PHYSICAL & THERMODYNAMIC PROPERTIES 19

Ethylene, propylene and butylene oxides

Major property data for three organic oxides are presented as part of our continuing series.

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☐ The organic oxides (ethylene, propylene and butylene oxide) are of significant economic importance. Primary use of ethylene oxide is for the production of ethylene glycol and higher alcohols with a myriad of uses (automotive antifreeze, explosives, resins, fibers, rubbers, plasticizers, etc.). It is also an important intermediate for pharmaceuticals, solvents and organic synthetics.

Propylene oxide is consumed in large production volumes for manufacture of urethane foams. Propylene oxide derivatives are also used for agricultural chemicals, textiles, cosmetics, petroleum, plastics, rubber and paints. Butylene oxide is a specialty chemical having application in polymers, detergents, lube additives and textiles.

Critical properties—Table 19—1

Critical properties are experimentally available for ethylene and propylene oxides [*4,10,413,653*] and are in close agreement. Critical properties for butylene oxide are estimated by the Lydersen and Riedel relationships (Eq. 16—1, 16—2 and 16—3 *). Testing of the estimation relationships with ethylene and propylene oxides produced fair agreement of theory and data. Deviations of 0.1 to 2.3%, 5.8 to 9.5% and 2.4 to 4.0% for critical temperature, pressure and volume, respectively, were encountered.

Heat of vaporization—Fig. 19—1

Heat of vaporization data in the region around the boiling point were extended by means of Watson's correlation (Eq. 1—1). The results from the various sources are in close agreement.

*See Part 1 of this series for equations starting with a boldfaced numeral "1", Part 2 for those with "2", etc. The footnote on p. 107 of the March 1, 1976 issue is a guide to locating Parts 1 through 18.

Vapor pressure—Fig. 19—2

Extensive data were found for ethylene and propylene oxide from the critical point to below the boiling point. Vapor pressure data were correlated and extended using the Cox-Antoine relation (Eq. 1—2). The deviations were less than 1% in most cases.

Heat capacities—Fig. 19—3, 19—4

Ideal gas heat-capacities are available for ethylene and propylene oxide. The agreement of results is good among the several sources, with average deviations being less than 1%.

In the absence of data, ideal gas heat-capacities for butylene oxide were estimated with the Rihani and Doraiswamy method (Eq. 18—1). Testing of the estimation method with the available data for ethylene and propylene oxide produced favorable comparisons with average deviations of 0.5% and 3.7%.

For ethylene and propylene oxide, liquid heat capacity data were extended with the density relation (Eq. 1—3, $n = 1$). Tests of the relation with the available data produced valid results with average deviations of only 4.4% and 2.5% for ethylene and propylene oxide.

Liquid heat capacity for butylene oxide at 20°C was estimated with the Johnson and Huang method [*14*]:

$$C_P = \Delta C_1 + \Delta C_2 + \Delta C_3 + \cdots \Delta C_n \quad (19—1)$$

where C_P = liquid heat capacity at constant pressure, cal/g-mol °K, and $\Delta C_1, \Delta C_2 \cdots \Delta C_n$ = heat capacity contribution of each atomic group, cal/g-mol °K.

Values for ΔC_1, ΔC_2, etc., are available in Reid and Sherwood [*14*] for the various atomic groups ($—CH_3$, $—CH_2$, —O—, etc.) making up the chemical compound. Application of the method to ethylene and

Text continues on p. 137

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:

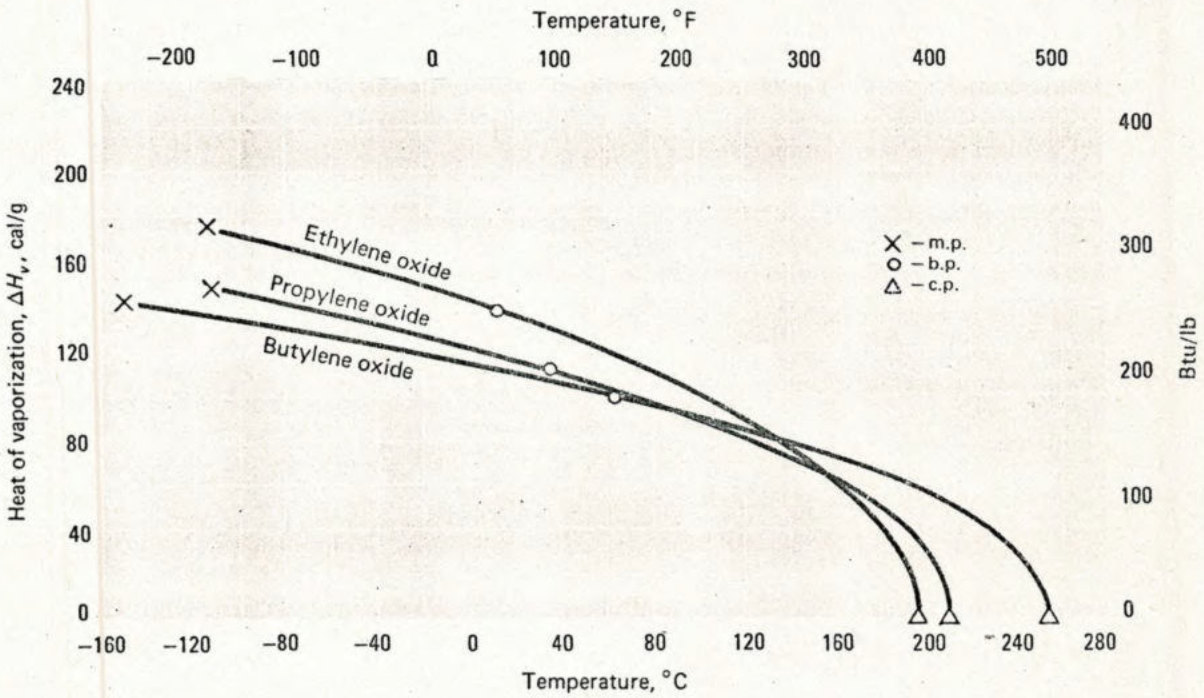
- ■ Data in this region are experimentally known.
- ◪ Experimental and correlated data used.
- ☐ All data in this region are correlated.

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 organic oxides — Table I

Identification	Ethylene oxide C_2H_4O	Propylene oxide C_3H_6O	Butylene oxide C_4H_8O
State (std. conditions)	gas	liquid	liquid
Molecular weight, M	44.05	58.08	72.10
Boiling point, T_b, °C	10.55	34.1	63.2
Melting point, T_m, °C	−112.5	−112.0	−150.0
Critical temp., T_c, °C	195.8	209.1	252.6*
Critical pressure, P_c, atm	70.97	48.6	43.3*
Critical volume, V_c, cm^3/g-mol	140.3	186.0	248.5*
Critical compressibility factor, Z_c	0.259	0.228	0.250*

*Estimated

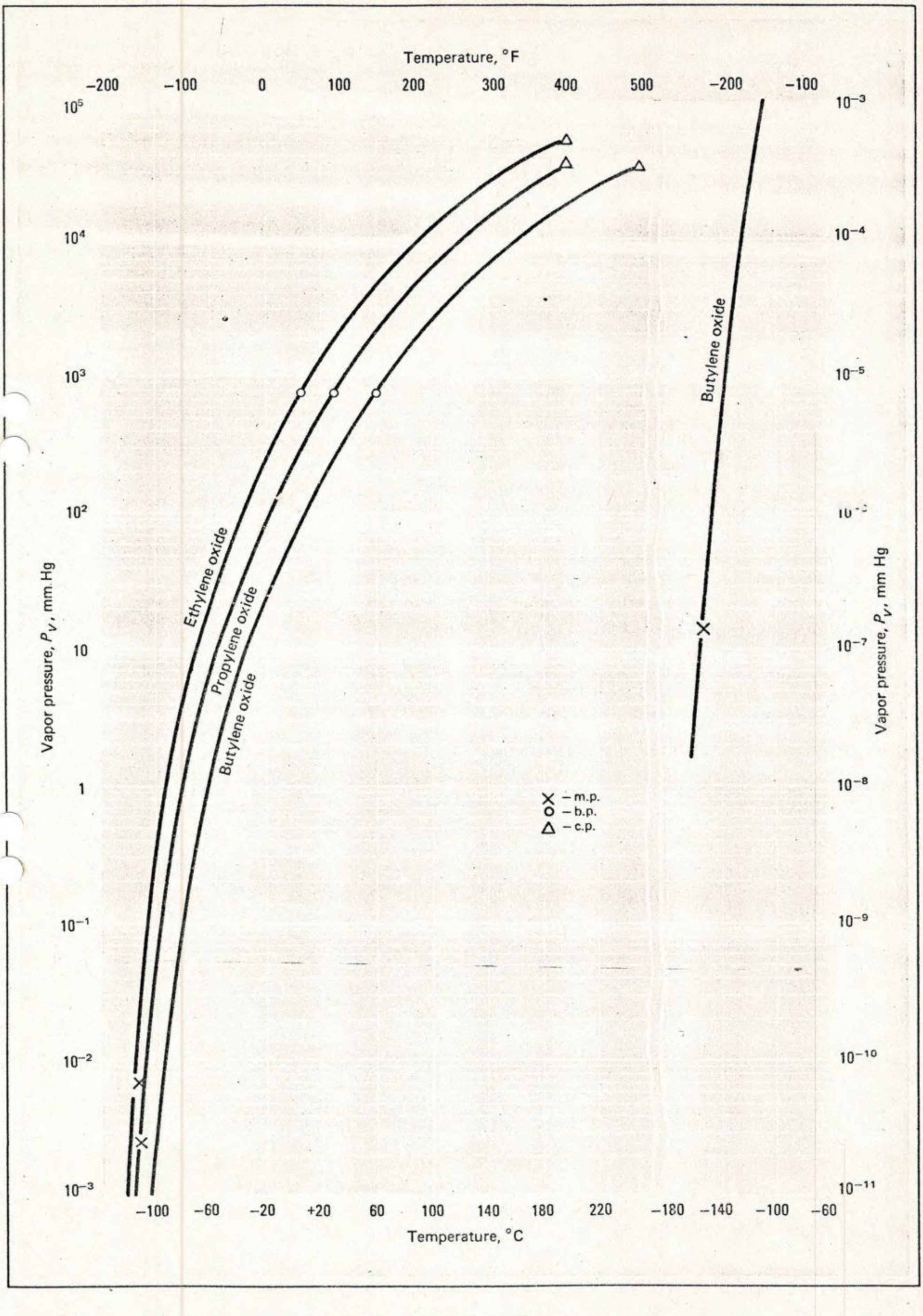


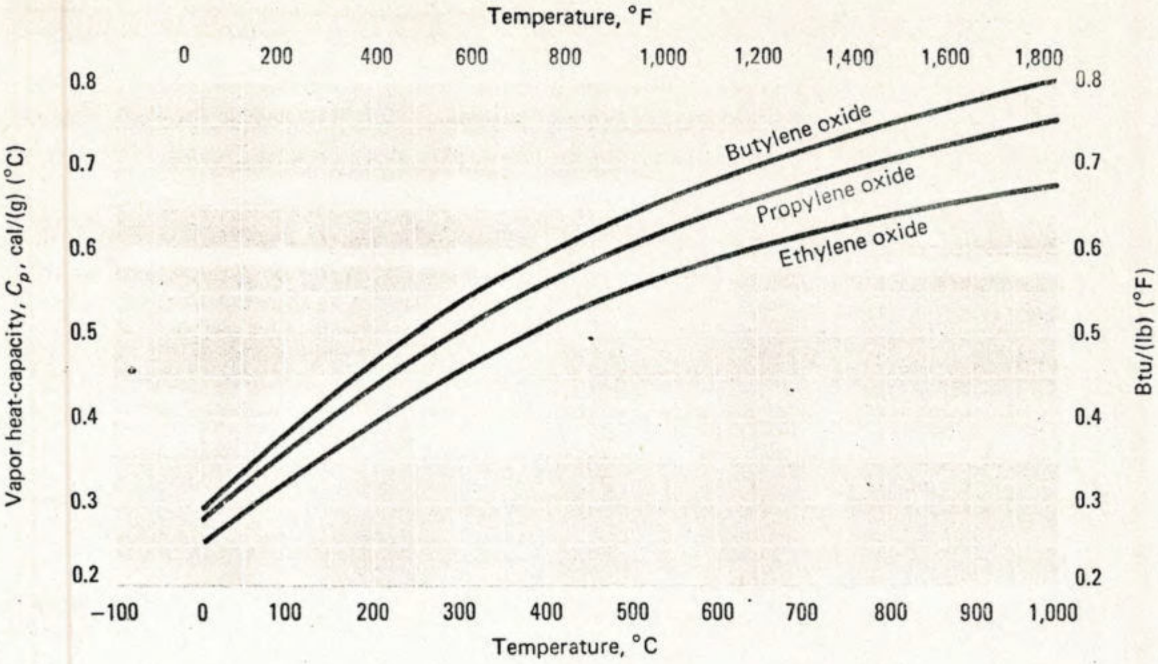
Heat of vaporization — Fig. 1

Fig. 19–1	Temperature range, °C m.p.–b.p.	b.p.–c.p.	References
Ethylene oxide	◪	◪	4, 10, 15, 309, 574, 657, 658, 659, 660
Propylene oxide	◪	☐	4, 656, 657, 658
Butylene oxide	◪	☐	4, 657

Vapor pressure — Fig. 2

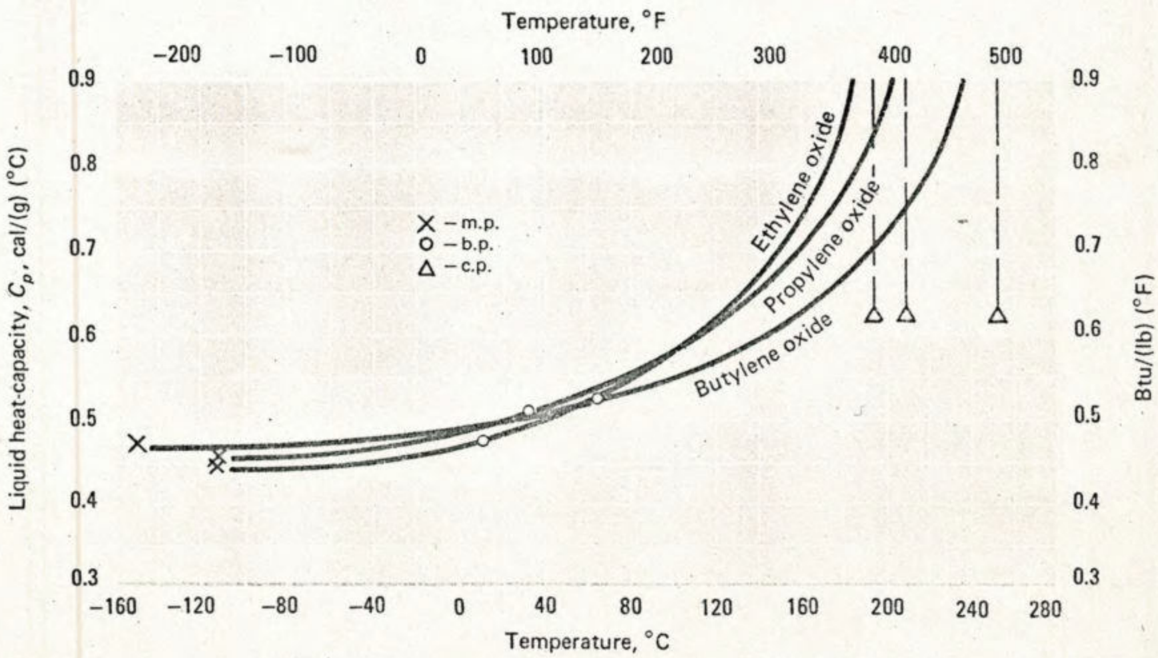
Fig. 19–2	Temperature range, °C m.p.–b.p.	b.p.–c.p.	References
Ethylene oxide	◪	■	4, 413, 415, 529, 548, 637
Propylene oxide	◪	■	4, 529, 637, 647, 653
Butylene oxide	◪	☐	4

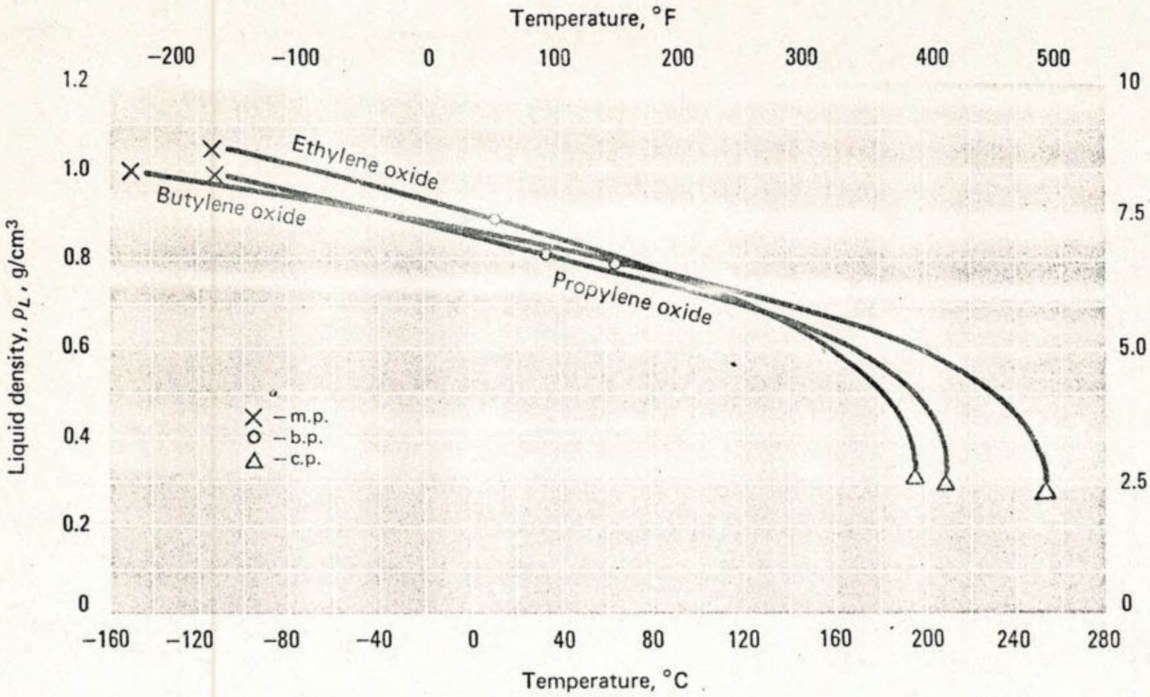

Temperature, °F
-200
-100
0
100
200
300
400
500
-200
-100
10^5
10^4
10^3
10^2
10
1
10^-1
10^-2
10^-3
10^-3
10^-4
10^-5
10^-7
10^-8
10^-9
10^-10
10^-11
Vapor pressure, P_V, mm Hg
Vapor pressure, P_V, mm Hg
Ethylene oxide
Propylene oxide
Butylene oxide
Butylene oxide
× – m.p.
o – b.p.
△ – c.p.
-100
-60
-20
+20
60
100
140
180
220
-180
-140
-100
-60
Temperature, °C



Vapor heat capacity			**Fig. 3**
Fig. 19–3	Temperature range, °C		References
	m.p.–b.p.	b.p.–c.p.	
Ethylene oxide	◪	◪	2, 10, 15, 416, 637, 650, 651, 652, 664
Propylene oxide	◪	◪	2, 15, 416, 649, 654
Butylene oxide	□	□	14, 655

Liquid heat capacity			**Fig. 4**
Fig. 19–4	Temperature range, °C		References
	m.p.–b.p.	b.p.–c.p.	
Ethylene oxide	◪	◪	4, 659
Propylene oxide	◪	□	4, 654, 659
Butylene oxide	□	□	14



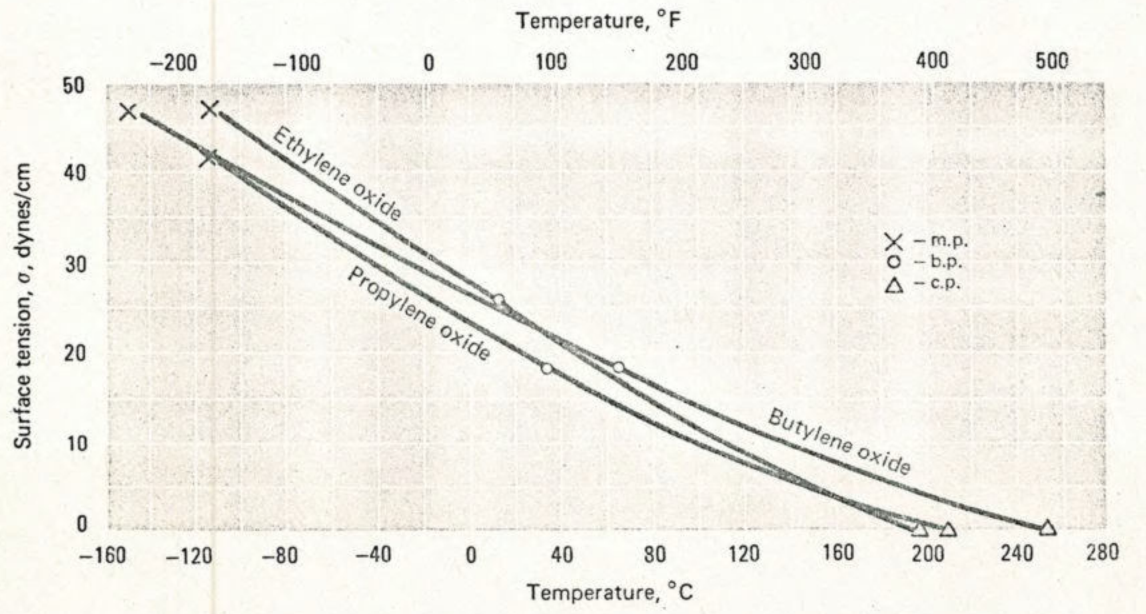


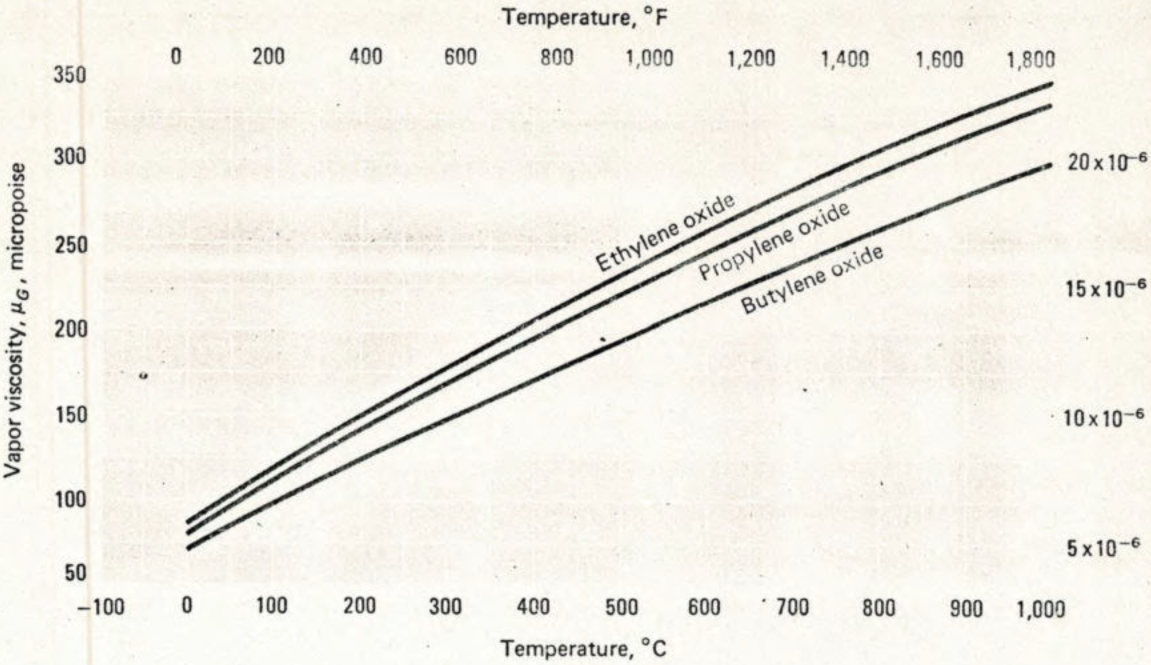
Liquid density — Fig. 5

Fig. 19–5	Temperature range, °C		References
	m.p.–b.p.	b.p.–c.p.	
Ethylene oxide	◪	◪	4, 10, 415, 637, 659
Propylene oxide	◪	◪	4, 659
Butylene oxide	◪	□	4

Surface tension — Fig. 6

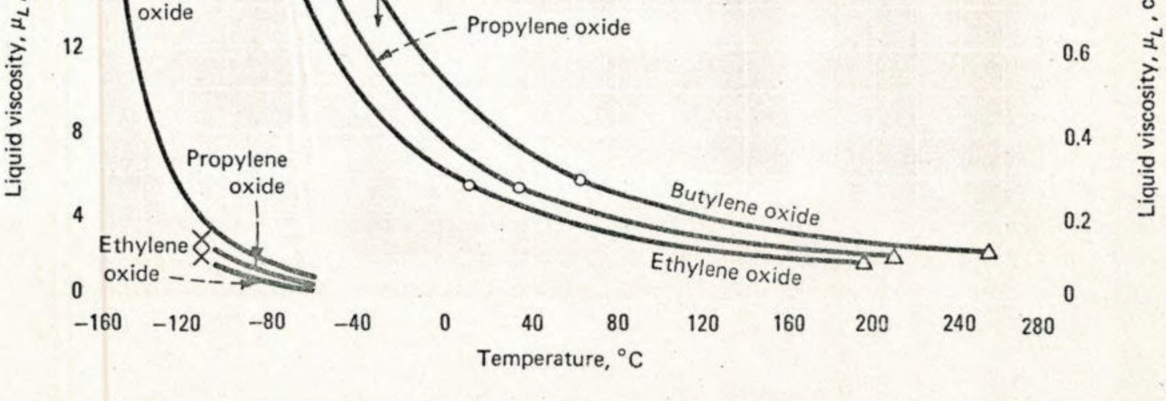
Fig. 19–6	Temperature range, °C		References
	m.p.–b.p.	b.p.–c.p.	
Ethylene oxide	◪	◪	2, 4, 10, 416, 574, 659
Propylene oxide	□	□	14
Butylene oxide	□	□	14

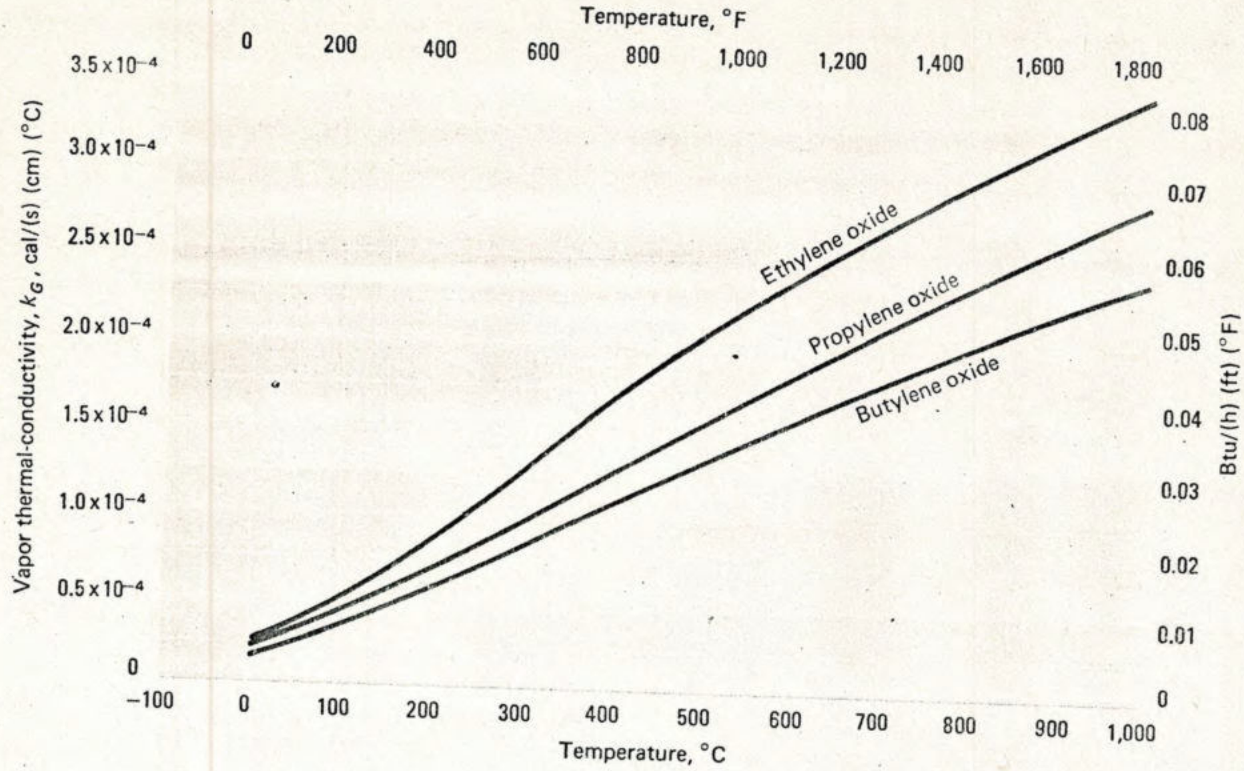




Vapor viscosity			**Fig. 7**
Fig. 19–7	Temperature range, °C 0–500	500–1,000	References
Ethylene oxide	☐	☐	14
Propylene oxide	☐	☐	14
Butylene oxide	☐	☐	14

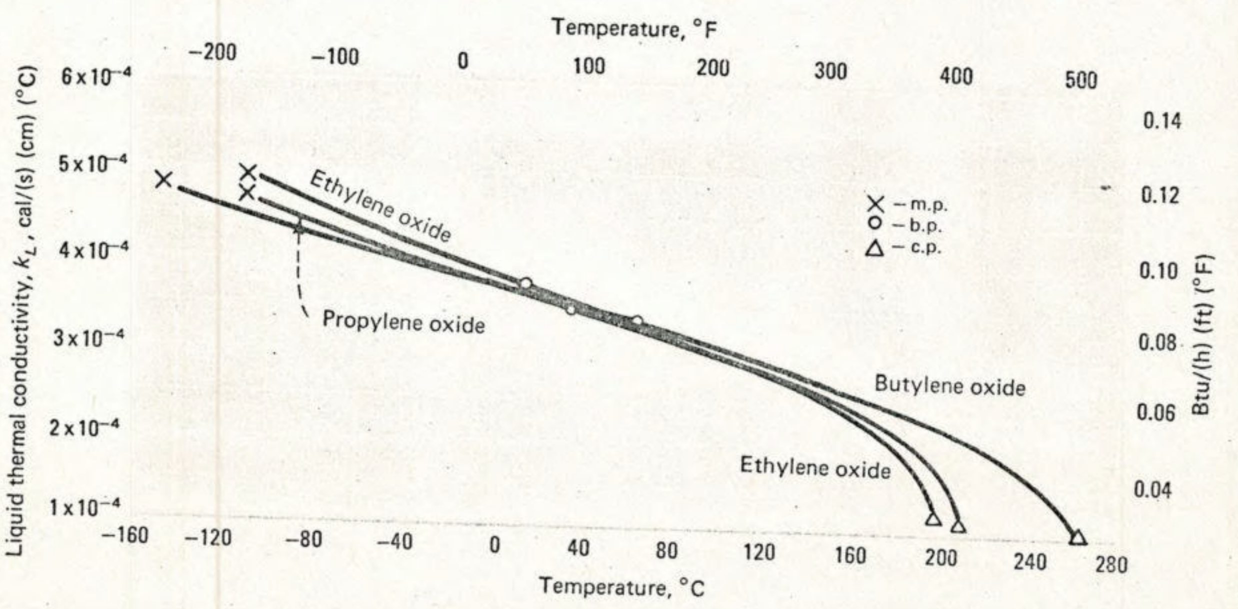
Liquid viscosity			**Fig. 8**
Fig. 19–8	Temperature range, C m.p.–b.p.	b.p.–c.p.	References
Ethylene oxide	☒	☒	2,4,10,415,416,637,657,658,653,660,661,663
Propylene oxide	☒	☐	4,637,657,658,659,661
Butylene oxide	☒	☐	4,657,658

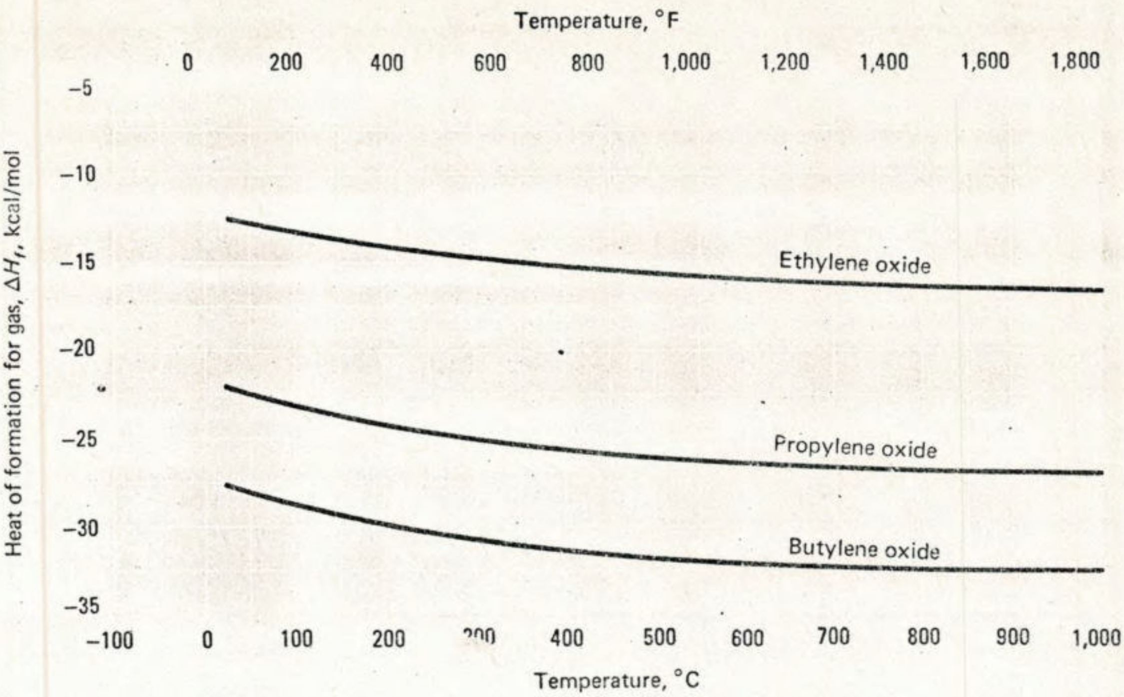




Vapor thermal conductivity			Fig. 9
Fig. 19–9	Temperature range, °C 0–500	500–1,000	References
Ethylene oxide	☑	☐	4, 10, 14, 515, 590, 625, 637, 648, 659
Propylene oxide	☐	☐	14
Butylene oxide	☐	☐	14

Liquid thermal conductivity			Fig. 10
Fig. 19–10	Temperature range, °C m.p.–b.p.	b.p.–c.p.	References
Ethylene oxide	☐	☐	14, 481
Propylene oxide	☐	☐	14, 481
Butylene oxide	☐	☐	14, 481



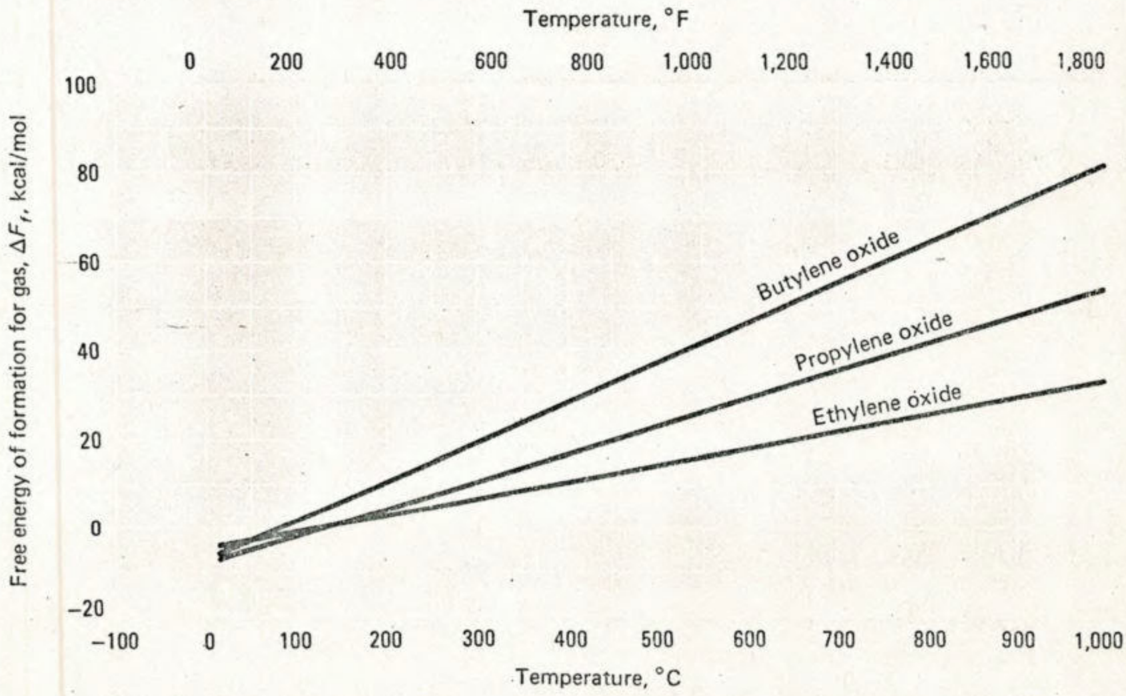


Heat of formation for gas **Fig. 11**

Fig. 19–11	Temperature range, °C 0–500	Temperature range, °C 500–1,000	References
Ethylene oxide	☑	☑	15,574
Propylene oxide	☑	☑	15,649,654
Butylene oxide	☐	☐	14

Free energy of formation for gas **Fig. 12**

Fig. 19–12	Temperature range, °C 0–500	Temperature range, °C 500–1,000	References
Ethylene oxide	☑	☑	15,574
Propylene oxide	☑	☑	15,649,654
Butylene oxide	☐	☐	14



propylene oxide produced favorable agreement of estimated and experimental data. Maximum variations of 1% and 4.9% were encountered.

The estimated value at 20°C for butylene oxide was extended to lower temperatures by using the same general shape of curves for ethylene and propylene oxide. Extension to higher temperatures was achieved with the density relation (Eq. 1—3, $n = 1$).

Density—Fig. 19—5

Liquid density data were extended with modified Rackett correlation (Eq. 15—1) to attain complete coverage of the saturated liquid phase. The correlation values were extremely close to experimental data; average deviations were less than 0.5% for each organic oxide.

Surface tension—Fig. 19—6

Surface tension data for ethylene oxide were correlated and extended with the Othmer relation (Eq. 9—2, $n = 1.19$). Predicted and experimental values were close with average deviations of less than 1%.

In the absence of experimental data, surface tension values for propylene and butylene oxide were estimated with the Brock and Bird correlation (Eq. 16—4). Testing of the correlation with data for ethylene oxide produced an average error of 5.7%.

Viscosity—Fig. 19—7, 19—8

Gas-phase viscosity values at atmospheric pressure for each organic oxide were estimated with the Stiel and Thodos correlation [*14*] for polar compounds without hydrogen bonding:

$$\mu_G = \frac{Z_c^{-2/3}}{\xi}[1.90T_r - 0.29]^{4/5} \qquad (19—2)$$

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

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

Z_c = critical compressibility factor

T_r = reduced temperature, T/T_c

Unfortunately, experimental data are lacking for a direct comparison of experimental and calculated results for the organic oxides. However, testing of the correlation with similar compounds (14 different esters and ethers) produced favorable comparison findings. Average deviations between estimated values and experimental data were less than 3%.

The Guzman-Andrade relation (Eq. 1—6) for log of viscosity versus reciprocal temperature was used to correlate and extend liquid viscosity data. The relation fitted the data quite adequately. Average deviations between the relation and data were 4% or less.

Thermal conductivity—Fig. 19—9, 19—10

The Misic and Thodos correlation (Eq. 10—2) was selected for extrapolation of experimental gas-phase thermal conductivity data for ethylene oxide. In the absence of experimental data, the same correlation was used to estimate gas-phase thermal conductivities for propylene and butylene oxide. The calculated and experimental results were in general agreement. Average deviations were 8.2%. Other correlations [*14*] produced greater deviations.

Liquid thermal conductivity values for each organic oxide were estimated with the Pachaiyappan and Vaidyanthan correlation (Eq. 16—7) at room temperature. These values were then extended with the modified Stiel and Thodos relation (Eq. 10—3) to achieve full coverage of the saturated liquid phase.

Heat and free energy of formation—Fig. 19—11, 19—12

Heat and free energy of formation of the ideal gas are available for ethylene and propylene oxide. The results from the several different sources agree. Average respective deviations are 0.1 and 0.36 kcal/mol.

In the absence of experimental data, heat and free energy of formation were estimated with the modified Verma and Dorsiswamy method (ΔH_f, Eq. 18—2) and Van Krevelen correlation (ΔF_f, Eq. 18—3). Application of the two estimation techniques to ethylene and propylene oxide produced agreement of calculated and experimental results. Average deviations of 0.8 to 1.7% and 4.8 to 5.1% were experienced.

References

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Carl L. Yaws—For biography, see *Chem. Eng.*, May 12, 1975, p. 97.