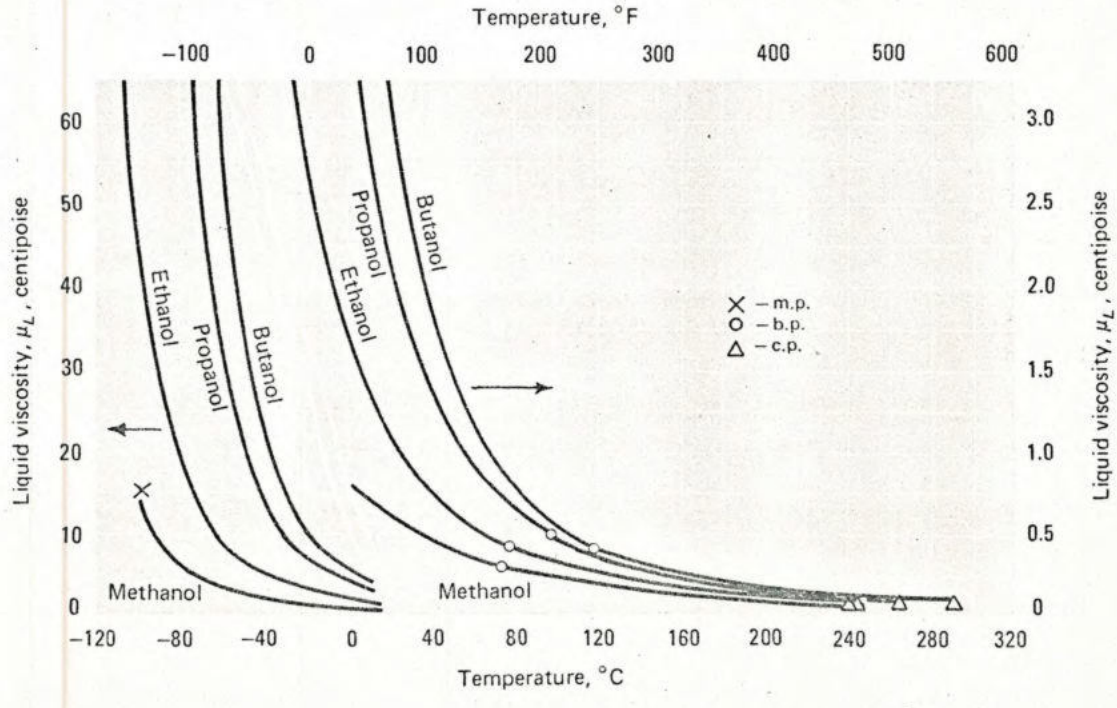


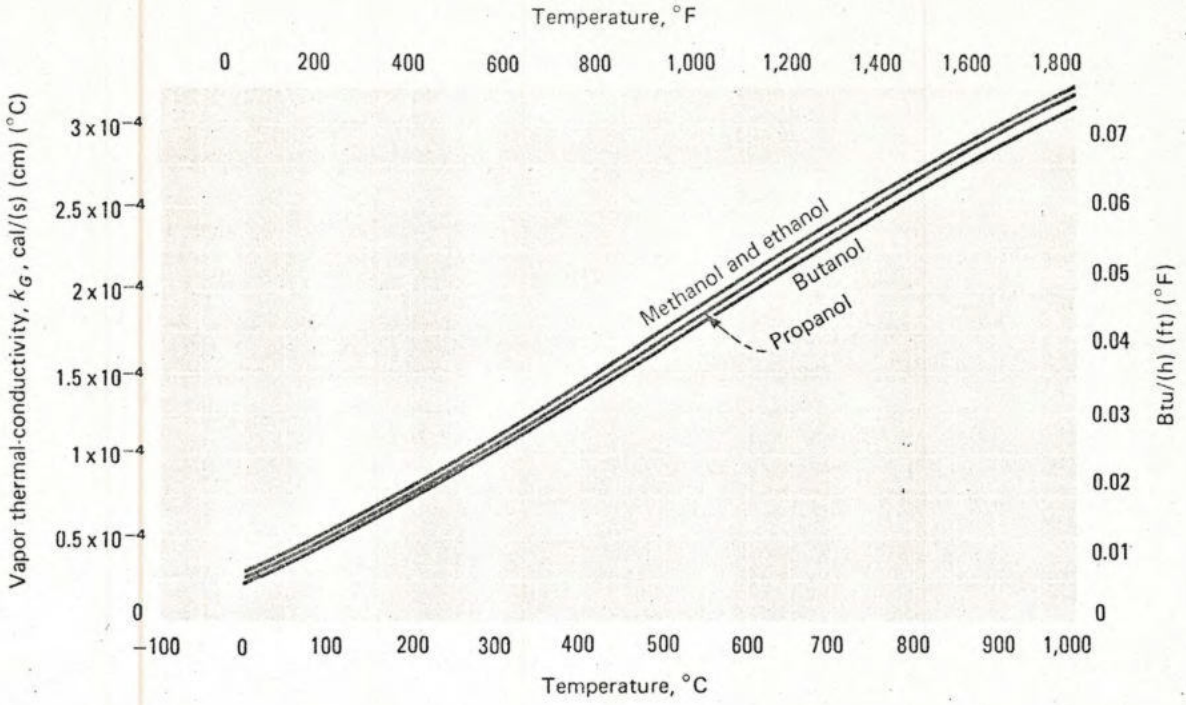
Vapor viscosity — Fig. 7

Fig. 20–7	Temperature range, °C		Reference
	0–500	500–1,000	
Methanol	◪	□	14,416,467,500,545,637,646,669,671,683,703
Ethanol	◪	□	9,14,416,467,545,637,646,671,683,703
Propanol	◪	□	9,14,416,467,545,637,646
Butanol	◪	□	416,545,637

Liquid viscosity — Fig. 8

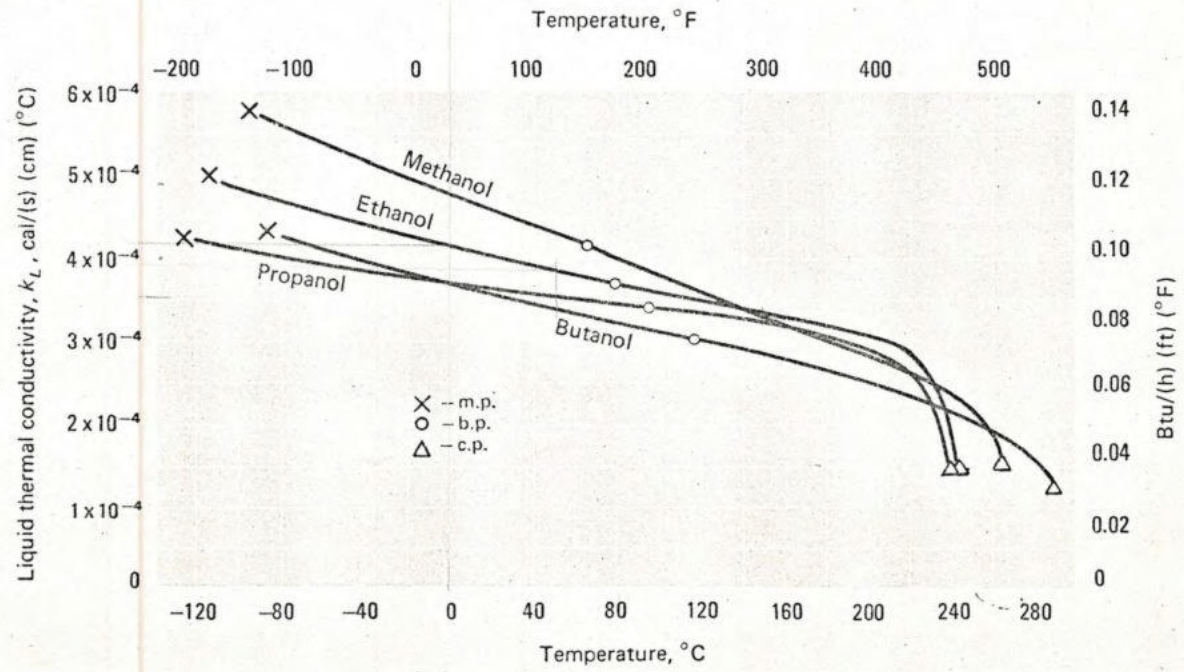
Fig. 20–8	Temperature range, °C		Reference
	m.p.–b.p.	b.p.–c.p.	
Methanol	■	■	6,9,14,415,416,467,484,637,646
Ethanol	◪	■	6,9,14,415,416,467,484,637
Propanol	◪	◪	6,9,14,415,416,467,484,637,646,679
Butanol	◪	□	6,9,14,415,416,467,484,637,646

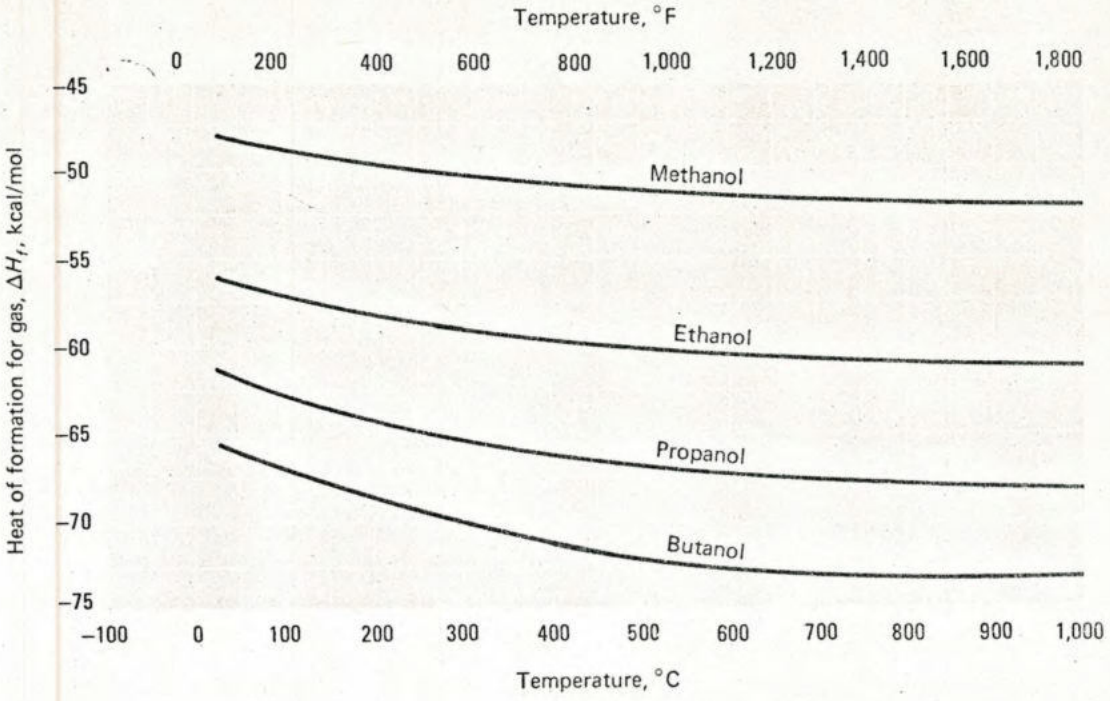




Vapor thermal conductivity			Fig. 9
Fig. 20–9	Temperature range, °C		Reference
	0–500	500–1,000	
Methanol	◪	□	6,9,14,19,515,574,587,637,669,646,674,677,682,695
Ethanol	◪	□	6,9,14,19,416,574,590,637,646,674,637,682,695
Propanol	◪	□	14,590,637,646,682
Butanol	◪	□	590,637,646,682

Liquid thermal conductivity			Fig. 10
Fig. 20–10	Temperature range, °C		Reference
	m.p.–b.p.	b.p.–c.p.	
Methanol	◪	◪	6,9,14,19,416,475,486,562,637,646,674,680,684,685,686,690,694
Ethanol	◪	◪	6,9,14,19,416,475,484,486,537,562,639,646,674,680,684,685,686,690,694
Propanol	◪	◪	9,14,475,486,562,637,646,668,680,684,685,686,690,694,704
Butanol	◪	◪	6,14,416,475,484,486,561,637,646,668,680,684,685,686,690,694



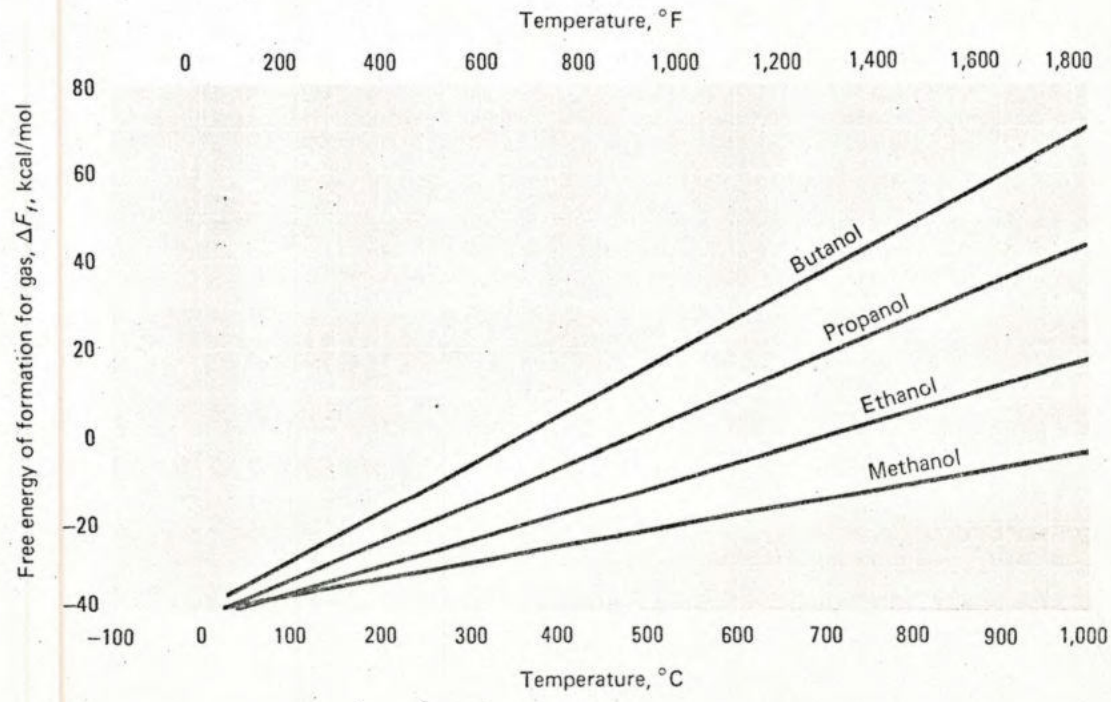


Heat of formation for gas — Fig. 11

Fig. 20–11	Temperature range, °C		Reference
	0–500	500–1,000	
Methanol	◪	◪	15,583,652,692
Ethanol	◪	◪	15,583,652,692
Propanol	◪	◪	15,676,692
Butanol	◪	◪	15,692

Free energy of formation for gas — Fig. 12

Fig. 20–12	Temperature range, °C		Reference
	0–500	500–1,000	
Methanol	◪	◪	15,652,692
Ethanol	◪	◪	15,652,692
Propanol	◪	◪	15,676,692
Butanol	◪	◪	15,692



equation (Eq. 15—1). In tests at temperatures near or below the boiling point, calculated and experimental values compared favorably. Average deviations of 1.1, 0.9, 1.5 and 1.8% were detected for methanol, ethanol, propanol, and butanol.

Surface Tension—Fig. 20—6

Surface tension data were culled from the recent tabulations of Jasper [*79*] and Vargaftik [*646*]. The Othmer relation correlated and extended the data to cover the full liquid phase. Values for n in the equation were 0.85, 0.93, 0.786 and 0.903 for methanol, ethanol, propanol and butanol. Correlation values for surface tension approached experimental ones, with average deviations of 0.32, 0.34, 0.1 and 0.15 dynes/cm.

Viscosity—Fig. 20—7, 20—8

Recent tabulations by Touloukian et al. [*703*] and Landbolt-Bornstein [*637*] were chosen as the primary sources for experimental gas viscosities at low pressure. At high temperature, the Stiel and Thodos correlation [*14, 545*] for polar compounds with hydrogen bonding was adopted to extend the data:

$$\mu_G = (0.755T_r - 0.055)Z_c^{-5/4}/\xi \qquad (20—1)$$

where μ_G = gas viscosity at low pressure (1 atm), micropoise

ξ = correlation parameter, $T_c^{1/6}/(M^{1/2}P_c^{2/3})$

M = molecular weight

T = temperature, °K

T_c = critical temperature, °K

T_r = reduced temperature, T/T_c

Z_c = critical compressibility factor

Tests of the correlation were favorable. Average deviations between calculated and experimental values were 2.4, 3.7, 3.0 and 3.8% for methanol, ethanol, propanol and butanol.

Liquid viscosity data were correlated and extended with the Guzman-Andrade relation (Eq. 1—6). For each alcohol, one straight line fitted the bulk of the data until temperatures approached the critical region. Experimental data in this region were available only for methanol and ethanol. Curves similar in shape to those of methanol and ethanol were adopted for propanol and butanol. In most cases, deviations from the experimental were less than 2.5%.

Thermal conductivity—Fig. 20—9, 20—10

Gas-phase thermal conductivities at low pressures (1 atm) were compiled from Touloukian et al. [*19*], Landbolt-Bornstein [*637*], and Vargaftik [*646*]. These were extended to high temperatures with a modified Misic and Thodos equation (Eq. 10—2). Estimates by this equation deviated from the smoothed data points by averages of 1.4, 2.5, 0.6 and 0.4% for methanol, ethanol, propanol and butanol.

For the saturated liquids, thermal conductivities were correlated and extended by the modified Stiel and Thodos relation (Eq. 10—3) to cover the complete liquid range. Average deviations from selected data [*19, 475, 637, 646*] were 1.2, 5.1, 3.7 and 2.1% for the four alcohols.

Heat and Free Energy of Formation—Fig. 20—11, 20—12

Heat and free energy of formation for the ideal gas of each alcohol were selected from Stull et al. [*15*] and Wilhoit and Zwolinski [*692*].

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