Physical Properties of Hydrocarbons

Part 12—C_2-C_4 Oxides

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As a group, the C_2 to C_4 oxides represent over two and one-half billion pounds of production. However, only a small part of this reaches the market place as an oxide. Of the two billion pounds of ethylene oxide produced in 1965, two-thirds went into producing ethylene glycol. The combination of giant plants and improved oxidation technology has made ethylene oxide one of the cheapest chemical intermediates, but its growth is largely tied to the slow growth of ethylene glycol in antifreeze.

Propylene oxide output has grown to 600 million pounds/year, spurred by its use in the fast-growing urethane foams market. This usage now consumes 200 million pounds/year, making it almost as large an outlet as propylene glycol.

Epichlorohydrin continues to be one of the top growth chemicals. About 80 percent of its 100 million pounds/year production goes into epoxy resins.

Butylene oxide has not achieved the major product status of the other three compounds. The much lower reactivity of its oxide group, coupled with a higher price will probably keep it a low volume specialty chemical.

Critical Properties. The critical properties of ethylene oxide[1] and propylene oxide[2] have been experimentally determined. The critical properties of butylene oxide and epichlorohydrin were estimated by the method of Lydersen, which sums up the contributions of each structural part of the molecule. When compared to experimental values for ethylene oxide and propylene oxide, this method gave only a few degrees error in the critical temperature and about 0.01 grams/ml error in the critical density. However, the error in the critical pressure was about 60 psi.

Vapor Pressure. There are extensive experimental data available on the vapor pressures of ethylene oxide[1,3,4,5,6,7,8] and propylene oxide[2,3,4,5,6] up to the critical point. The only vapor pressure information on butylene oxide is a product bulletin.[9] The vapor pressure of epichlorohydrin has been determined only up to the boiling point.[10,11,12] A Cox chart plot was used to extrapolate the data to the critical point.

TABLE 12-1—C_2-C_4 Oxides

	Boiling Point, °C	Melting Point, °C	Molecular Weight	Critical Properties		
				°C T_c	psia P_c	g/ml d_c
Ethylene Oxide	10.6	−112.5	44.05	195.8	1043	0.315
Propylene Oxide	34.2	−112.1	58.08	209	714	.312
Epichlorohydrin	116.1	− 57.2	92.53	323*	721*	.381*
1,2-Butylene Oxide	63	.....	72.10	243*	630*	.290*

* Estimated

Heat of Vaporization. The heat of vaporization of ethylene oxide has been experimentally determined over the entire temperature range.[1,8] The heat of vaporization has been determined only at the boiling point for propylene oxide,[5,6,13] butylene oxide,[9] and epichlorohydrin.[10] These data have been extrapolated over the entire temperature range by the method of Watson.

Heat Capacity. The vapor heat capacity of ethylene oxide has been accurately determined.[14] For the other three compounds, the vapor heat capacity has been calculated by the recently proposed method of Rihani and Doraiswamy.[15] For ethylene oxide, this method gave errors of less than 2 percent.

The liquid heat capacity of ethylene oxide is available over a wide temperature range.[5,7] For the other three compounds, the liquid heat capacity has been calculated at 20° C by the method of Johnson and Huang[16] and extrapolated over the range by the method proposed by Chow and Bright.[16] The error is normally ± 10 percent.

Density. The density of ethylene oxide has been experimentally determined up to the critical temperature.[1,5] Propylene oxide is reported from —40° C to +50° C.[6,17] The INTERNATIONAL CRITICAL TABLES give the density of epichlorohydrin from 0° C to 115° C.[18] The density of butylene oxide is available only at 25° C.[9] The data have been extended to the critical point by the method of Lydersen, Greenkorn and Hougen.[16] Calculated values compared to experimental values gave an average error of less than 1 percent.

Viscosity. Because of the complete lack of vapor viscosity data in the literature, the values were calculated by the method of Bromley and Wilke.[16] The error is normally only a few percent.

The limited liquid viscosity data on ethylene oxide,[5,6] propylene oxide,[5,6,17] butylene oxide,[9] and epichlorohydrin[10,11,18] have been extrapolated over the temperature

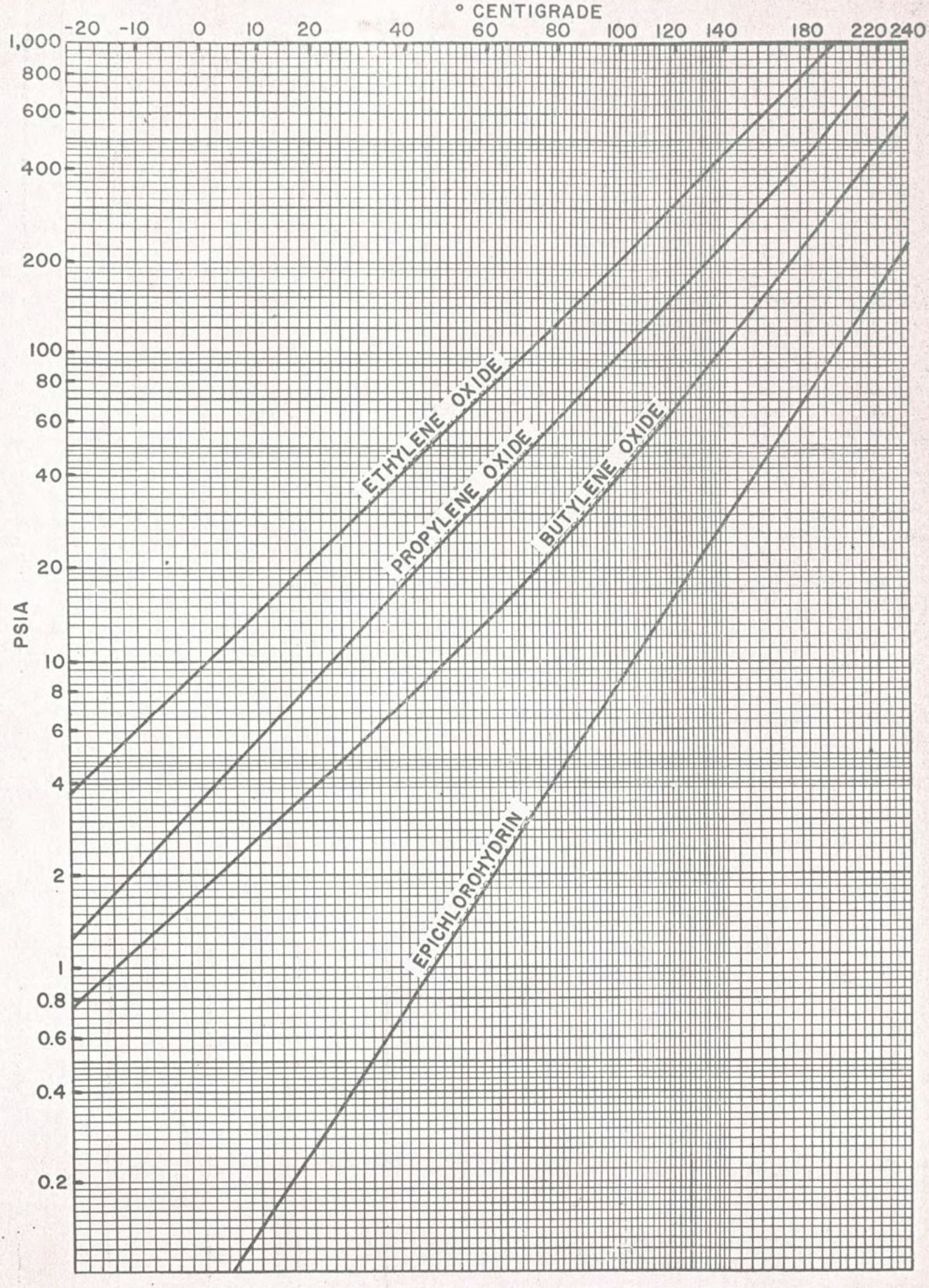

Fig. 12-1—Gives vapor pressure of C_2-C_4 oxides from −20°C to + 240°C.

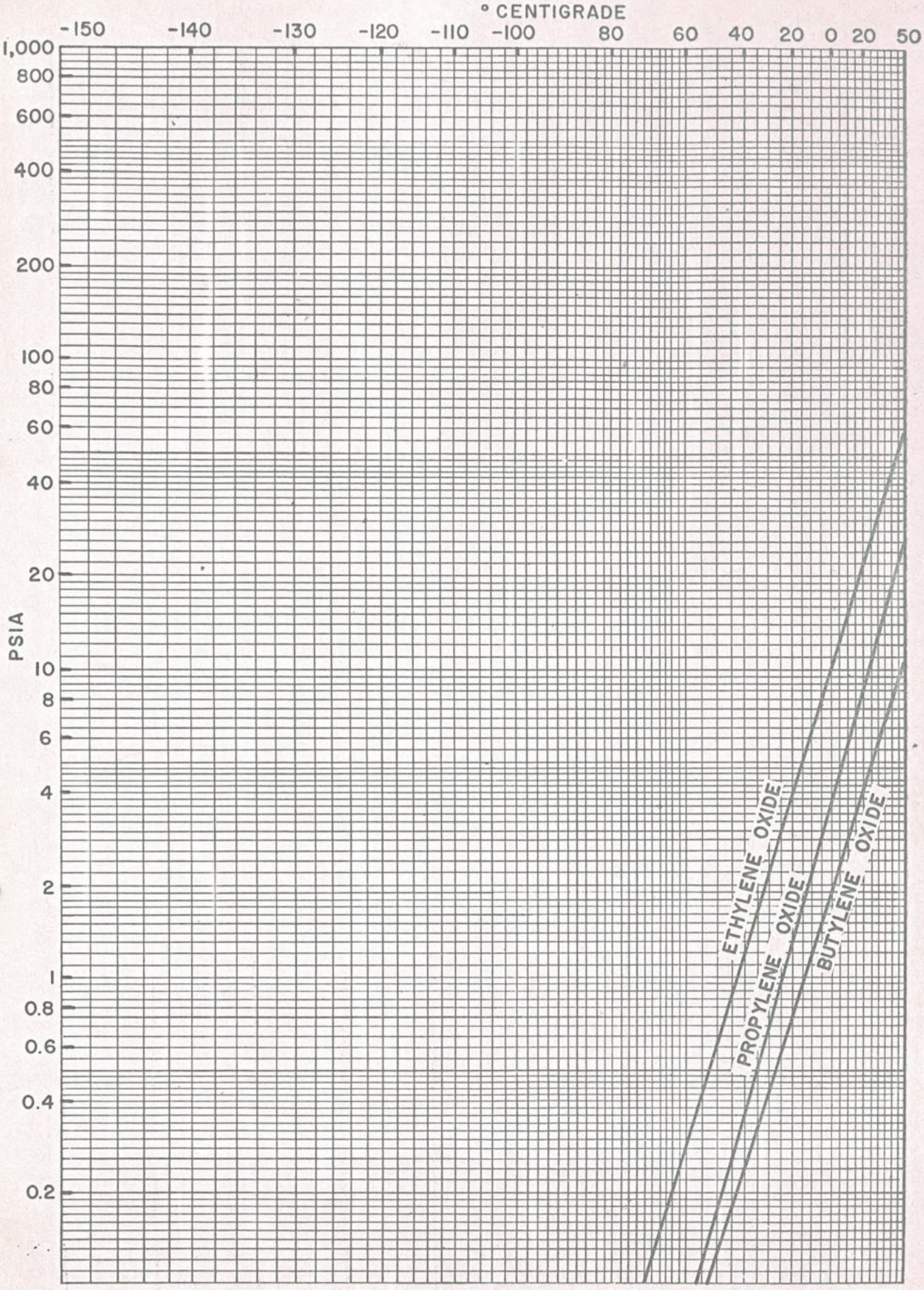

Fig. 12-2—Gives vapor pressure of C_2-C_4 oxides from −70°C to + 50°C.

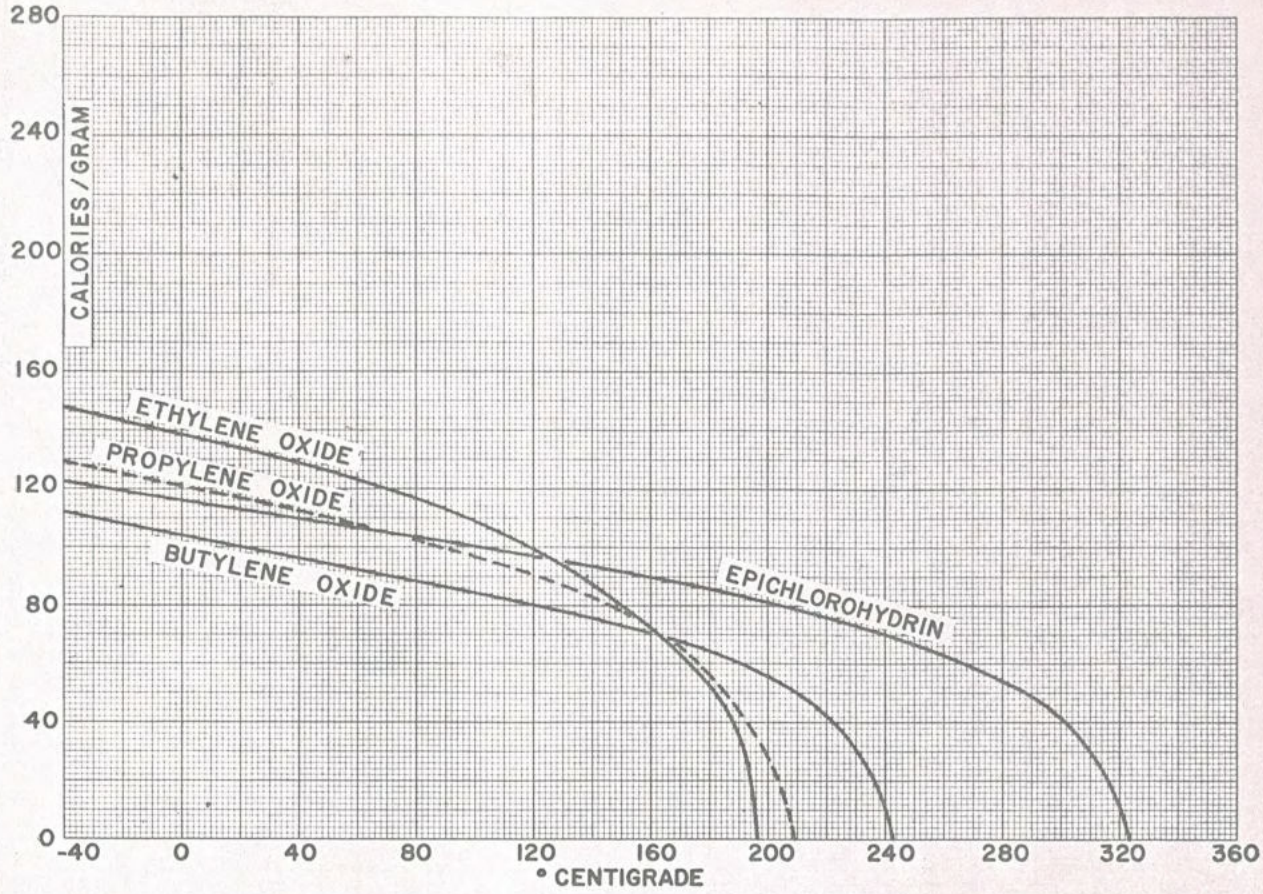

Fig. 12-3—Shows heat of vaporization of C_2-C_4 oxides from −40°C to + 320°C.

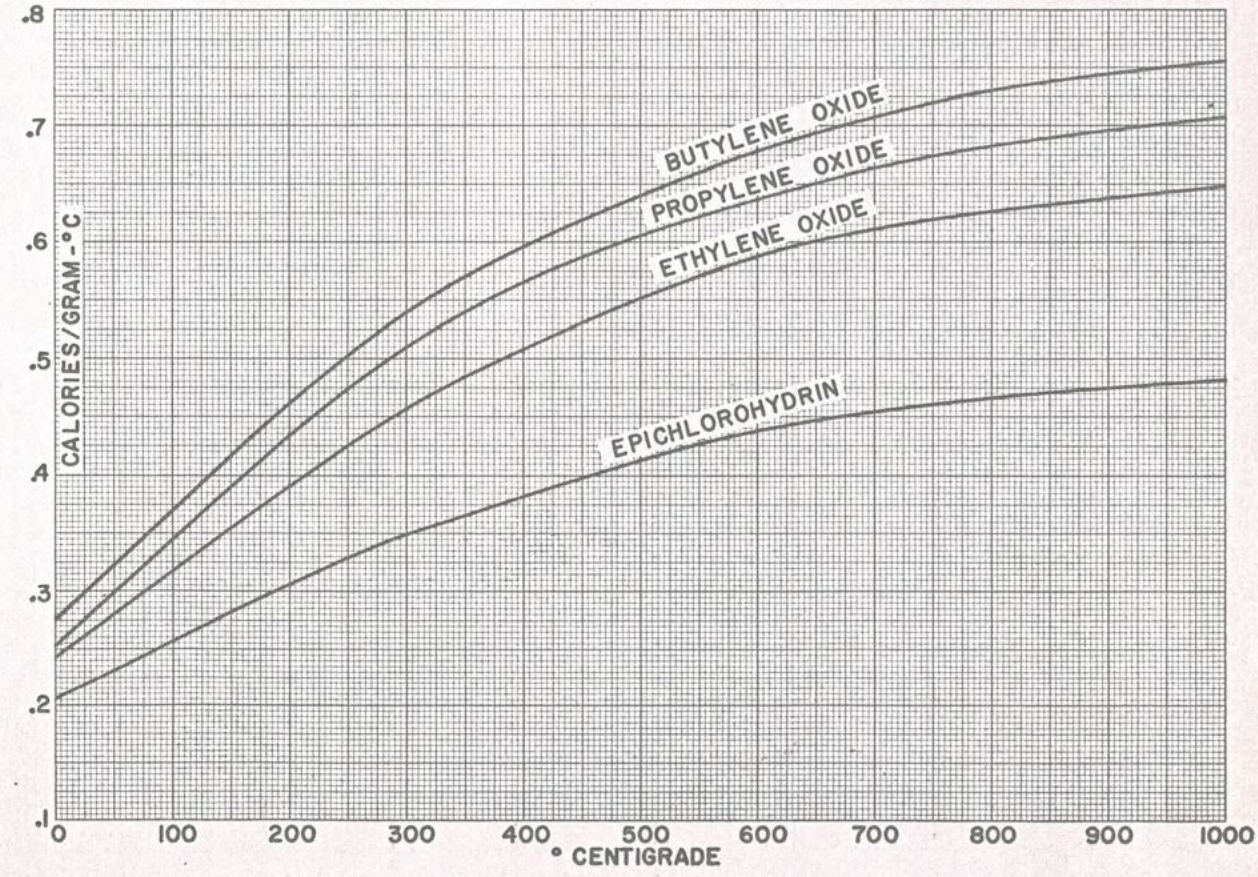

Fig. 12-4—Shows vapor heat capacity of C_2-C_4 oxides from 0°C to + 1,000°C.

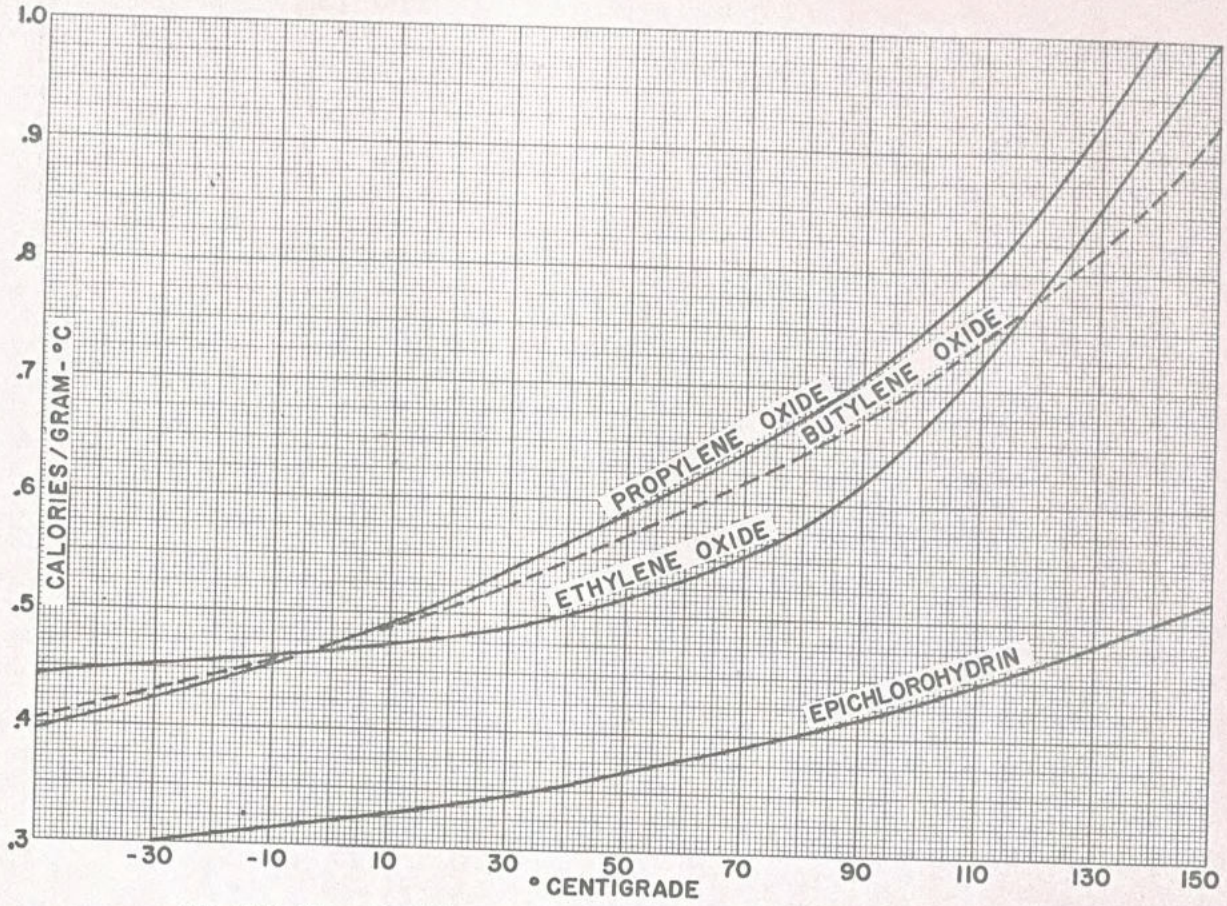

Fig. 12-5—Shows liquid heat capacity of C_2C_4 oxides from $-50°C$ to $+ 150°C$.

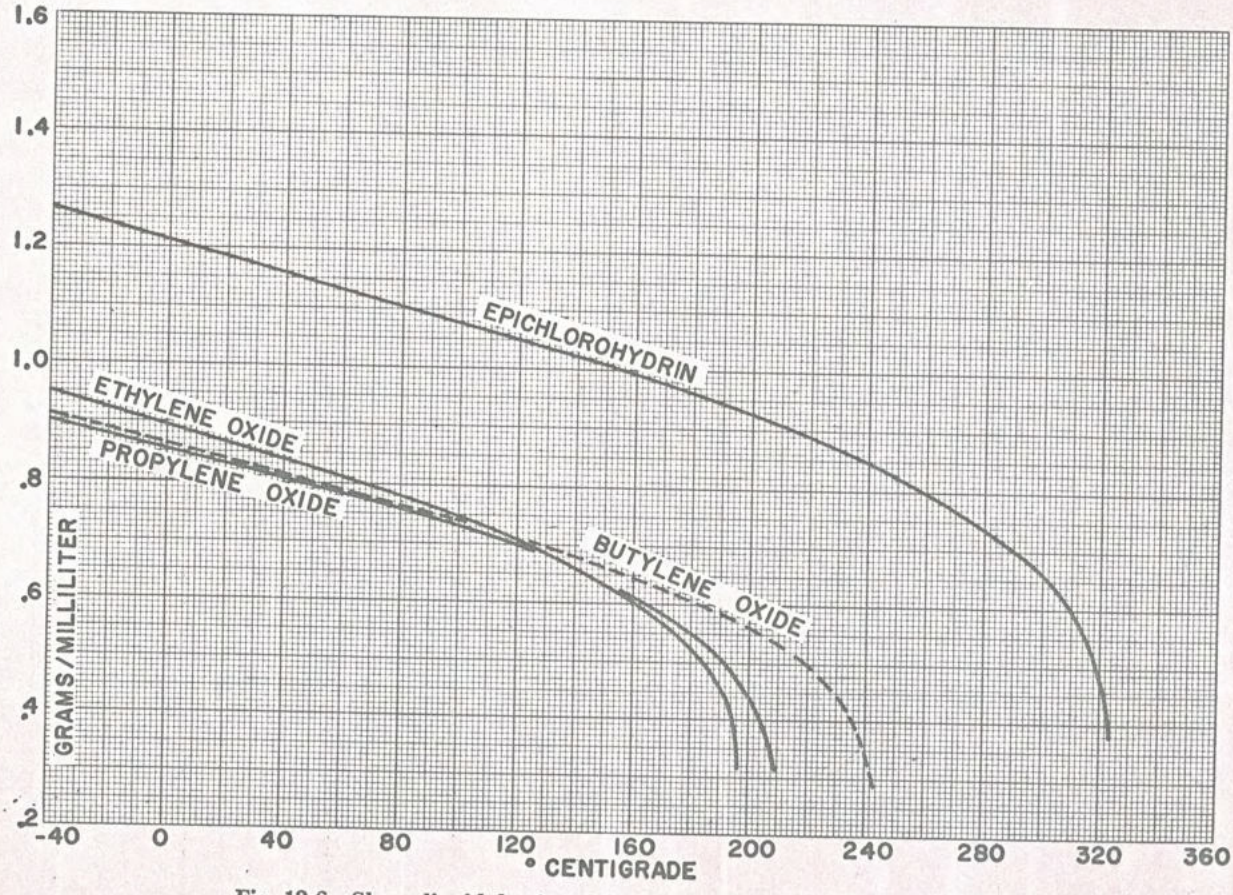

Fig. 12-6—Shows liquid density of C_2-C_4 oxides from $-40°C$ to $+ 320°C$.

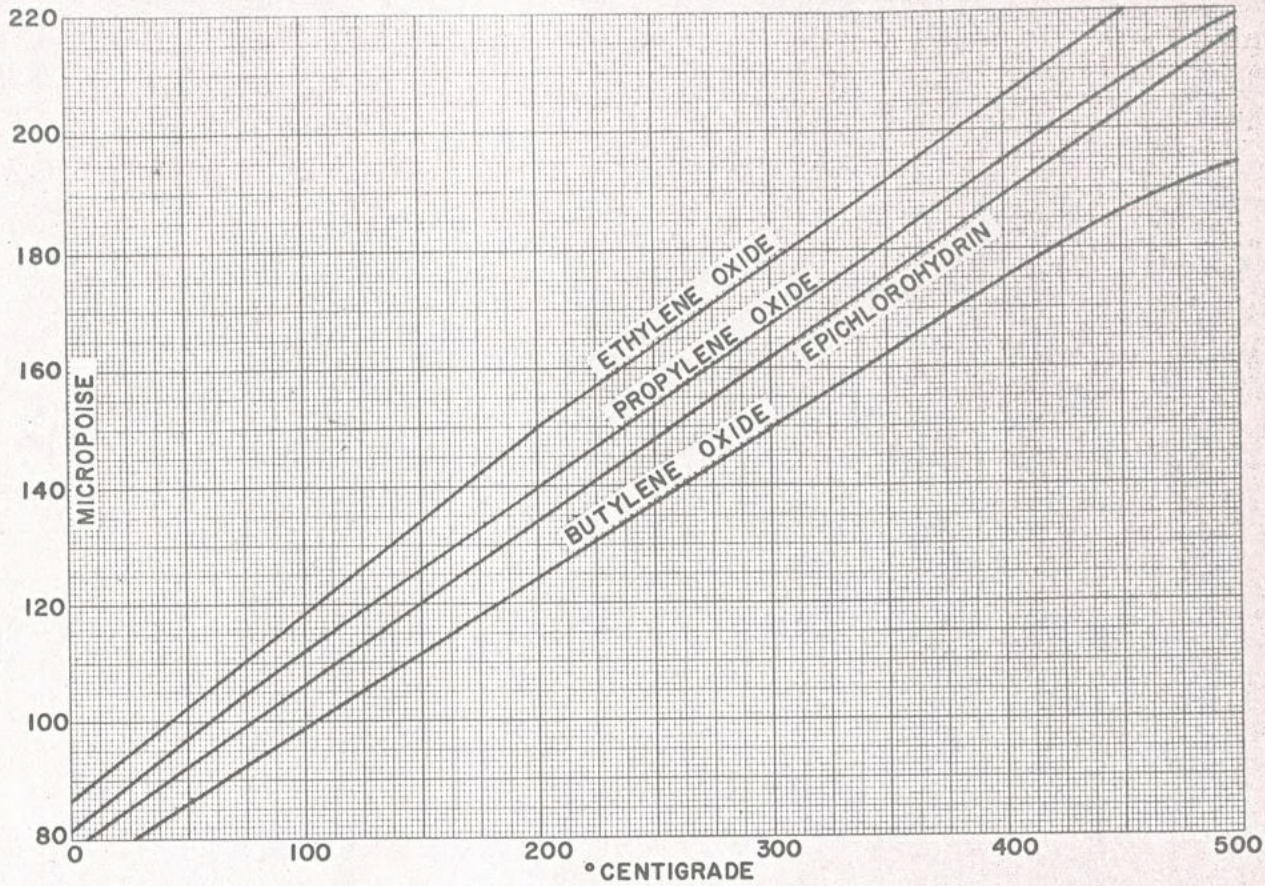

Fig. 12-7—Shows vapor viscosity of C_2-C_4 oxides from 0°C to + 500°C.

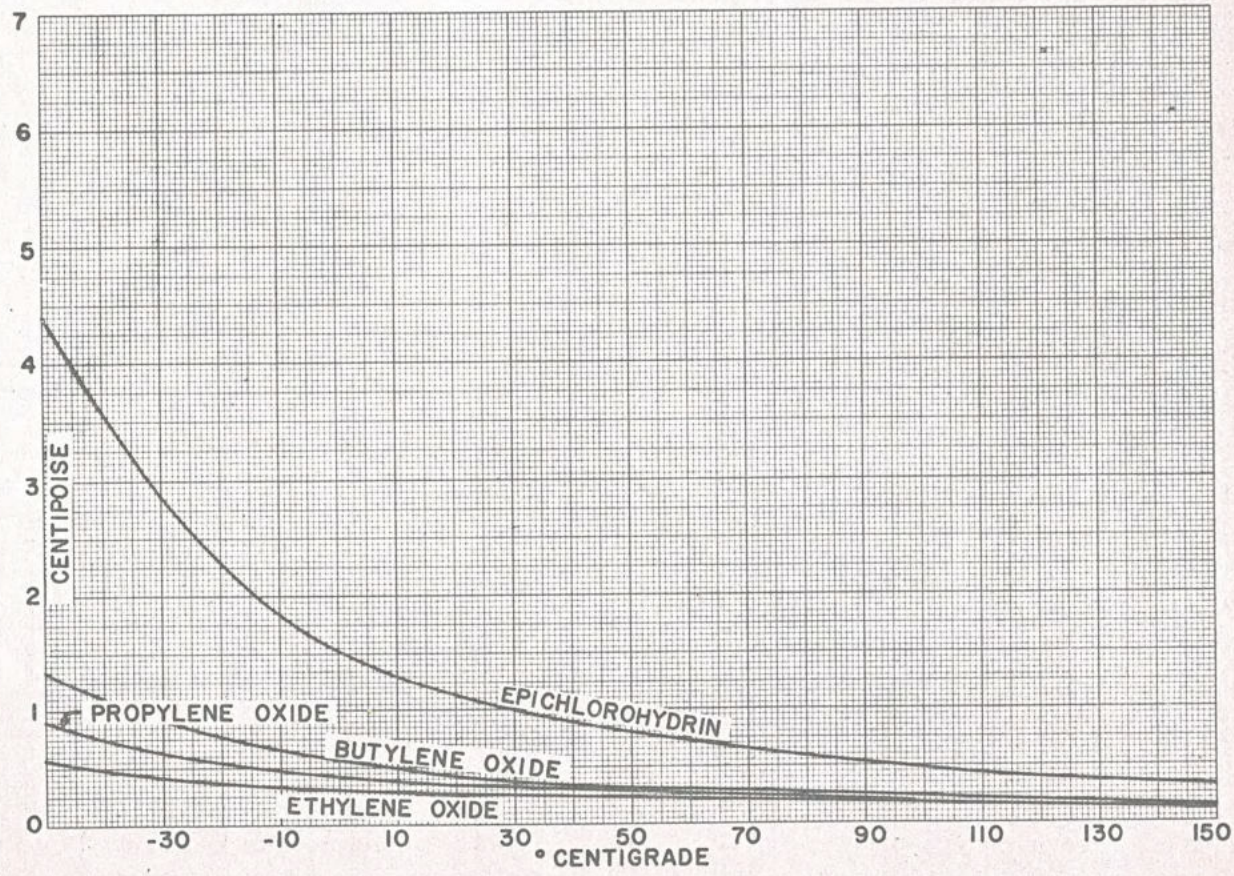

Fig. 12-8—Shows liquid viscosity of C_2-C_4 oxides from —50°C to + 150°C.

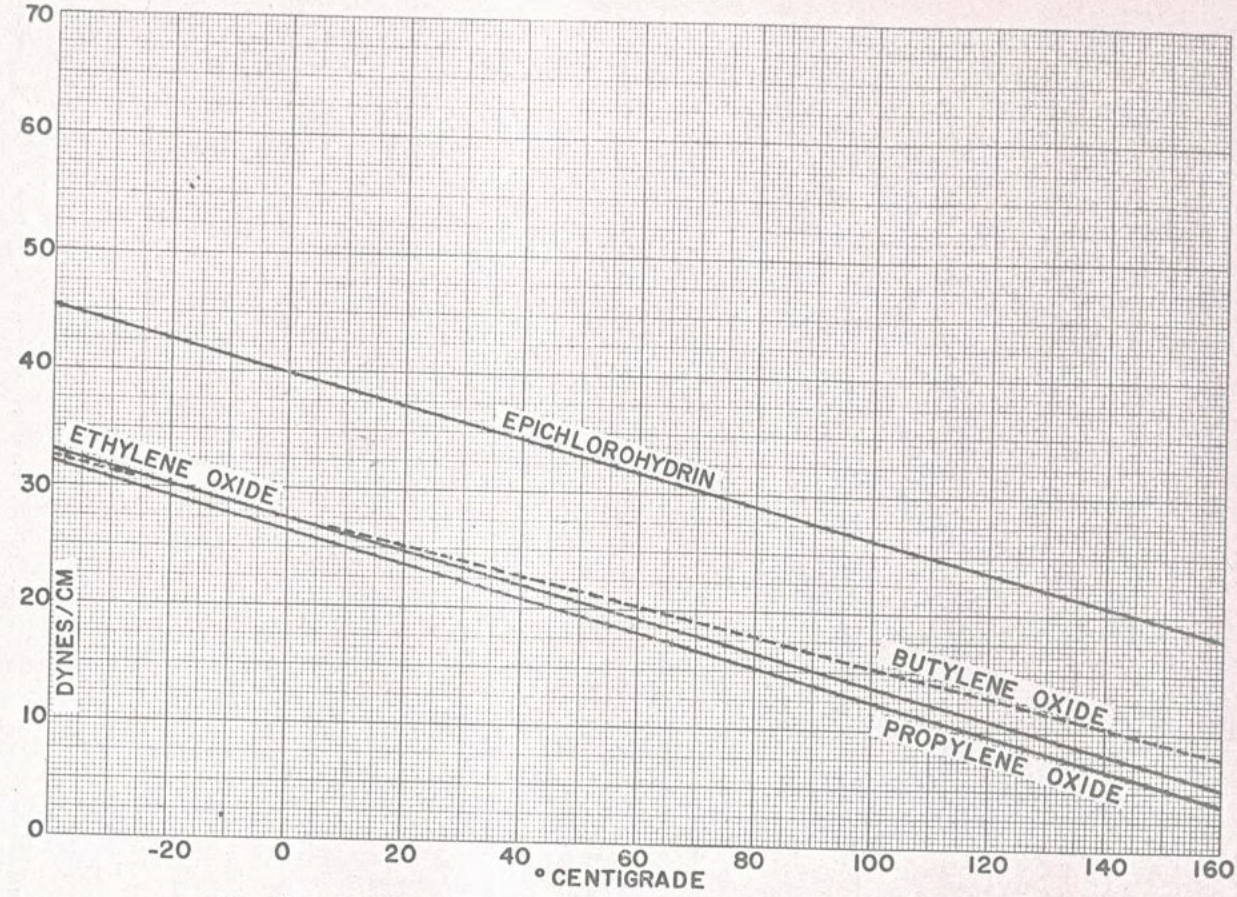

Fig. 12-9—Shows surface tension of C_2-C_4 oxides from −40°C to + 160°C.

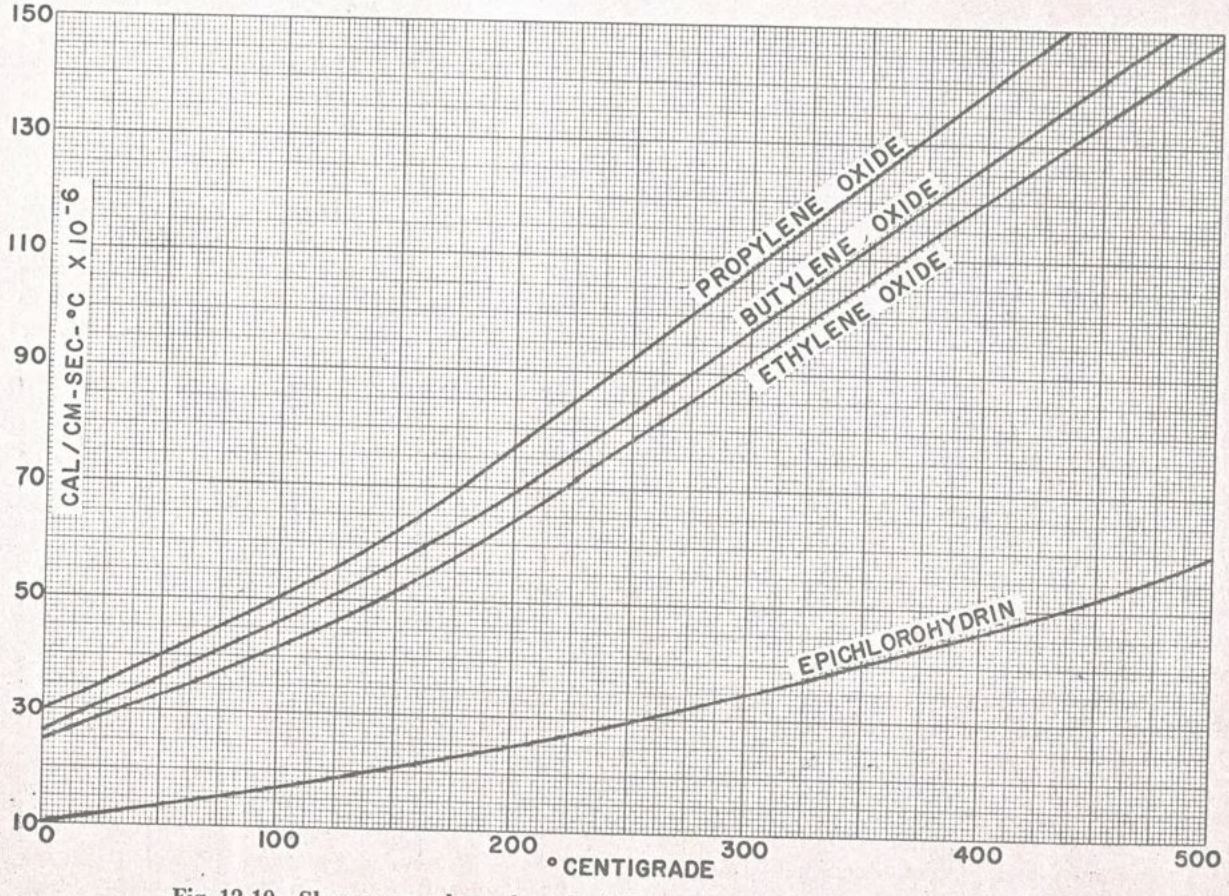

Fig. 12-10—Shows vapor thermal conductivity of C_2-C_4 oxides from 0°C to + 500°C.

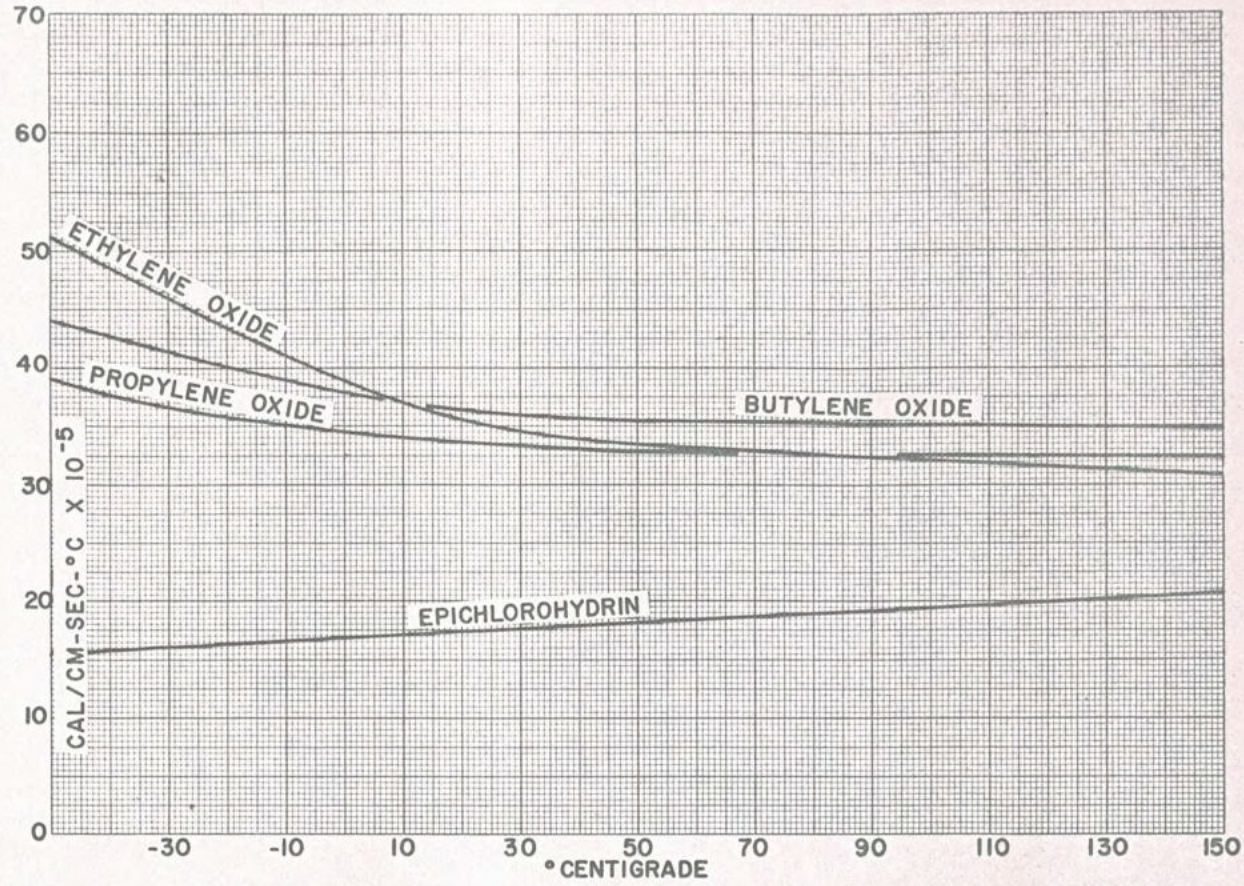

Fig. 12-11—Shows liquid thermal conductivity of C_2-C_4 oxides from −50°C to + 150°C.

range by plotting the log of the viscosity against the reciprocal of the temperature.

Surface Tension. The surface tension of ethylene oxide has been reported from —50° C to +20° C.[5] Epichlorohydrin is covered from 10° C to 90° C.[18] The method proposed by Sugden[19] was used to calculate the surface tension of propylene oxide and butylene oxide at 25° C. In this method,

$$s = \left(\frac{[P]\ (d_l - d_v)}{M} \right)^4$$

where

s = surface tension, dynes/cm
$[P]$ = parachor, which can be calculated from the molecular structure
d_l = density of liquid, grams/ml
d_v = density of vapor, grams/ml
M = molecular weight

When compared with experimental values for ethylene oxide and epichlorohydrin, the author found errors of 3.6 percent and 7.4 percent, respectively. The data for all four compounds were extended over the temperature range by the nomograph method of Kharbanda.[20] This normally gives errors of less than 5 percent.

Thermal Conductivity. The only thermal conductivity data reported are for ethylene oxide vapor from 0° C to 70° C.[5] Consequently, the thermal conductivities have been calculated by the methods used in previous articles for the vapor[21] and liquid[22] thermal conductivity. When compared to the experimental ethylene oxide data, the calculated vapor thermal conductivity gave an average error of 0.7 percent.

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Indexing Terms: Butylene Oxide-9, Computations-4, Epichlorohydrin-9, Ethylene Oxide-9, Heat-7, Liquid Phase-5, Physical Properties-7, Pressure-6, Properties/Characteristics/-7, Propylene Oxide-9, Temperature-6, Vapor Phase-5.

Part 13 will appear in an early issue.