

Physical Properties of Hydrocarbons

Part 7—Chlorinated Aliphatics

Part 8—Primary Alcohols

Part 9—Thermal Conductivity of C₁ to C₄ Hydrocarbons

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UNLIKE MANY of the petrochemicals that have become major products only in the past decade, the primary alcohols—methanol, ethanol, propanol and butanol—have been important industrial chemicals for many years. They are mature products whose growth in the future will be less than 5 percent per year. Their present combined output of 5 billion pounds per year can be attributed to the combination of years of availability, low price, good solvent characteristics, and versatility as raw materials for other chemical products.

The steady move toward production of these alcohols from hydrocarbons represents a good example of how petrochemical technology is continuing to broaden its scope at the expense of other raw material sources.

Methanol's 2.5 billion pounds/year use places it at the top of the list for alcohols. With almost half of it going into formaldehyde production, its future growth would appear to be the best of the four.

Ethanol is a close second to methanol, with about half of its 2 billion pounds/year going into acetaldehyde. But herein lies its major weakness. Direct oxidation of ethylene is rapidly becoming the major route to acetaldehyde, and ethanol's other chemical and solvent uses will be hard pressed to offset the loss of this market.

TABLE 8-1—Primary Alcohols

Compound	Boiling Point (°C)	Melting Point (°C)	Molecular Weight	Critical Properties		
				°C T _c	psia P _c	g/ml d _c
Methanol	64.5	-97.5	32.04	240.0	1155	0.272
Ethanol	78.4	-114	46.07	243.1	924	.275
Propanol	97.8	-127	60.09	263.6	749	.275
Butanol	117.8	-89.8	74.12	289.8	640	.270

Propanol and butanol together account for over 400 million pounds/year in production. Their versatility as solvents and raw materials for ethers, acetates, etc., enable them to have a broad end use pattern.

Because these four alcohols have been industrially important for many years, their physical properties have been extensively studied in the 0-100° C range. The engineer often encounters the alcohols in aqueous solution in plant processes and so data on the physical properties of both the pure compounds and the aqueous solutions have been included in this article.

Vapor Pressure. The vapor pressures of all four compounds up to the critical point have been extensively studied. Stull² presents data for all four compounds from -20° C to the critical temperature. There are a number of good bulletins published by alcohol manufacturers which include good physical property tables. Probably the best of these are the product booklets of Commercial Solvent Corporation.^{2,3} Such thorough compilations provide design engineers with a wealth of useful information. Recent experimental work by Ambrose⁴ on the high temperature and critical range vapor pressures of propanol and butanol give slightly different results than most previous data reported in the more common handbooks. This is especially true for the critical pressure of butanol, which Ambrose reports as 640 psia; as compared with the normally reported 700-710 psia. The author considers Ambrose's data to be the most reliable.

Figure 8-2 shows the vapor pressure of various aqueous concentrations of methanol⁵ and ethanol.⁶ The International Critical Tables⁶ are a good source of more extensive data on aqueous solution vapor pressures of the alcohols.

Heat of Vaporization. The heat of vaporization of both methanol and ethanol from 0° C to their critical point

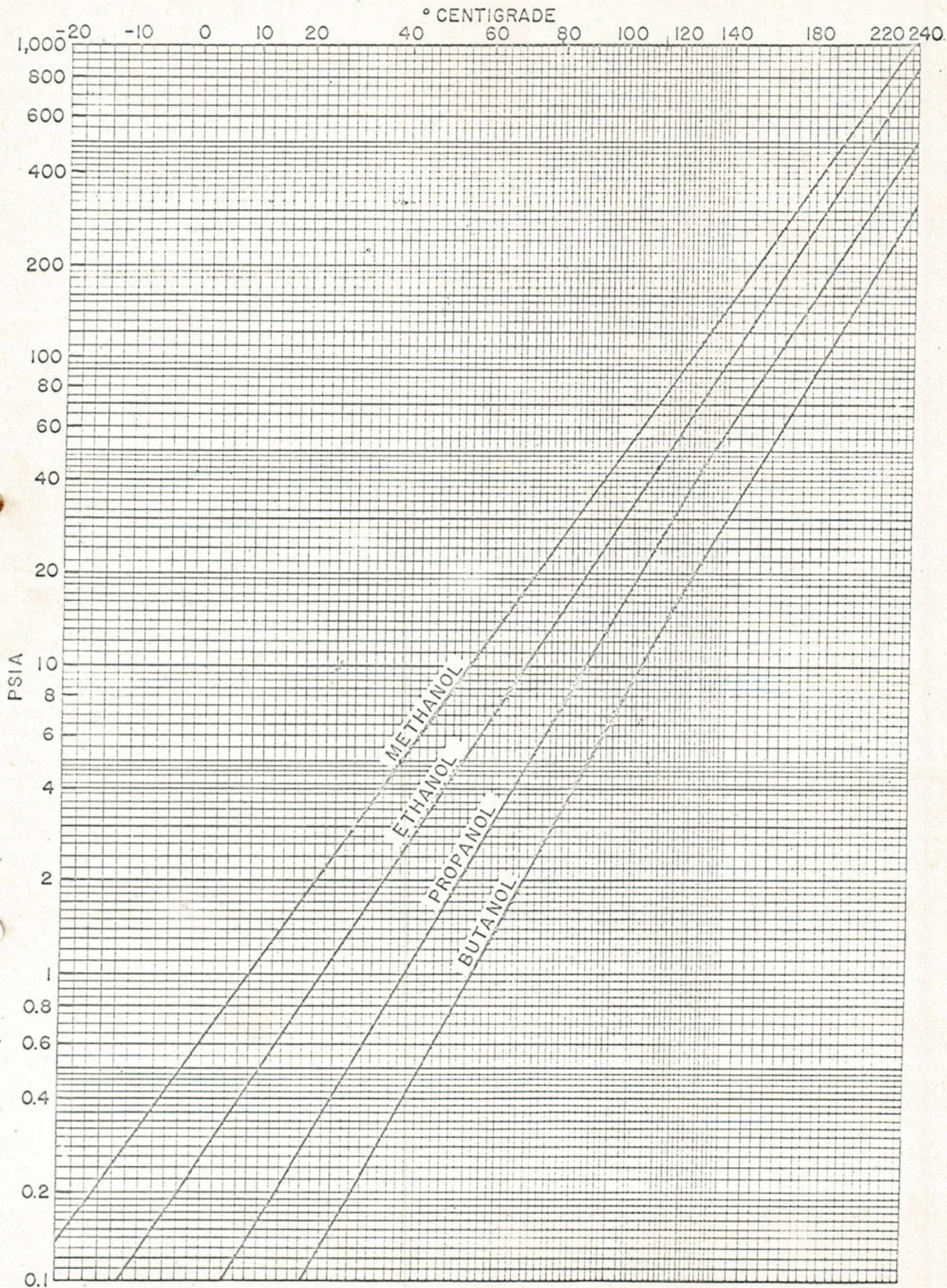


Fig. 8-1—Gives vapor pressure over a range of -20°C to $+240^{\circ}\text{C}$.

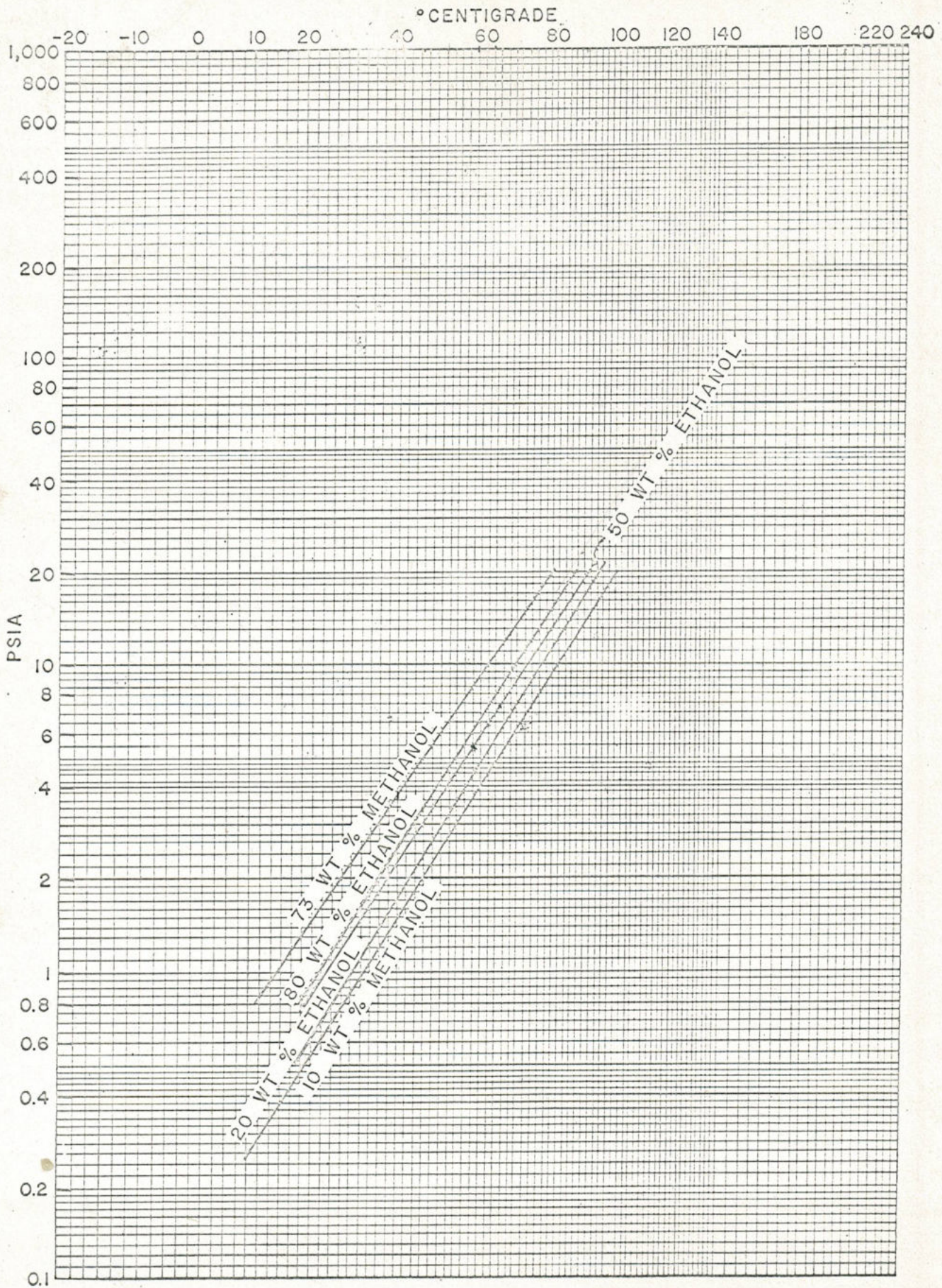


Fig. 8-2—Gives vapor pressure over a range of +10° C to +100° C.

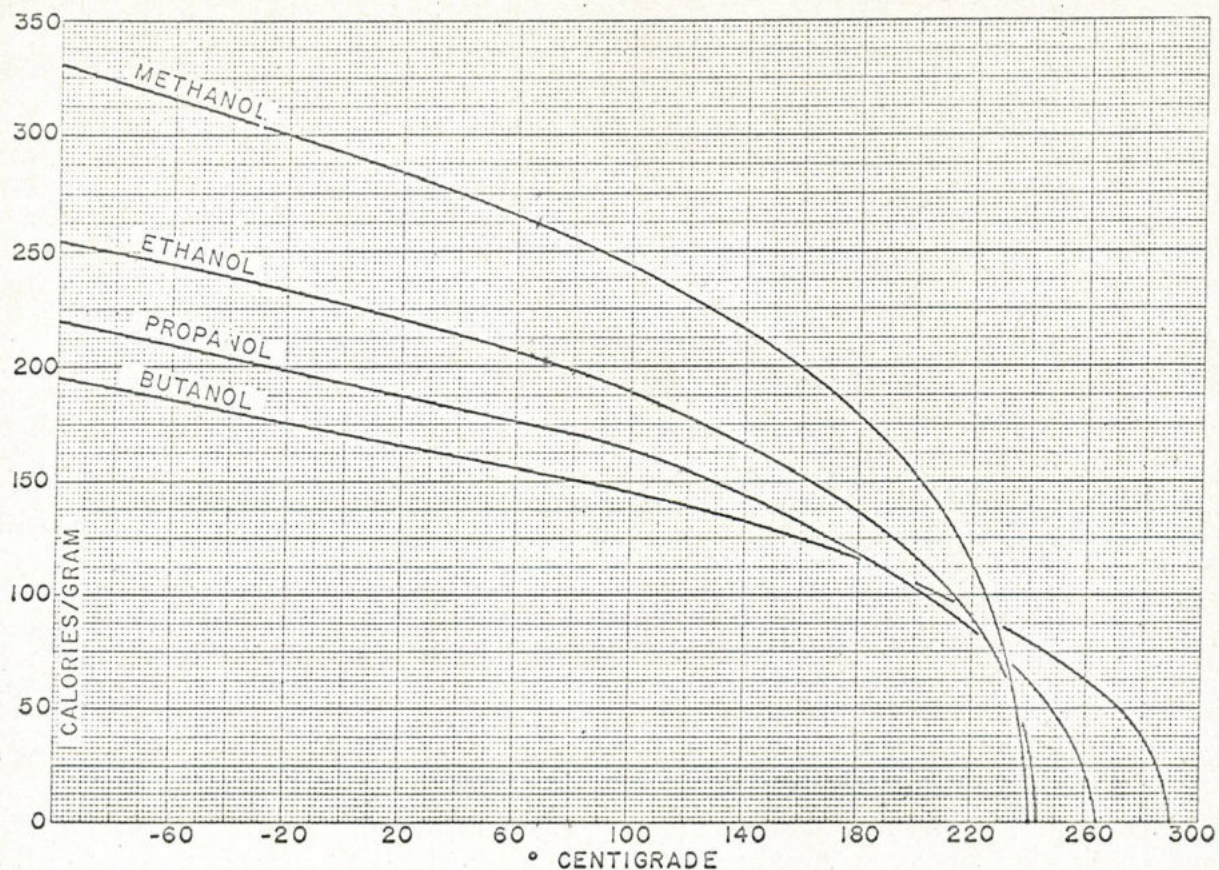


Fig. 8-3—Gives heat of vaporization over range of -100° C to +280° C.

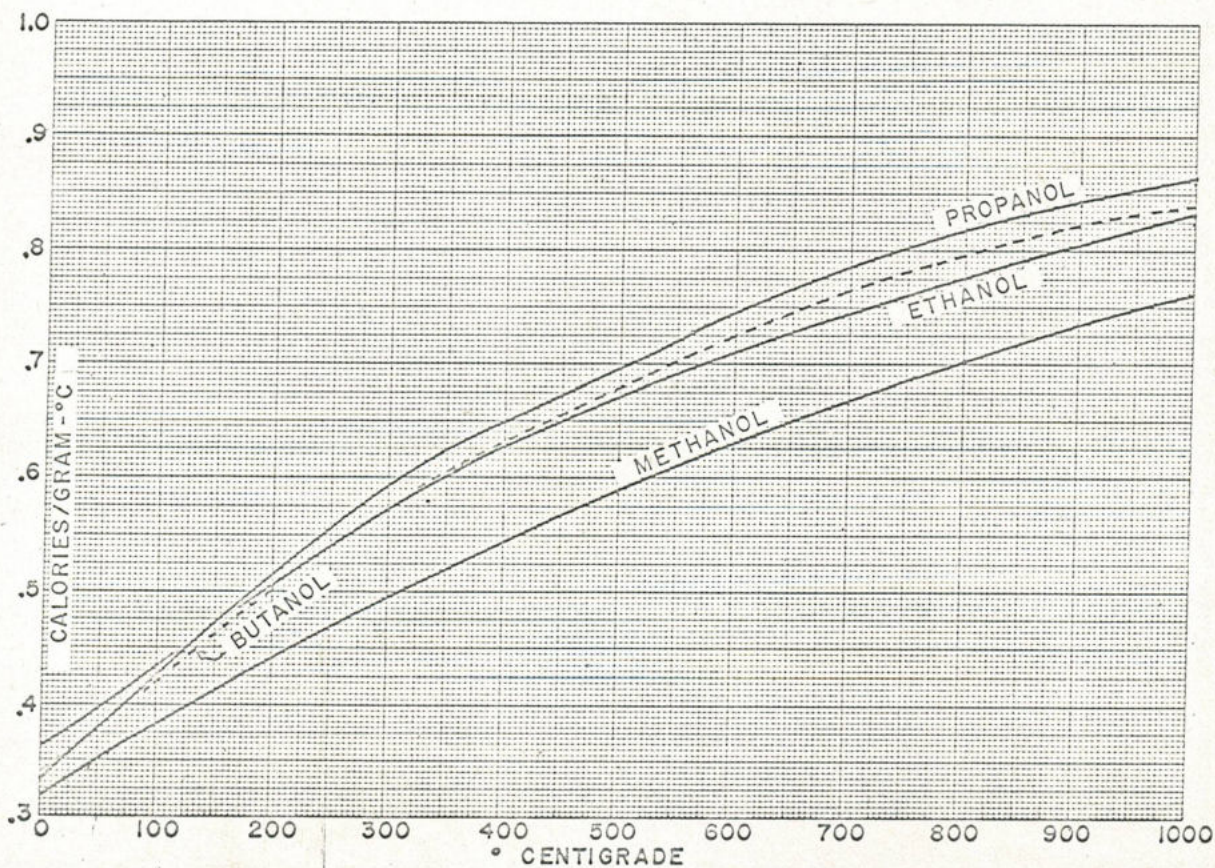


Fig. 8-4— Gives vapor heat capacity over range of 0° C to +1,000° C.

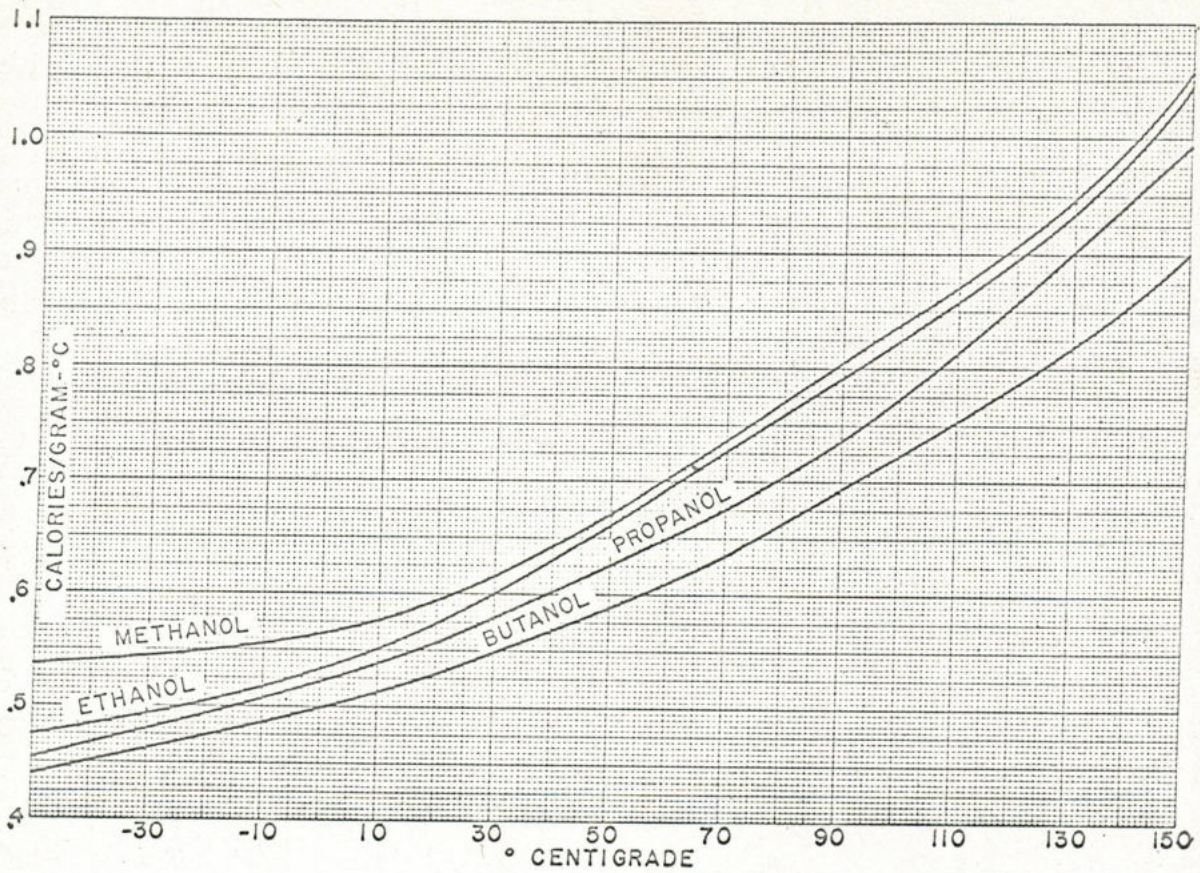


Fig. 8-5—Gives liquid heat capacity over a range of -60°C to $+150^{\circ}\text{C}$.

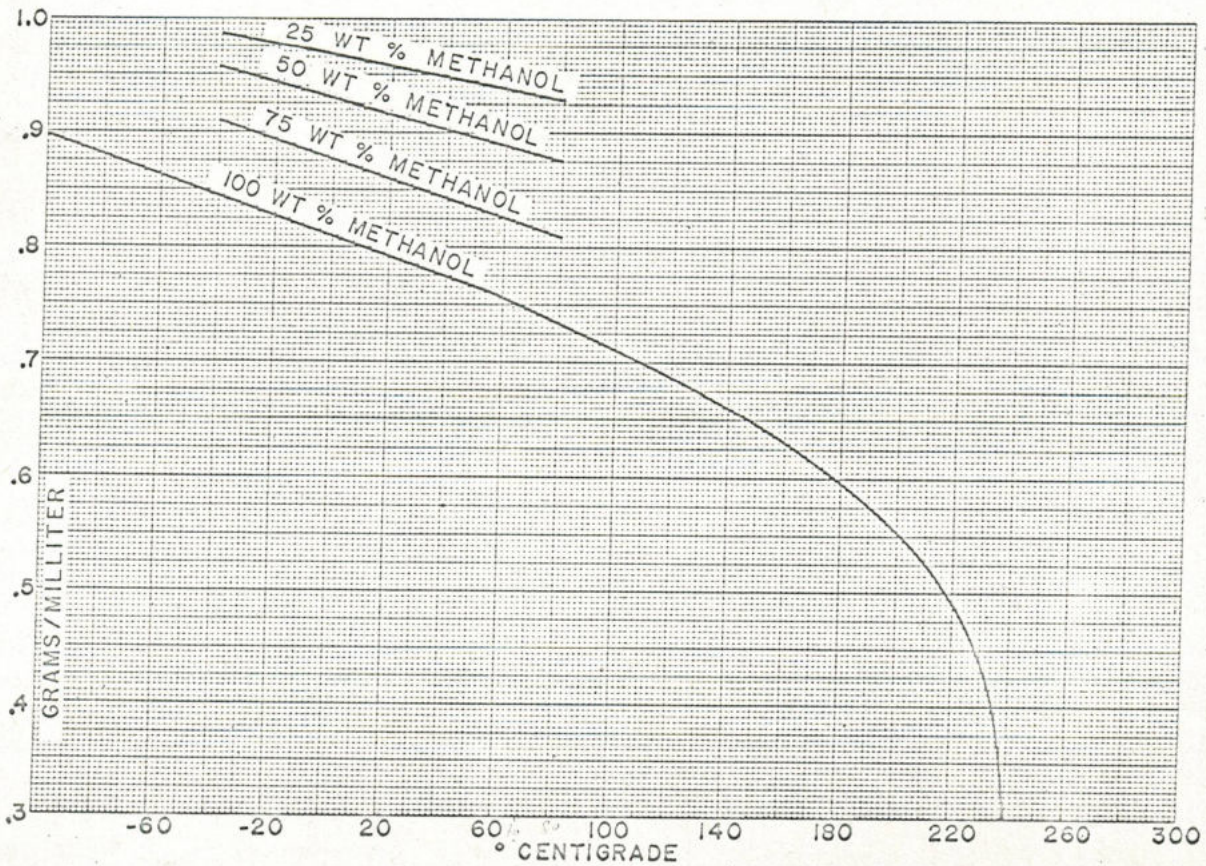


Fig. 8-6A—Gives liquid density of methanol solutions over a range of -40°C to $+80^{\circ}\text{C}$.

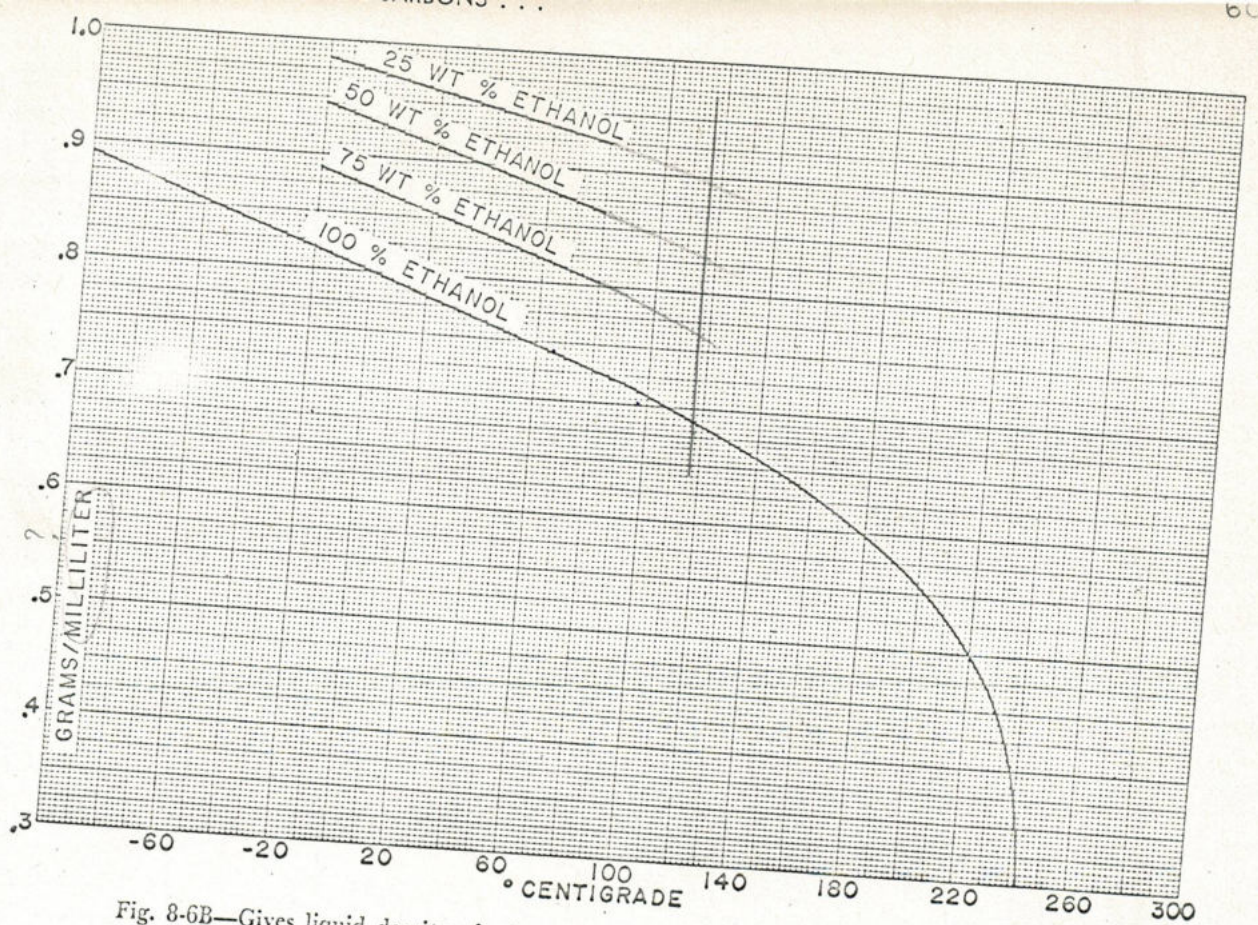


Fig. 8-6B—Gives liquid density of ethanol solutions over a range of -20°C to $+80^{\circ}\text{C}$.

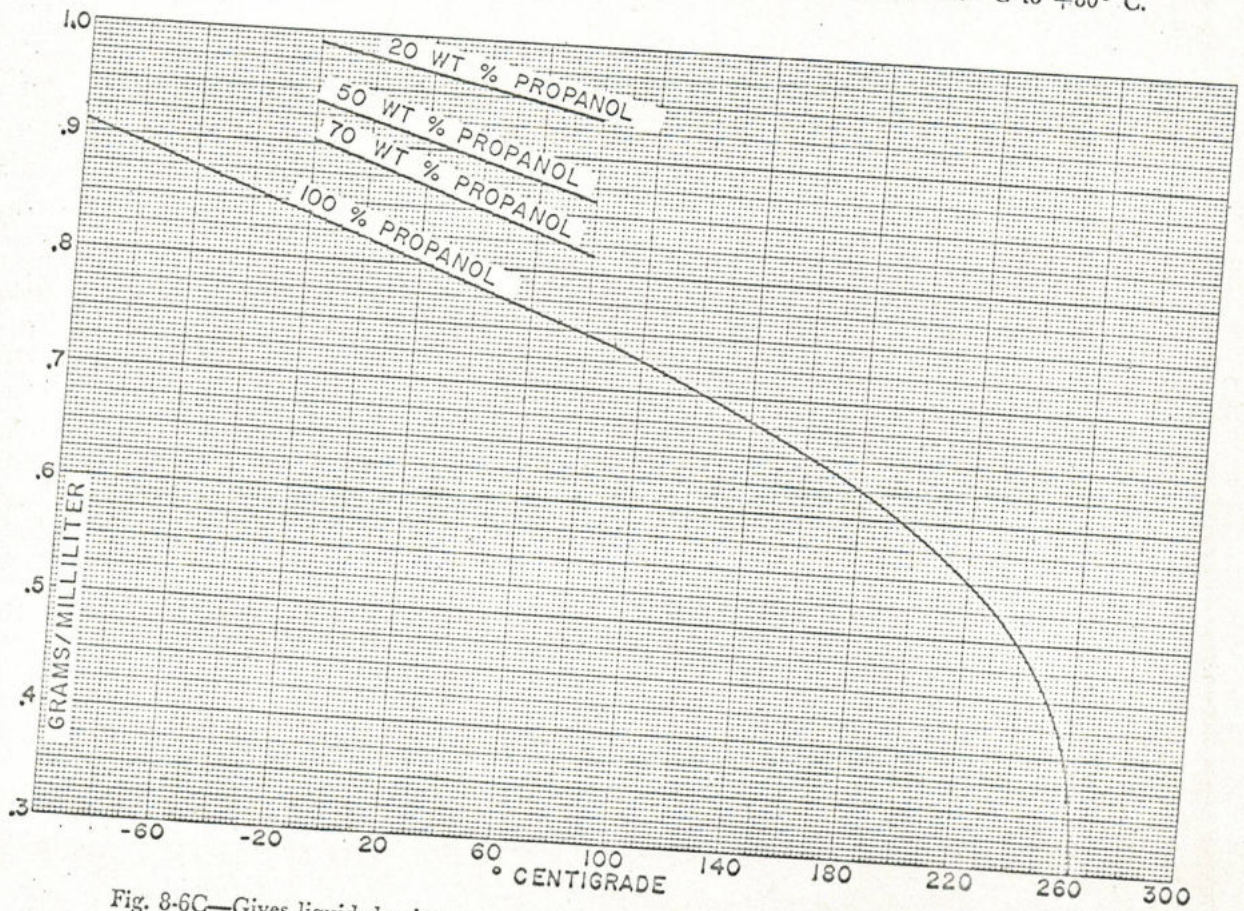


Fig. 8-6C—Gives liquid density of propanol solutions over a range of -20°C to $+80^{\circ}\text{C}$.

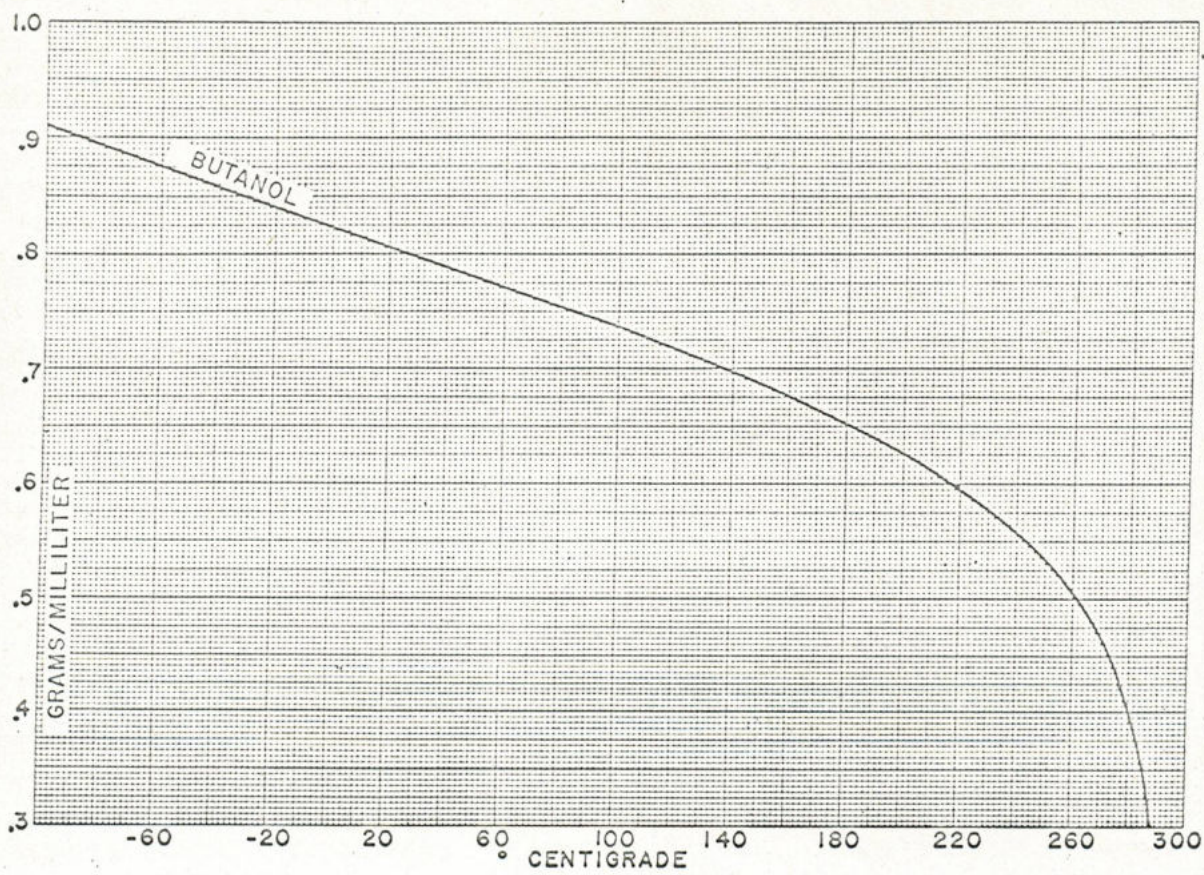


Fig. 8-6D—Gives liquid of butanol over a range of -80° C to +290° C.

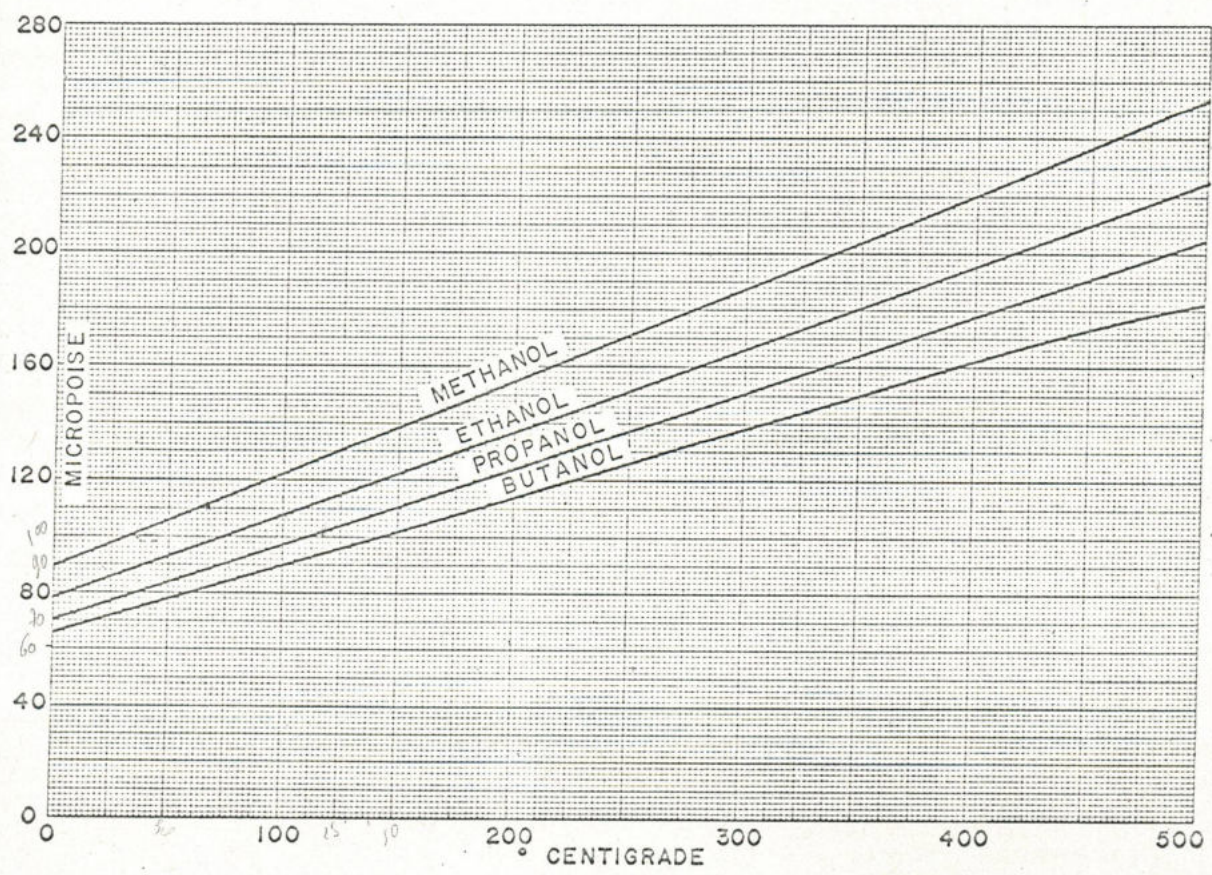


Fig. 8-7—Gives vapor viscosity over a range of 0° C to +500° C.

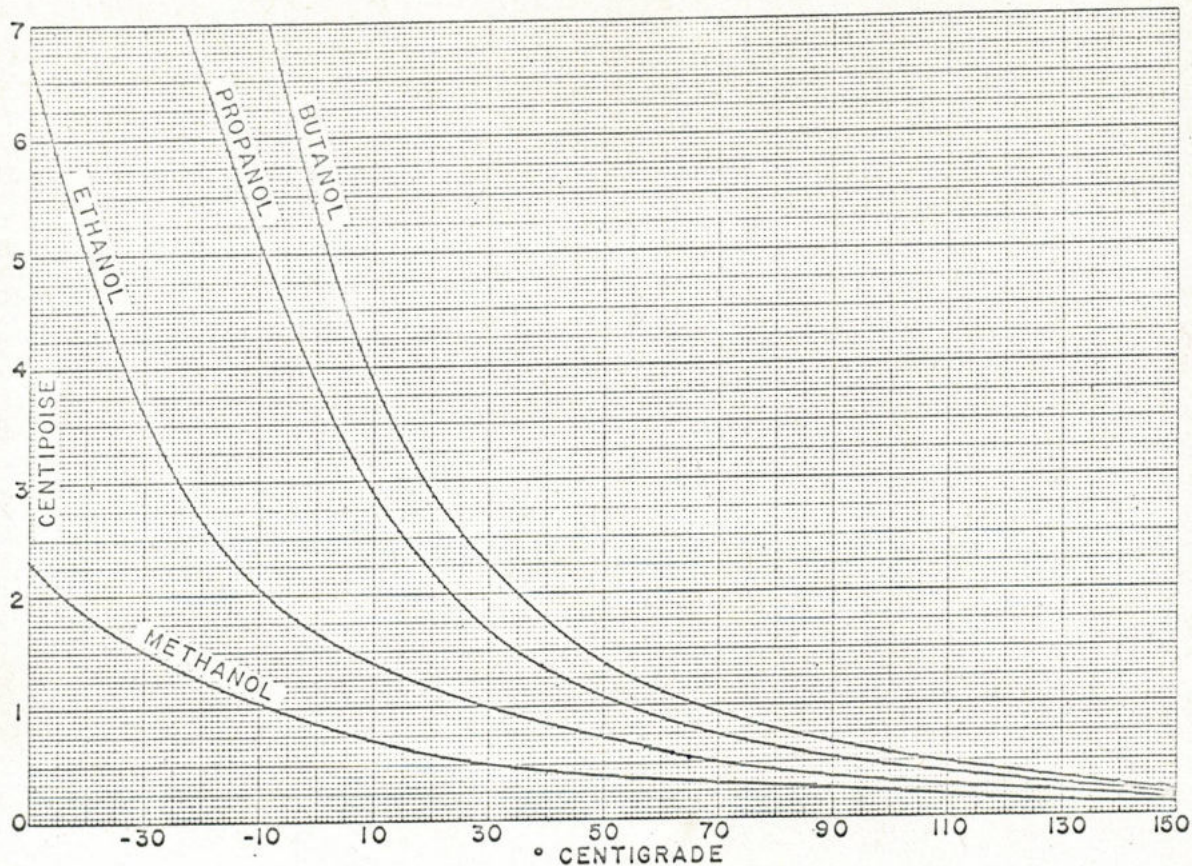


Fig. 8-8A—Gives liquid viscosity over a range of -30°C to $+150^{\circ}\text{C}$.

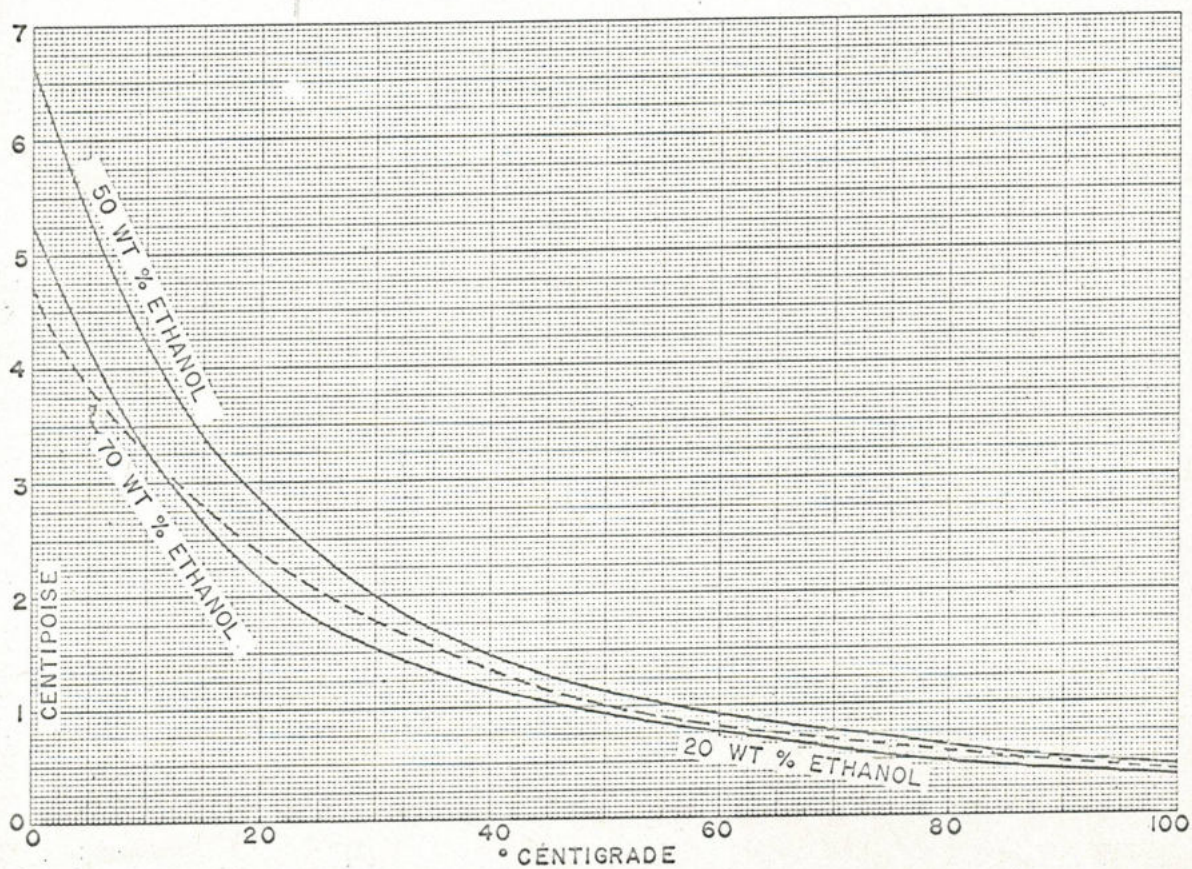


Fig. 8-8B—Gives liquid viscosity of ethanol solutions over a range of 0°C to $+100^{\circ}\text{C}$.

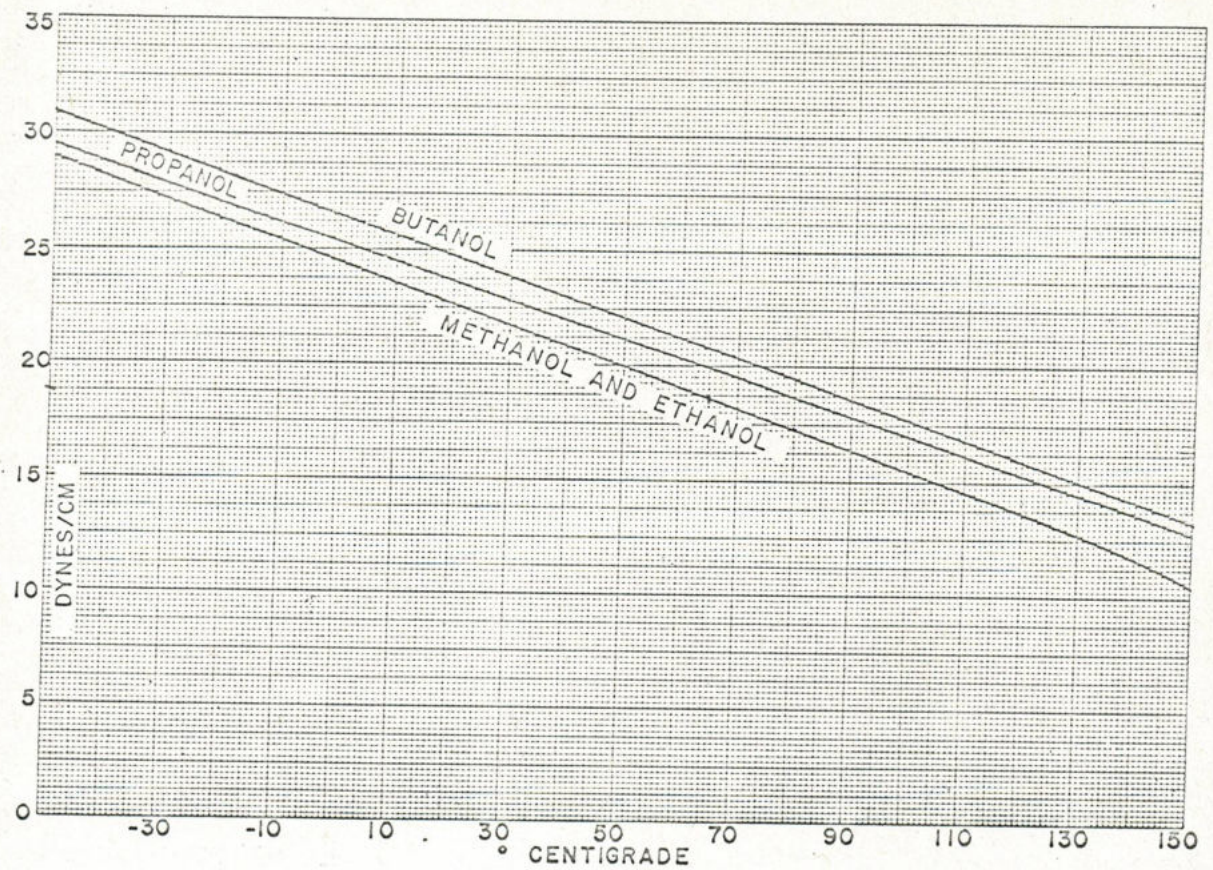


Fig. 8-9—Gives surface tension over a range of -60° C to +150° C.

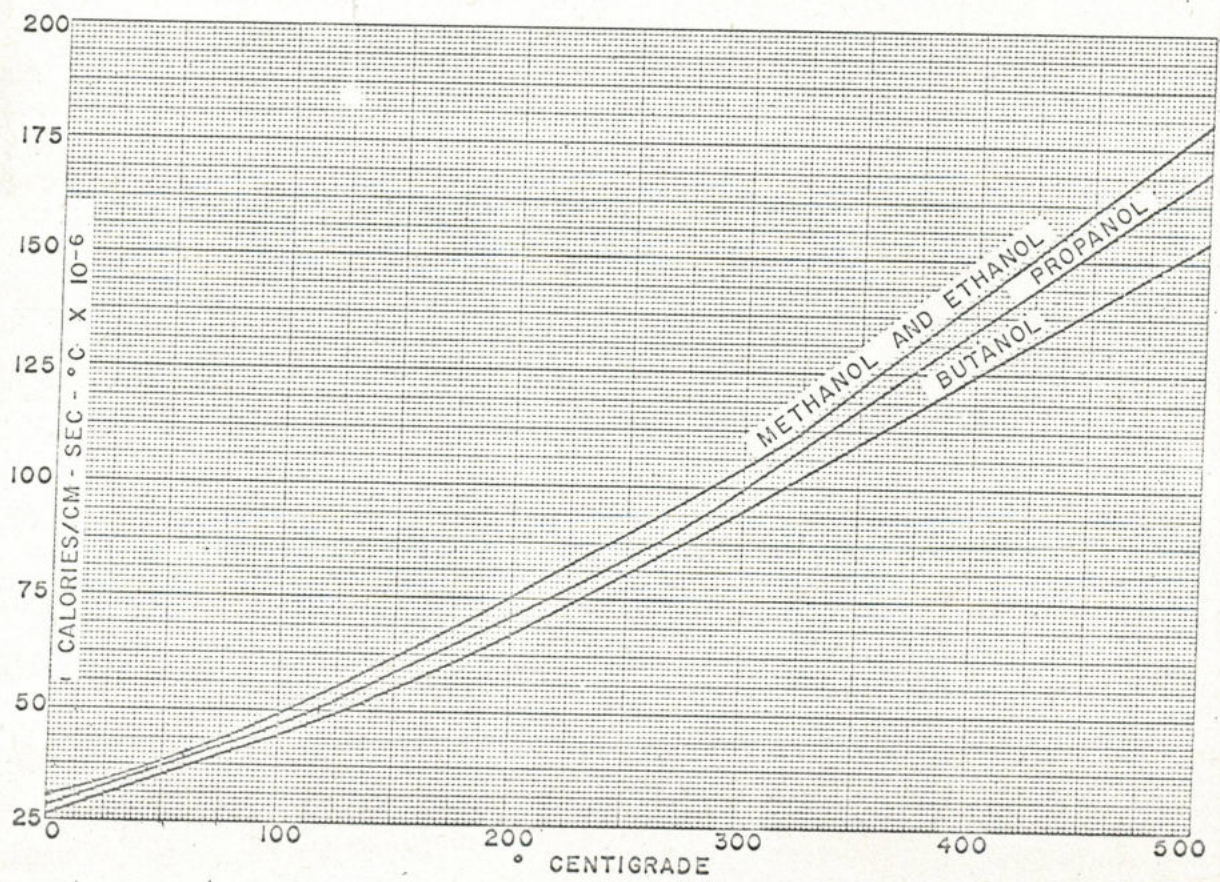


Fig. 8-10—Gives vapor thermal conductivity over a range of 0° C to +500° C.

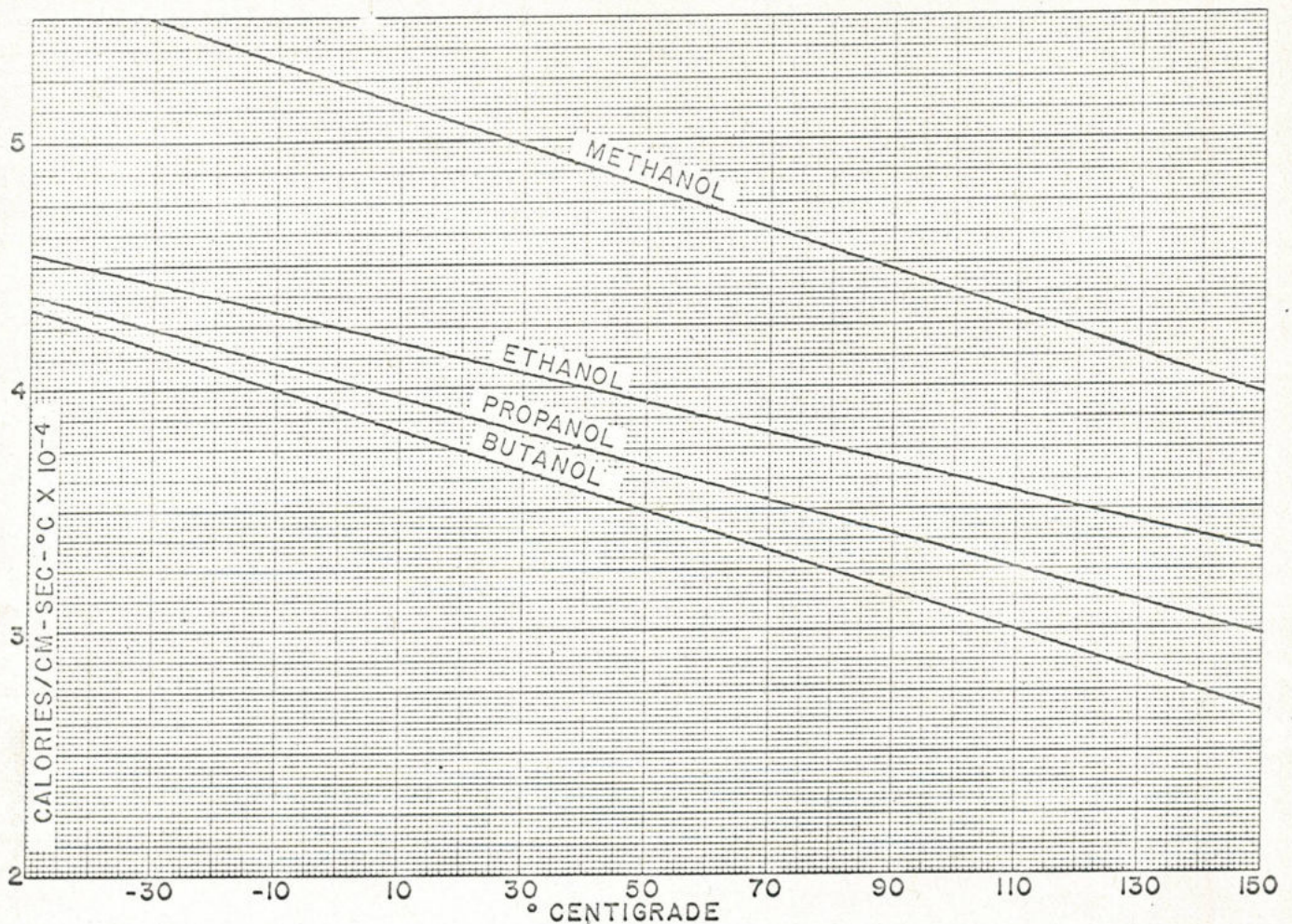


Fig. 8-11A—Gives liquid thermal conductivity over a range of -30°C to $+150^{\circ}\text{C}$

has been reported in the literature.^{2,3,6,7} The data have been extended to -100°C by use of the Watson equation, which relates the change in heat of vaporization to the reduced temperature. The percent error is normally about 1 percent. For propanol, the extensive data of Cosner⁸ have been supplemented with the data of Mathews⁹ and Williamson.¹⁰ Once again, the low temperature data have been determined by use of the Watson equation. Data for butanol are available only at the boiling point and have been extrapolated to the high and low temperature ranges by the Watson equation. The error should be only 1-3 percent, except for temperatures within 10° of the critical point.

Heat Capacity. The vapor heat capacity of methanol, ethanol, and propanol is available from the compilation of Kobe.^{11,12} The vapor heat capacity for butanol was estimated over the entire temperature range by the method of Dobratz, which is based upon the stretching and bending vibration contributions of the various bonds in the molecule. The error expected by using this method for alcohol compounds is less than 5 percent.

The liquid heat capacities are available over a wide

temperature range for methanol,^{2,3,7} ethanol,^{3,6,7} and propanol.^{6,7} The limited data available on butanol⁸ have been expanded by the estimation method proposed by Chow and Bright.

$$C_p = b/w^{2.8}$$

where

C_p = liquid heat capacity

b = a constant. For butanol, $b = 0.00187$

w = Watson density expansion factor

For the other three alcohols, this method gave an average error of 4.1 percent and a maximum error of 7 percent.

Density. The liquid density of the pure alcohols is available from a number of literature sources.^{2,3,6,7} For high temperatures up to the critical point, there are several good sources for propanol^{4,8} and butanol.⁴ It is rather surprising that the densities of all four compounds are very close in the 0 - 100°C range, varying from one another by only a few percent.

The aqueous densities of the alcohols are also very similar. The densities of methanol,² ethanol,³ and propanol¹³ solutions in the -20 to $+80^{\circ}\text{C}$ range at various con-

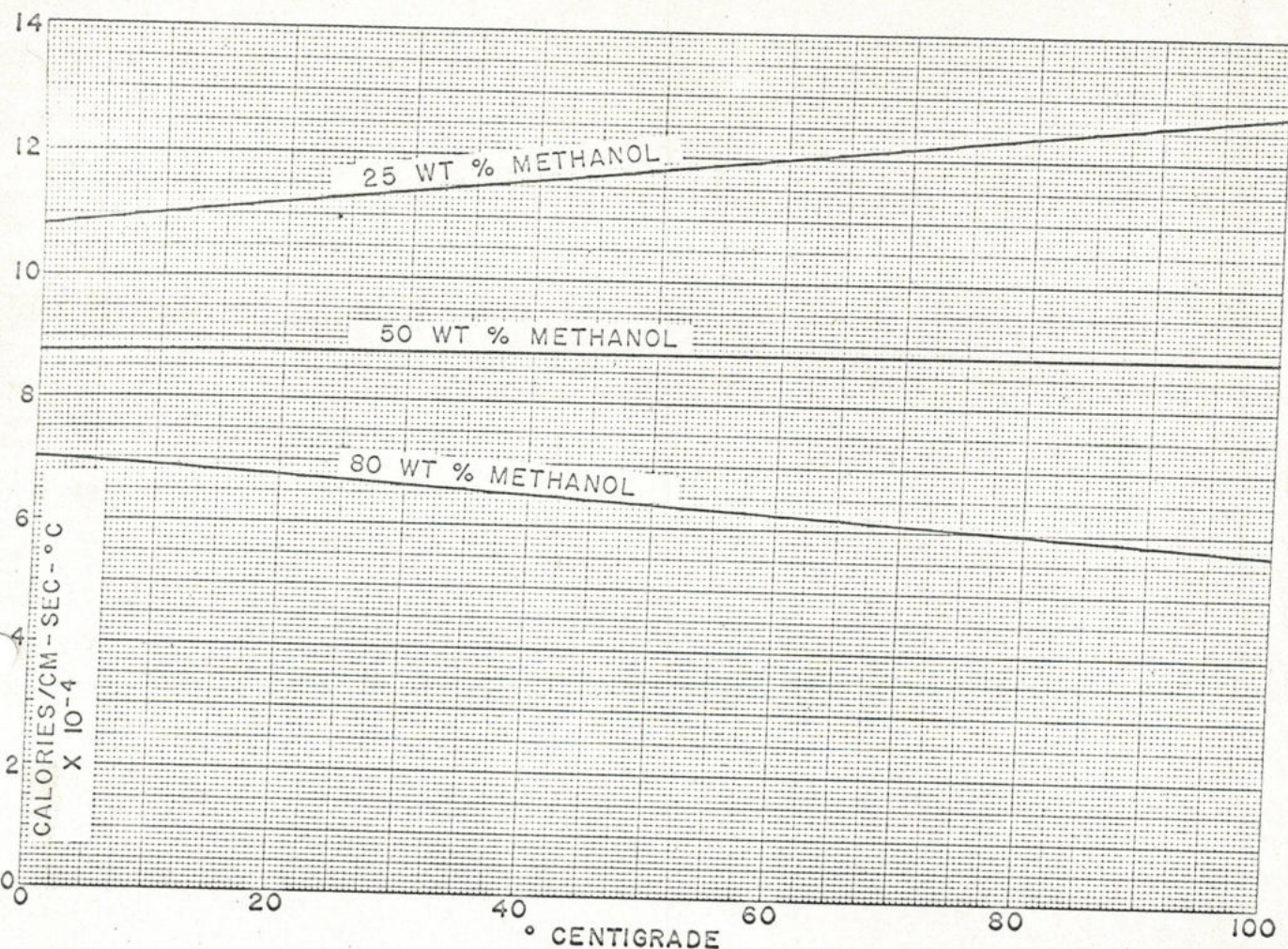


Fig. 8-11B—Gives liquid thermal conductivity for methanol solutions over a range of 0° C to +100° C.

centrations are presented to show the effect of water dilution on the densities.

Viscosity. The vapor viscosity data from the literature¹⁴ are extended over the temperature range by the method of Bromley and Wilke, which relates viscosity to the critical properties and the reduced temperature. The error should be less than 3 percent in the 0-500° C range.

The liquid viscosity of all four compounds is available from the literature.^{2, 3, 6, 7, 13, 14, 15} The viscosity of aqueous ethanol^{3, 6} is presented in Figure 8-8B.

Surface Tension. The best source for the surface tension of all four compounds over a wide temperature range is the International Critical Tables.⁶ It is interesting that methanol and ethanol have virtually identical surface tensions over the entire temperature range.

Thermal Conductivity. There are very little literature data available on the vapor thermal conductivity of the primary alcohols. However, Thodos and Owens¹⁶ have developed an excellent estimation method which allows calculation of the thermal conductivity in the 0-200° C range with an error of less than 1 percent. At higher

temperatures the method is not quite as accurate but still gives errors well below 5 percent.

The liquid thermal conductivities are available in the literature for all four compounds.^{17, 18, 19, 20} However, the results vary widely from source to source: The author has chosen the accumulated data of Robbins and Kingrea as the most reliable. This discrepancy among sophisticated investigators merely emphasizes the extreme difficulty of making accurate liquid thermal conductivity measurements above room temperature.

The literature also reports data for the liquid thermal conductivity of aqueous methanol² and propanol.¹⁸ The relative insensitivity of 50 percent aqueous solutions to temperature changes can be explained by the fact that the thermal conductivity of water increases as the temperature increases, whereas the thermal conductivity of pure methanol or propanol decreases with increasing temperature. The net result is to virtually cancel the change in each component.

LITERATURE CITED

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- 2 "Synthetic Methanol," Commercial Solvents Corp.
- 3 "Industrial Ethyl Alcohol," Commercial Solvents Corp.
- 4 Ambrose, D., *Journal of the Chemical Society* 1963, pp. 3614-25.
- 5 Othmer, D. F., *Industrial and Engineering Chemistry* 37 (3), pp. 299-303 (1945).

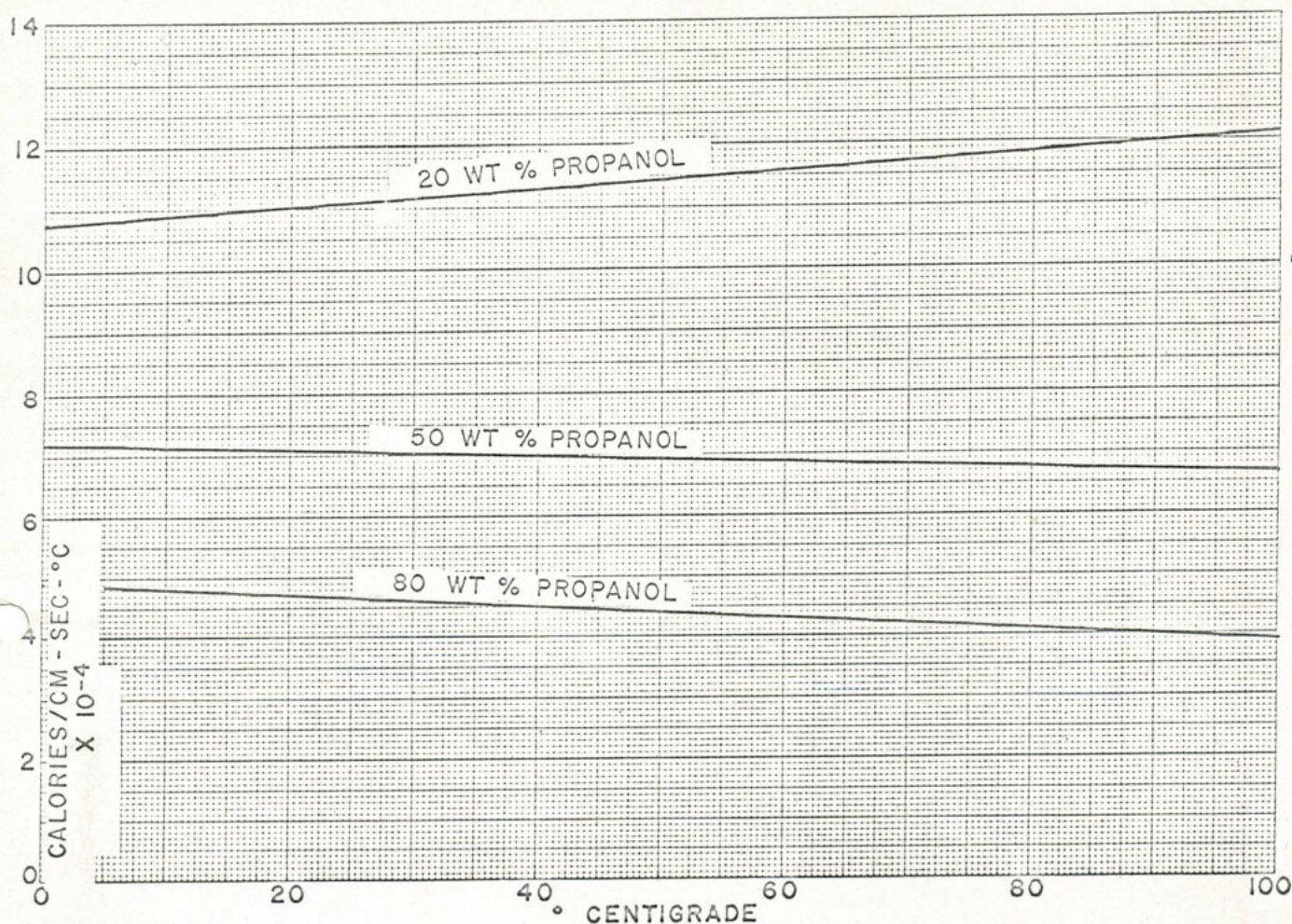


Fig. 8-11C—Gives liquid thermal conductivity for propanol solutions over a range of 0° C to +100° C.

- ⁶ International Critical Tables, McGraw-Hill Book Co., Inc. (1926).
⁷ Timmermans, J., *Physico-Chemical Constants of Pure Organic Compounds*, Elsevier Publishing Co., Inc., New York (1950).
⁸ Cosner, J. L., *Journal of Chemical and Engineering Data* 6, pp. 360-3 (1961).
⁹ Mathews, J. F., *Journal of Physical Chemistry* 65, pp. 758-762 (1961).
¹⁰ Williamson, K. D., *Journal of Chemical Physics* 26, pp. 1409-11 (1957).
¹¹ Kobe, K. A., *Petroleum Refiner* 29 (9), pp. 135-9 (1950).
¹² *Ibid.* 30 (8), pp. 119-22 (1951).
¹³ Mikhail, S. Z., *Journal of Chemical and Engineering Data* 8 (3), pp. 323-8 (1963).
¹⁴ Reid, R. C. and Sherwood, T. K., *The Properties of Gases and Liquids*, McGraw-Hill Book Co., New York (1958).
¹⁵ "Butanol and Isobutanol Product Bulletin," Dow Badische Chemical Co.
¹⁶ Owens, E. J. and Thodos, G., *AIChE Journal* 6 (4), pp. 676-681 (1960).
¹⁷ Sakiadis, B. C., *Engineering Experiment Station Bulletin No. 34*, Louisiana State University (1952).
¹⁸ Bates, O. K., *Industrial and Engineering Chemistry* 37, pp. 193-5 (1945).
¹⁹ Mason, H. L., *Transaction of the ASME*, pp. 817-821 (July 1954).
²⁰ Robbins, L. A. and Kingrea, C. L., *API, Division of Refining*, 42 (III) pp. 52-61 (1962).



About the author

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Prior installments in the Physical Properties of Hydrocarbons series include:

- Part 1—Methane-Ethane-Propane-Butane, July 1965
 Part 2—C₂ to C₄ Monoolefins, August 1965
 Part 3—C₂ to C₄ Alkynes, September 1965
 Part 4—C₂ to C₄ Diolefins, October 1965
 Part 5—Chlorinated Methanes, February 1966

- Part 6—Chlorinated Ethylenes, June 1966
 Part 7—Chlorinated Aliphatics, July 1966

Part 9 will appear in an early issue and will cover the Thermal Conductivity of C₁ to C₄ Hydrocarbons.