Physical Properties of Hydrocarbons

PART 28—Ethers

Robert W. Gallant,
The Dow Chemical Co., Plaquemine, La.

Ethyl ether is the best known of the ether compounds because of its wide usage as an anesthetic. However, this is a small part of the 90 million pounds consumed each year. Most ethyl ether is used as a chemical intermediate or a solvent. Methyl ether finds markets in such areas as refrigerants, spray propellants, and extraction. Propyl ether and butyl ether are not presently commercial products. Their high price makes it difficult for them to compete as solvents and extractants with the cheaper ethers and ketones.

These products are generally produced by the dehydration of the appropriate alcohol, and are often byproducts of alcohol production.

Critical Properties and Vapor Pressure. The critical properties of methyl ether[1,2,3] and ethyl ether[2,4] have been determined experimentally. Estimation methods have been used to calculate the critical properties of propyl and butyl ether. The method of Lydersen[5], used for the critical temperature, gives an error of only a few degrees. The Vowles method[5] gives an error of 5-10 psi for the critical pressure and about 0.001 grams/ml for the critical density.

Stull[2] presents data on the vapor pressures up to the critical point for methyl and ethyl ether. The vapor pressures of propyl ether[2] and butyl ether[3] have been measured only to the boiling point. The vapor pressure up to the critical point was estimated by the method described by Miller.[6] For ethyl ether this method yielded an average error of 1.5 percent.

Heat of Vaporization. Jones and Bowden[7] have measured the heat of vaporization of ethyl ether up to its critical point. The heat of vaporization at the boiling point has been determined for methyl ether[8] and butyl ether.[9] The method of Giacalone[5] was used to estimate the heat of vaporization of propyl ether, with a probable error of 2 percent. Kharbanda's nomograph was used to extend the data over a wide temperature range.[10] When compared to the experimental data for ethyl ether, this method gave an average error of 2.2 percent.

Heat Capacity. The vapor heat capacities of methyl ether[11] and ethyl ether[11,12] have been determined up to 727° C. The method of Rihani and Doraiswamy[11] has been used to calculate the vapor heat capacities over the 0 to 1000° C range, with a probable error of 1 percent.

The liquid heat capacity of ethyl ether has been experimentally determined from −100° C to the critical point.[3,13] Kennedy and coworkers[1] present data on methyl ether from −133° C to −33° C. No data are available for propyl and butyl ether. The method proposed by Johnson and Huang was used to estimate the heat capacity at 20° C,[5] with a probable error of 2 percent. The data were extended over a broader temperature by the equation, density times heat capacity equals a constant. For methyl and ethyl ether, this method gave an average error of 8.7 percent. Below the boiling point, the error was only 4.8 percent.

Density. The liquid densities of methyl ether[3,5] and ethyl ether[3,13] have been measured up to the critical point. Densities are available from 0° C to 30° C for propyl and butyl ether.[3] Lydersen's method was used to calculate the densities up to the critical point. The probable error is about 1 percent.

TABLE 28-1—Physical Properties of Ethers

	Boiling Pt., °C	Freezing Pt., °C	Molecular Weight	Critical Properties °C t_c	PSIA P_c	g/ml d_c
Methyl Ether	−24.9	−141	46.07	126.9	763	0.2714
Ethyl Ether	34.6	−116	74.12	193.8	522	0.2625
Propyl Ether	90.0	−122	102.17	254*	414*	0.258*
Butyl Ether	142.4	−98	130.22	307*	345*	0.255*

* Estimated.

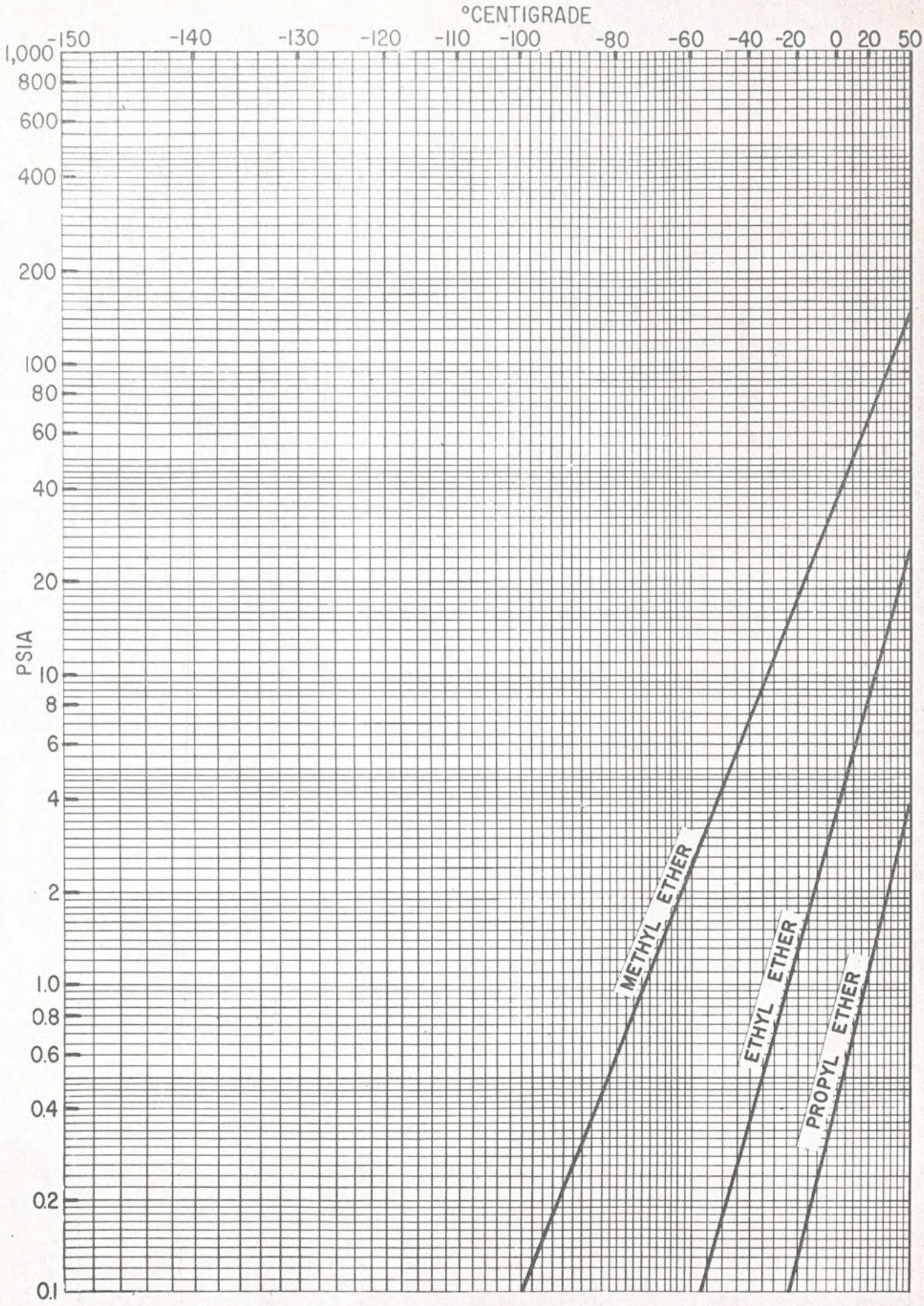


Fig. 28-1—Gives vapor pressure of ethers from −150°C to +50°C.

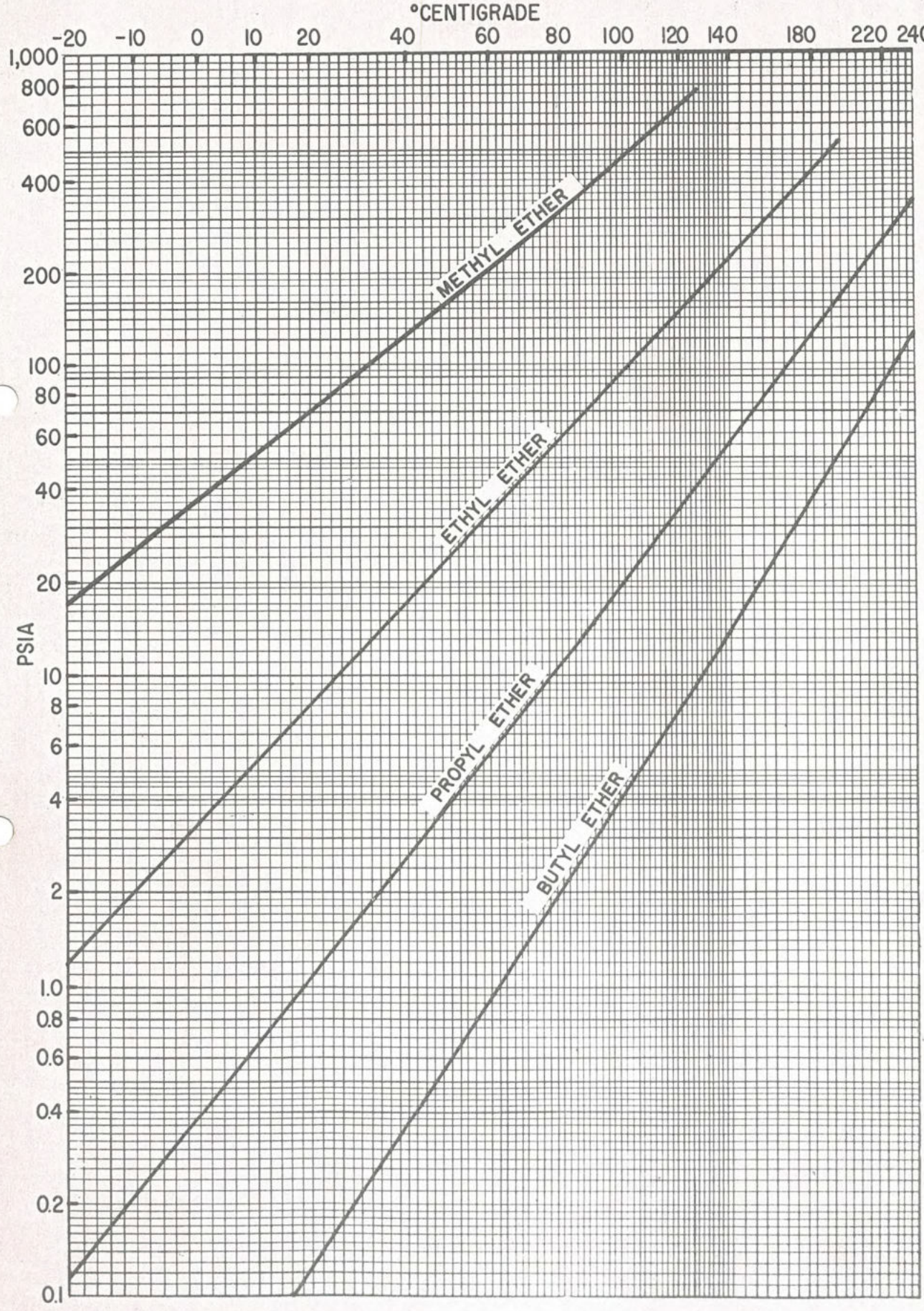


Fig. 28-2—Gives vapor pressure of ethers from −20°C to +240°C.

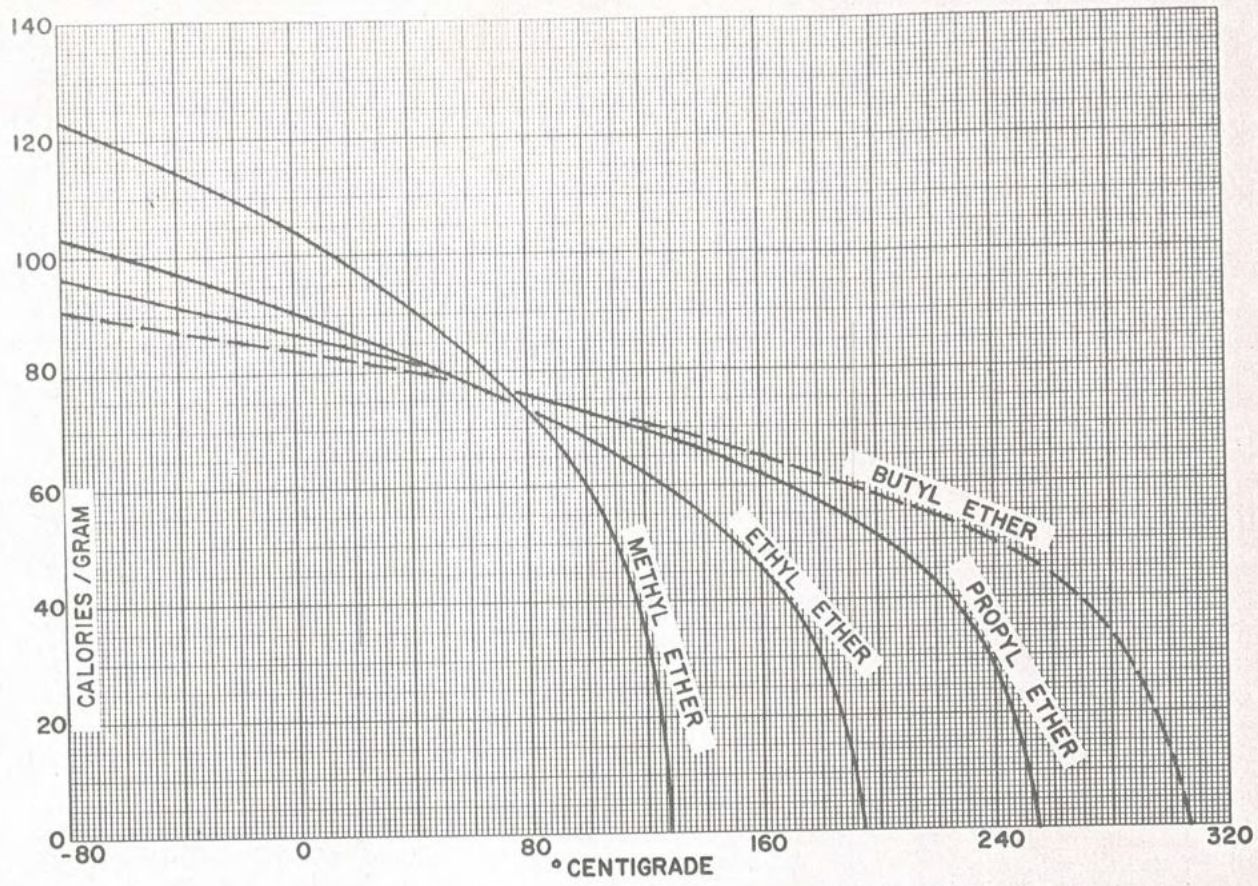


Fig. 28-3—Gives heat of vaporization of ethers from —80°C to +300°C.

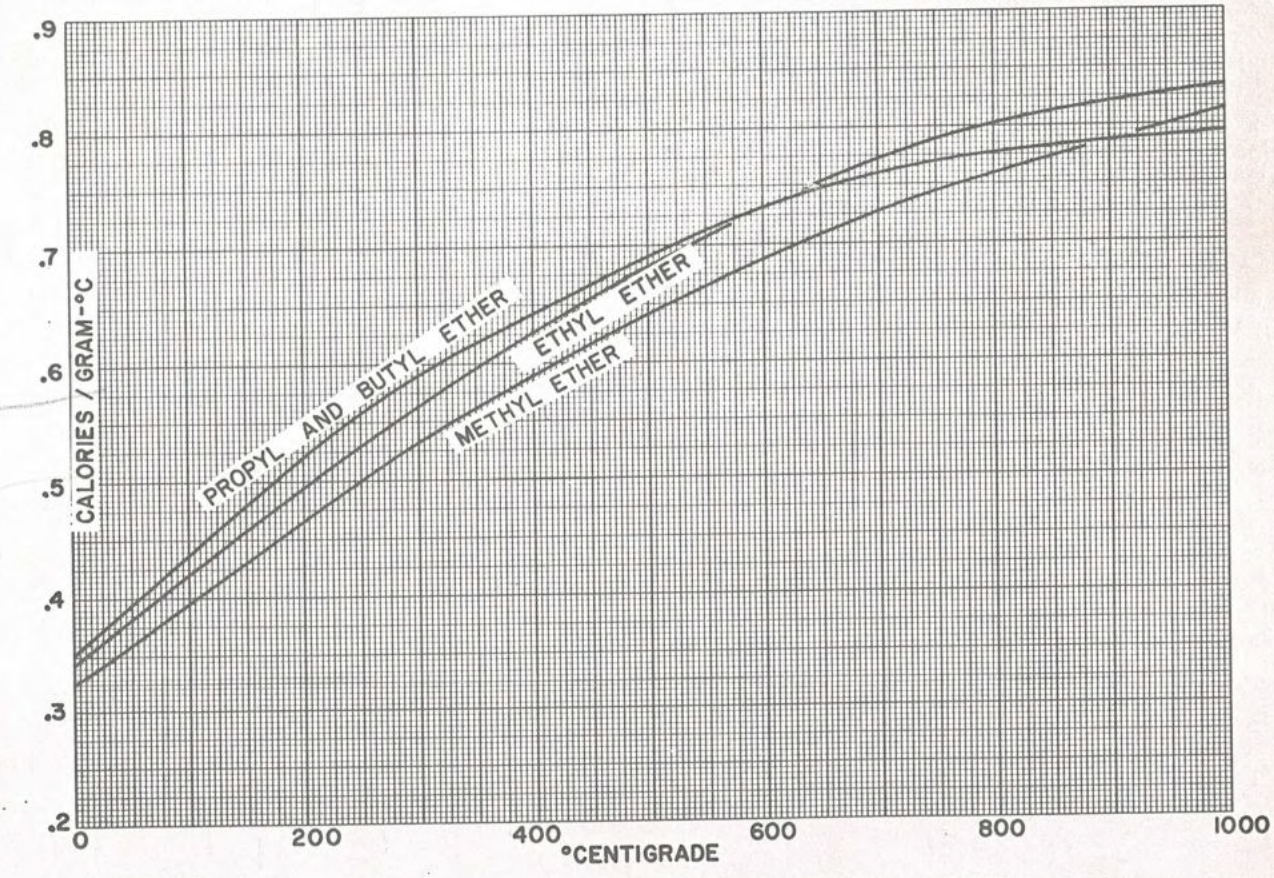


Fig. 28-4—Gives vapor heat capacity of ethers from 0°C to 1,000°C.

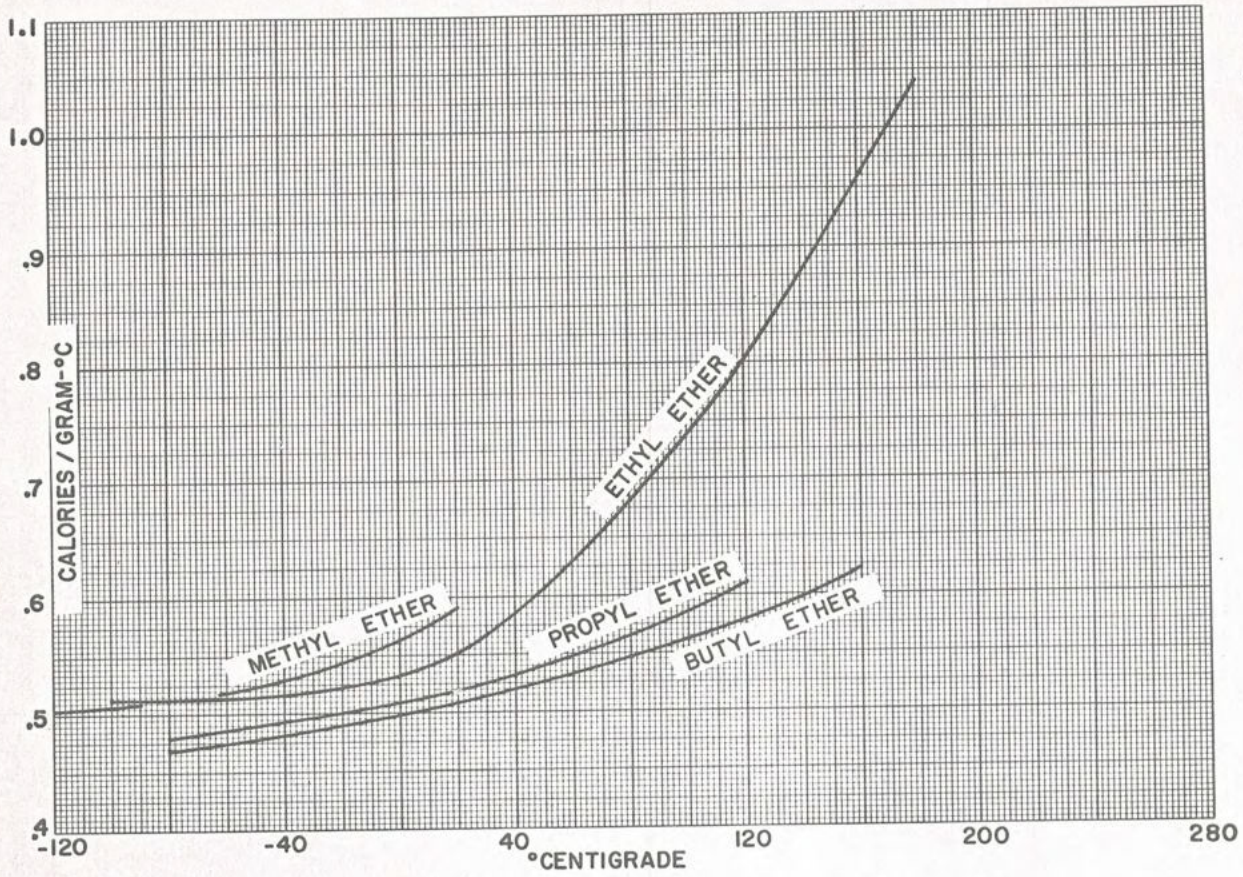


Fig. 28-5—Gives liquid heat capacity of ethers from —120°C to +180°C.

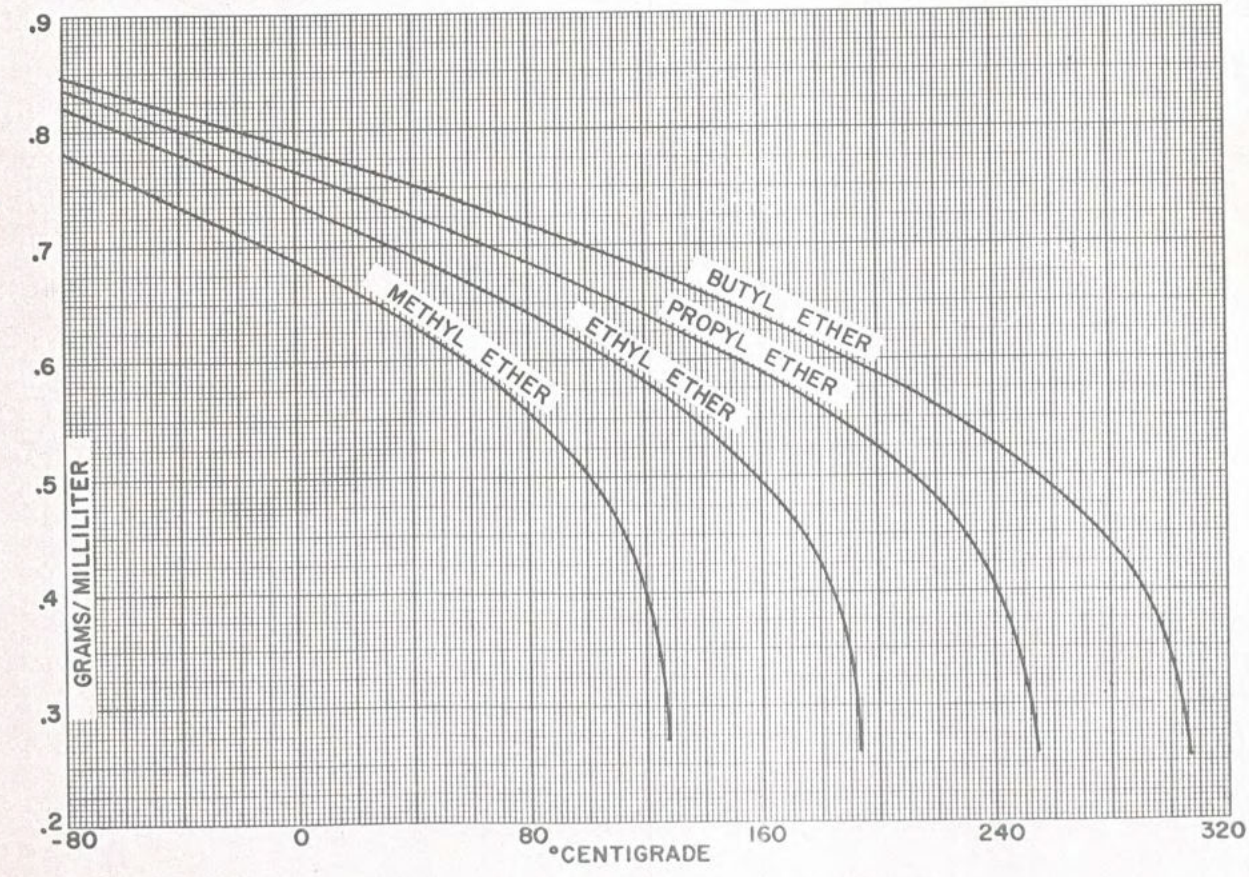


Fig. 28-6—Gives liquid density of ethers from —80°C to +300°C.

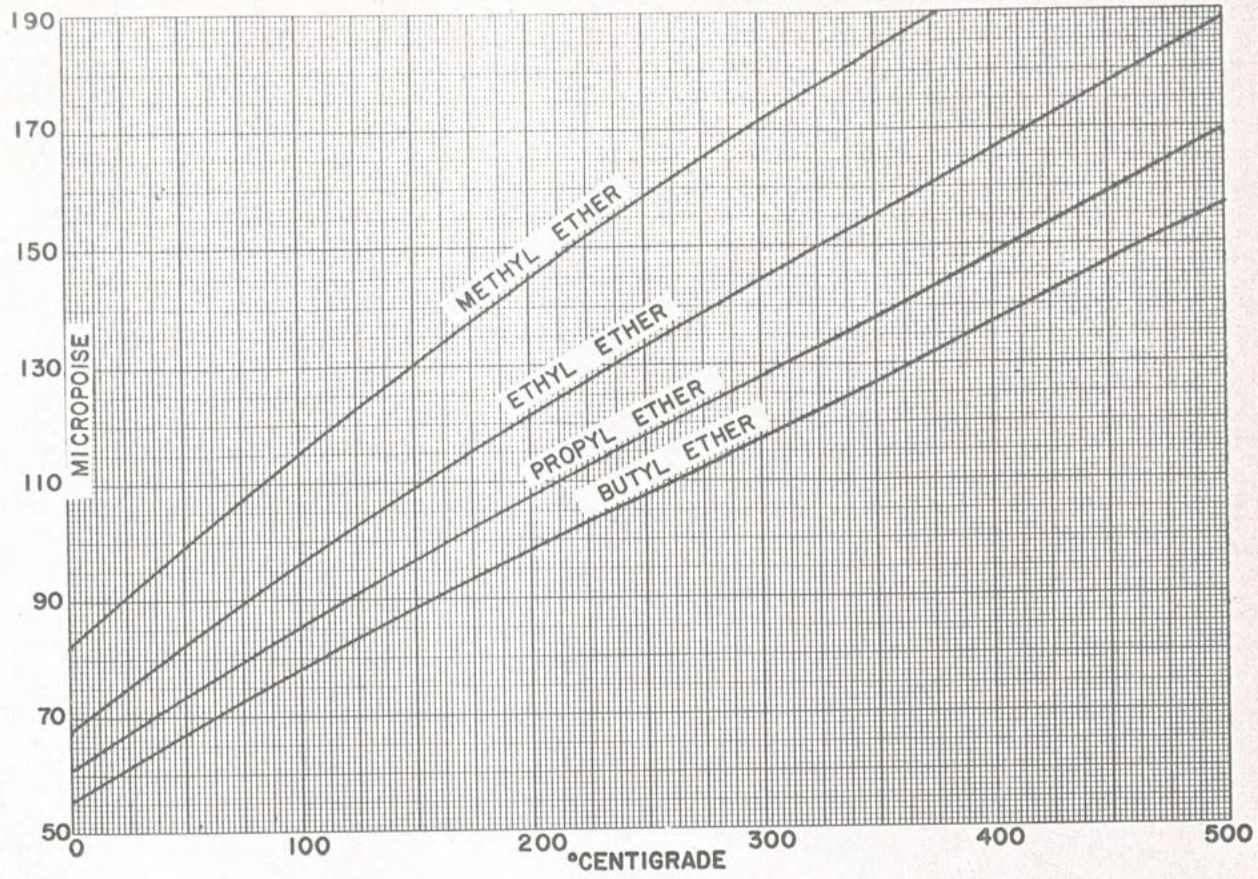


Fig. 28-7—Gives vapor viscosity of ethers from 0°C to 500°C.

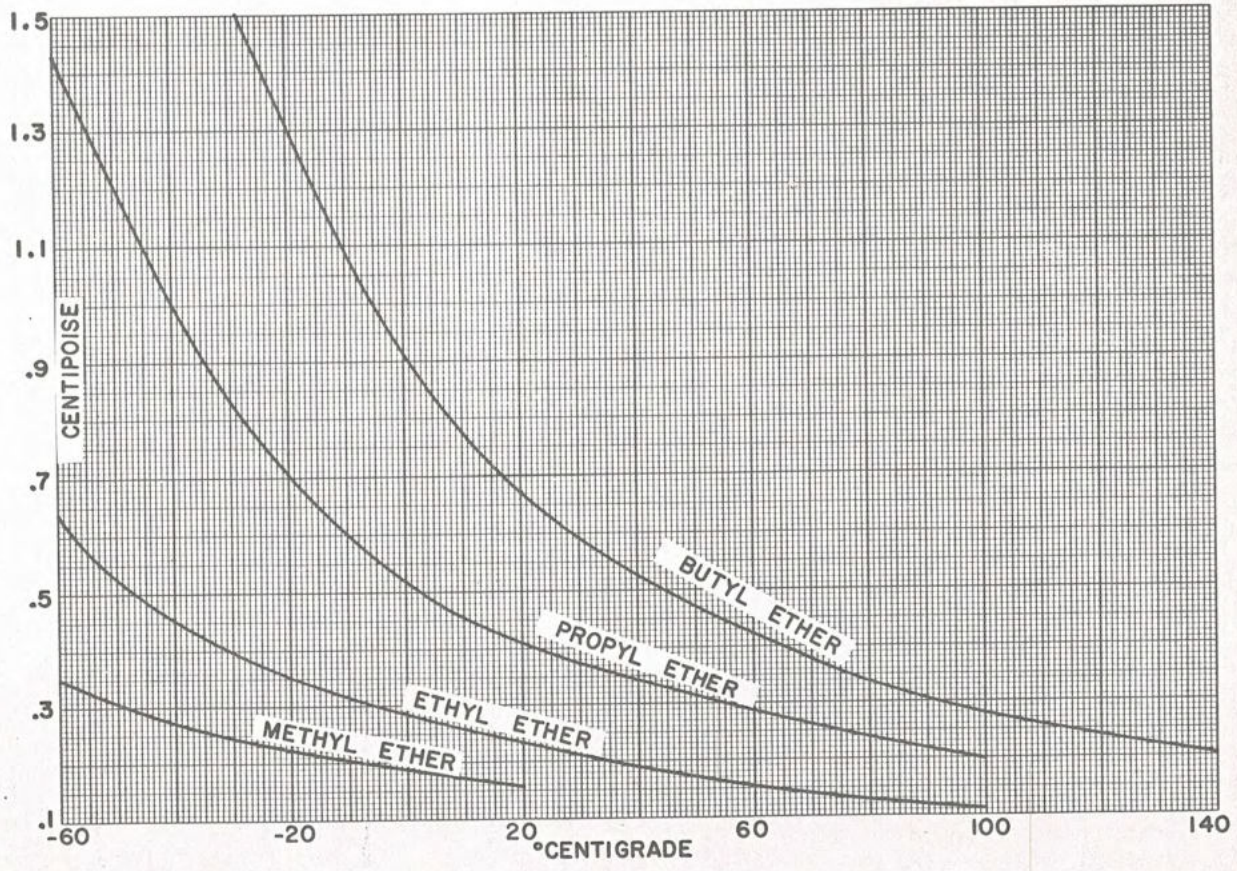
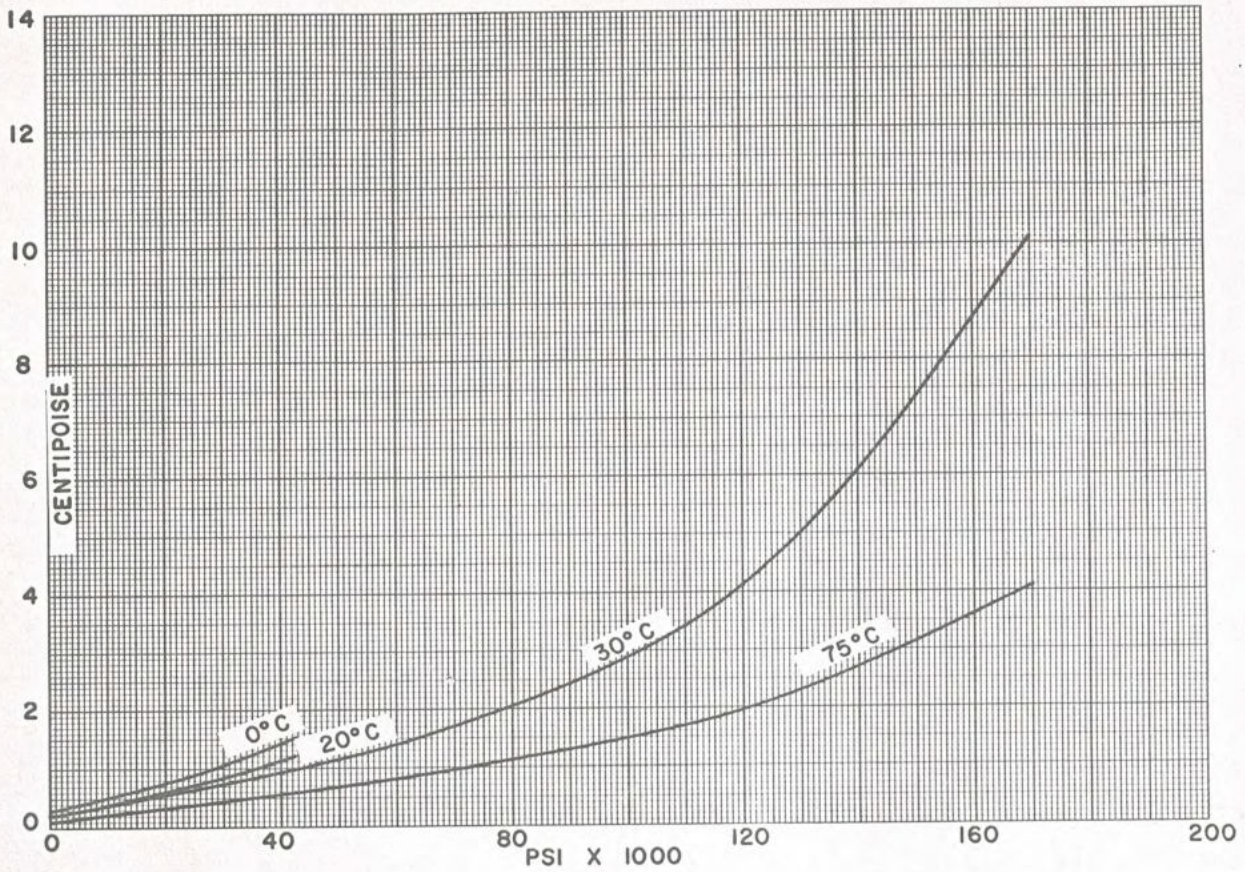


Fig. 28-8—Gives liquid viscosity of ethers from —60°C to +140°C.



Fig, 28-9—Gives pressure effect on liquid viscosity of ethyl ether from 0 psi to 170,000 psi.

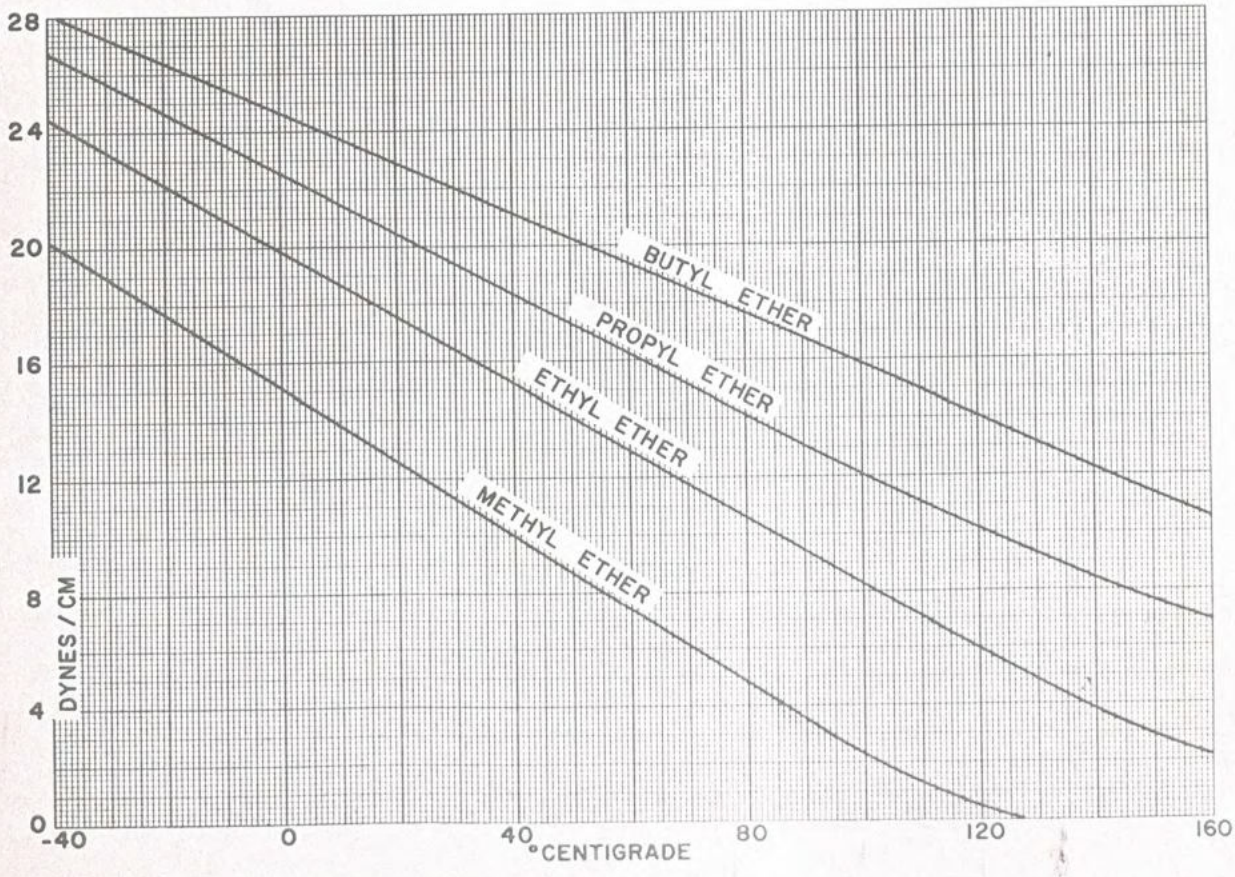


Fig. 28-10—Gives surface tension of ethers from —40° C to +160° C.

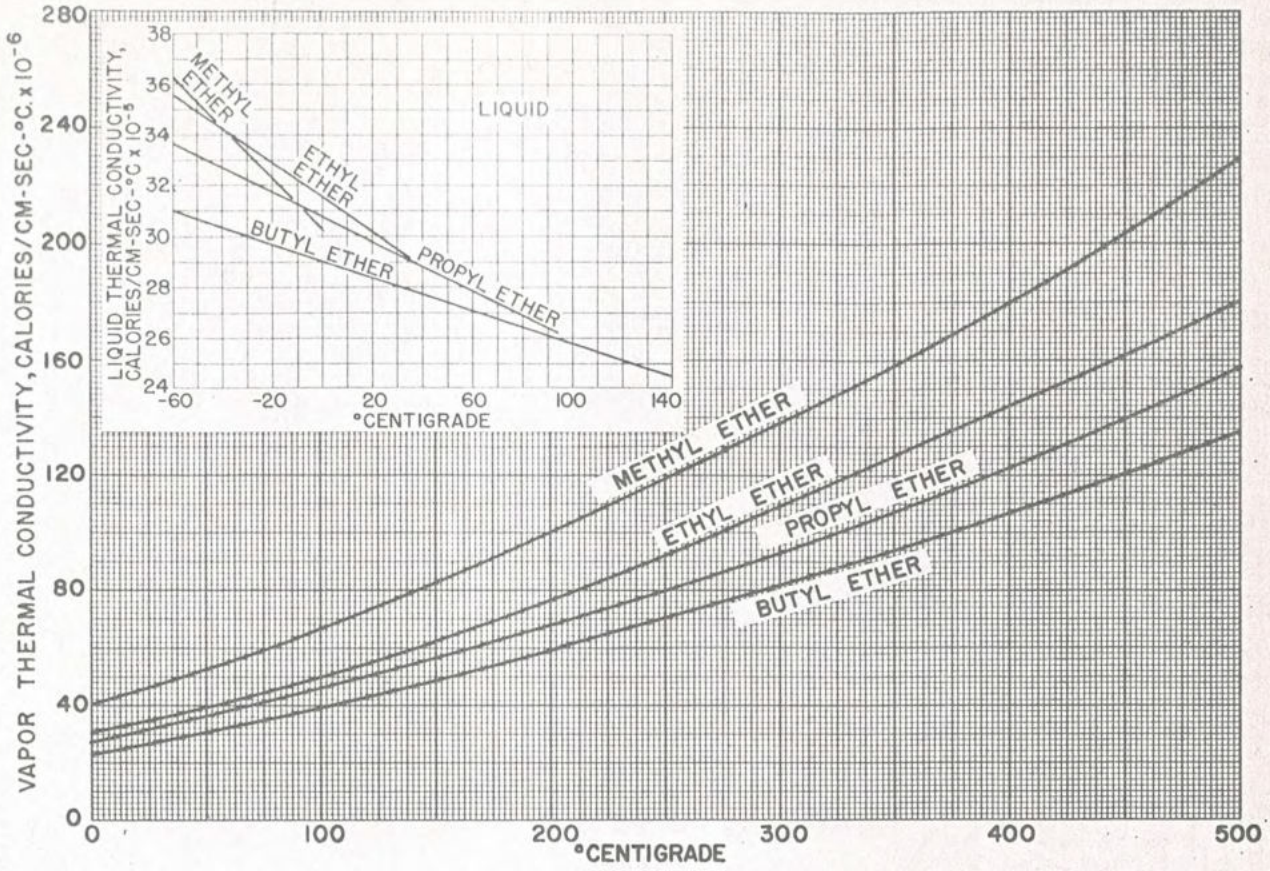


Fig. 28-11—Gives vapor and liquid thermal conductivity of ethers from —60°C to +500°C.

Viscosity. The method of Bromley and Wilke[14] was used to calculate the vapor viscosities. When compared with experimental data on methyl ether[5,15] and ethyl ether,[5,13] the average error was 2.7 percent.

Liquid viscosity data are available for ethyl ether[13] from −110° C to +100° C, for propyl ether[13] from 0° C to 90° C, and for butyl ether[3] at room temperature. The method of Thomas[5] was used to estimate the viscosities at various temperatures of methyl ether and butyl ether. Comparison with 12 experimental points showed an average error of 6.4 percent. Below the boiling point, the average error for eight points was 4.6 percent.

Fig. 28-9 shows the effect of pressure on the liquid viscosity of ethyl ether over the 0-75° C range.[13]

Surface Tension. The surface tension has been measured for methyl ether near its critical point;[16] for ethyl ether from 0° to the critical point; [7, 13, 17] for propyl and butyl ether from 20° C to 60° C.[16] Sugden's method,[17] used to estimate the surface tension over a wider temperature range, gave an average error of 5 percent when compared to eight experimental values.

Thermal Conductivity. Gribkova has measured the vapor thermal conductivity at 100° C of ethyl, propyl, and butyl ether.[19] The estimation method of Owens and Thodos gave an average error of 4.3 per cent when compared to this data.[20]

Jobst has measured the liquid-thermal conductivities from −100° C to close to the boiling point of ethyl, propyl, and butyl ether.[21] Mason has determined the thermal conductivity from 0-30° C for ethyl ether.[22] The thermal conductivity of methyl ether was estimated by the method of Robbins and Kingrea.[23]

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Indexing Terms: Butyl Ether-9, Computations-4, Ethyl Ether-9, Heat-7, Liquid Phase-5, Methyl Ether-9, Physical Properties-7, Pressure-7, Properties/Characteristics-7, Propyl Ether-9, Temperature-6, Vapor Phase-5.

Part 29, "Acetates," will appear in an early issue.