Physical Properties of Hydrocarbons

Part 10—C_3-C_4 Alcohols

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The C_3 — C_4 secondary alcohols have uses similar to the primary alcohols previously presented. They are good solvents and are cheap starting materials for other products.

Isopropyl alcohol is the favorite starting material for production of acetone. Over one-half of its 1.5 billion pounds annual production goes into acetone production.

The consumption of the three C_4 alcohols (isobutyl alcohol, *sec*-butyl alcohol, and *tert*-butyl alcohol) as solvents and intermediates is about 300 million pound/year and will probaby not grow very rapidly.

The physical properties of these four compounds have been studied fairly extensively by experimenters. There is, however, an unusually wide spread in the critical pressures reported by various experimenters. The data used here are that of Krone[1] for *tert*-butyl alcohol and Ambrose[2] for the other three compounds. The reported values for *tert*-butyl alcohol varied from 576 to 720 psia.

Vapor Pressure. The vapor pressures of all four compounds are available from several sources.[1,2,3,4,5] As noted earlier, there is considerable discrepancy in the data near the critical temperature.

Heat of Vaporization. Except for the extensive data for *tert*-butyl alcohol,[1] experimental data are available only over the range of 20 — 100° C for the compounds.[6,7,8,9] The data have been extrapolated over the temperature range by the method of Watson, which relates the heat of vaporization to the reduced temperature.

Heat Capacity. The vapor heat capacity is reported for isopropyl alcohol,[10,11] *sec*-butyl alcohol,[9] and *tert*-butyl alcohol[9] over a wide temperature range. The heat capacity of isobutyl alcohol was calculated from the stretching and bending vibrations by the method of Dobratz.

The liquid heat capacity is available over the entire temperature range only for isopropyl alcohol.[4,12,13] The limited data for the other compounds were extrapolated by the method of Chow and Bright. For *sec*-butyl alcohol, there were no liquid heat capacity data, and so they were estimated at 20° C by the method of Johnson and Huang, and then extrapolated over the temperature range. The error by these methods should be less than 10 percent.

TABLE 10-1—Secondary Alcohols

Alcohols	Boiling Point (°C)	Melting Point (°C)	Molecular Weight	Critical Properties		
				°C T_c	Psia P_c	g/ml d_c
Isopropyl	82.5	− 86	60.09	235.3	691	0.275
Isobutyl	108.0	−108	74.12	277	623	.270
Sec-butyl	99.5	−114.7	74.12	263	608	.270
Tert-butyl	82.5	25.3	74.12	235	614	.259

Density. Ambrose[2] and Costello[17] present experimental data for the liquid density of all four compounds. These data were supplemented by the data of Krone[1] for *t*-butyl alcohol, and by data from the standard reference handbooks.[4,5,14]

Viscosity. Except for isopropyl alcohol,[15] there are no extensive vapor viscosity data available. Consequently, the estimation method of Bromley and Wilke was used for all four compounds. Comparisons of calculated values with experimental values for isopropyl alcohol gave an average error of 1.3 percent.

Experimental liquid viscosity data are available for all but *sec*-butyl alcohol in the 0 — 100° C range.[4,5,15,16] The data for *sec*-butyl alcohol in the 0 — 100° C range were estimated by the method of Souders, which relates the viscosity to the density and molecular structure. The error is normally about 10 percent. The data for all four compounds have been extrapolated over the —50° to +150° C range by plotting the reciprocal of the absolute temperature against the logarithm of the viscosity. This method yields errors of less than 5 percent.

Surface Tension. Surface tension data are available for all four compounds over a wide temperature range.[4,5,14]

Thermal Conductivity. There are almost no experimental data available for either the vapor or the liquid thermal conductivities of these alcohols. Consequently, estimation methods were used to calculate the values presented in Fig. 10-9 and 10-10. The method of Thodos and Owens, used for the vapor thermal conductivity, is extremely accurate, yielding errors of about 1 percent. The method of Robbins and Kingera for liquid thermal conductivities is not quite as good but will give errors of less than 10 percent, and probably more like 3-4 percent. Thus, the values determined by these two estimation methods are more reliable than most existing experimental data.

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[15] Reid, R. C. and Sherwood, T. K., The Properties of Gases and Liquids, McGraw-Hill Book Company, New York (1958).
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[17] Costello, J. M., and Bowden, S. T., *Recveil*, 77, pp. 36-46 (1958).

Figures 10-1 through 10-10 appear on following pages

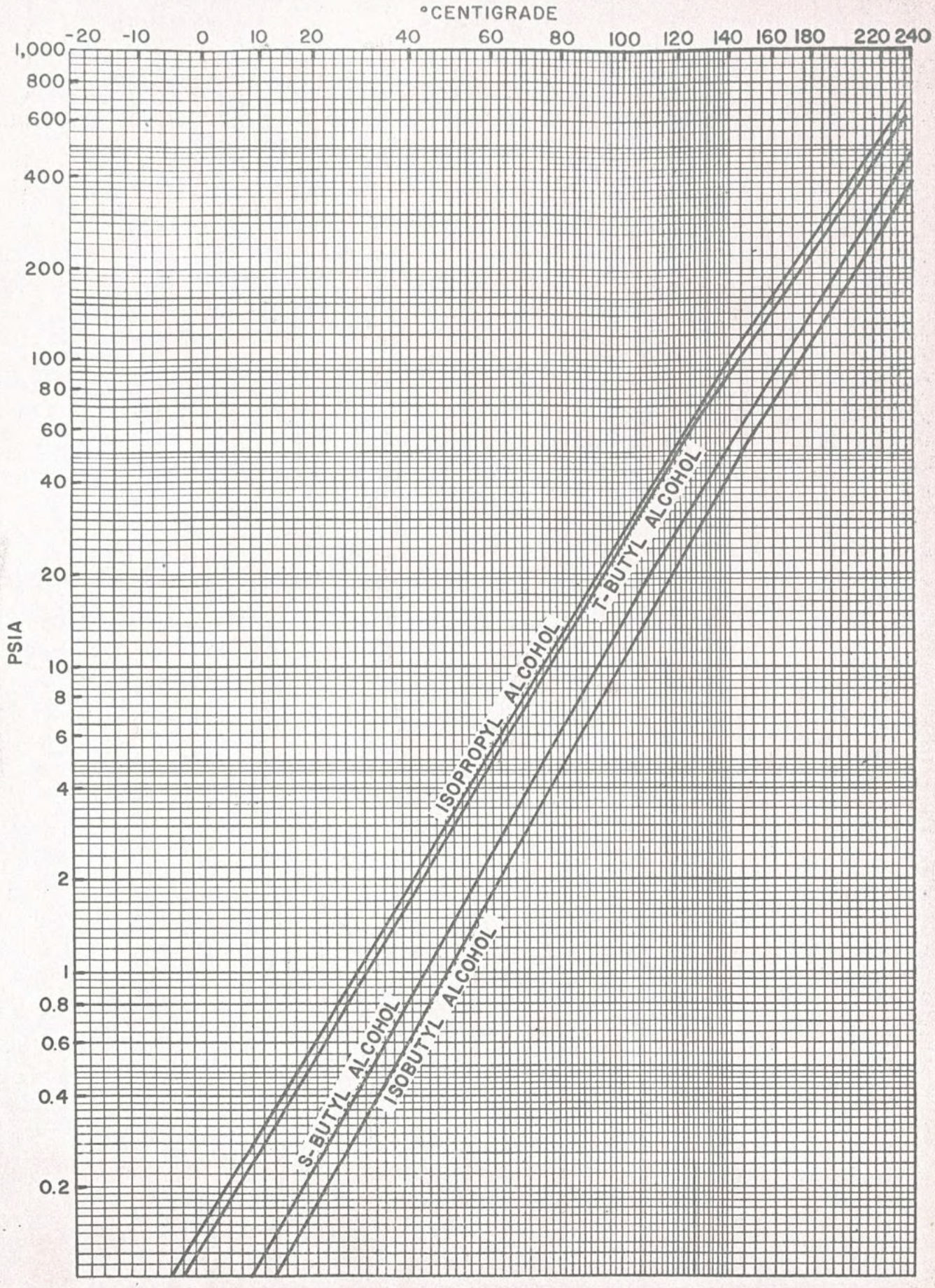

Fig. 10-1—Gives vapor pressure over a range of 0°C to + 240°C.

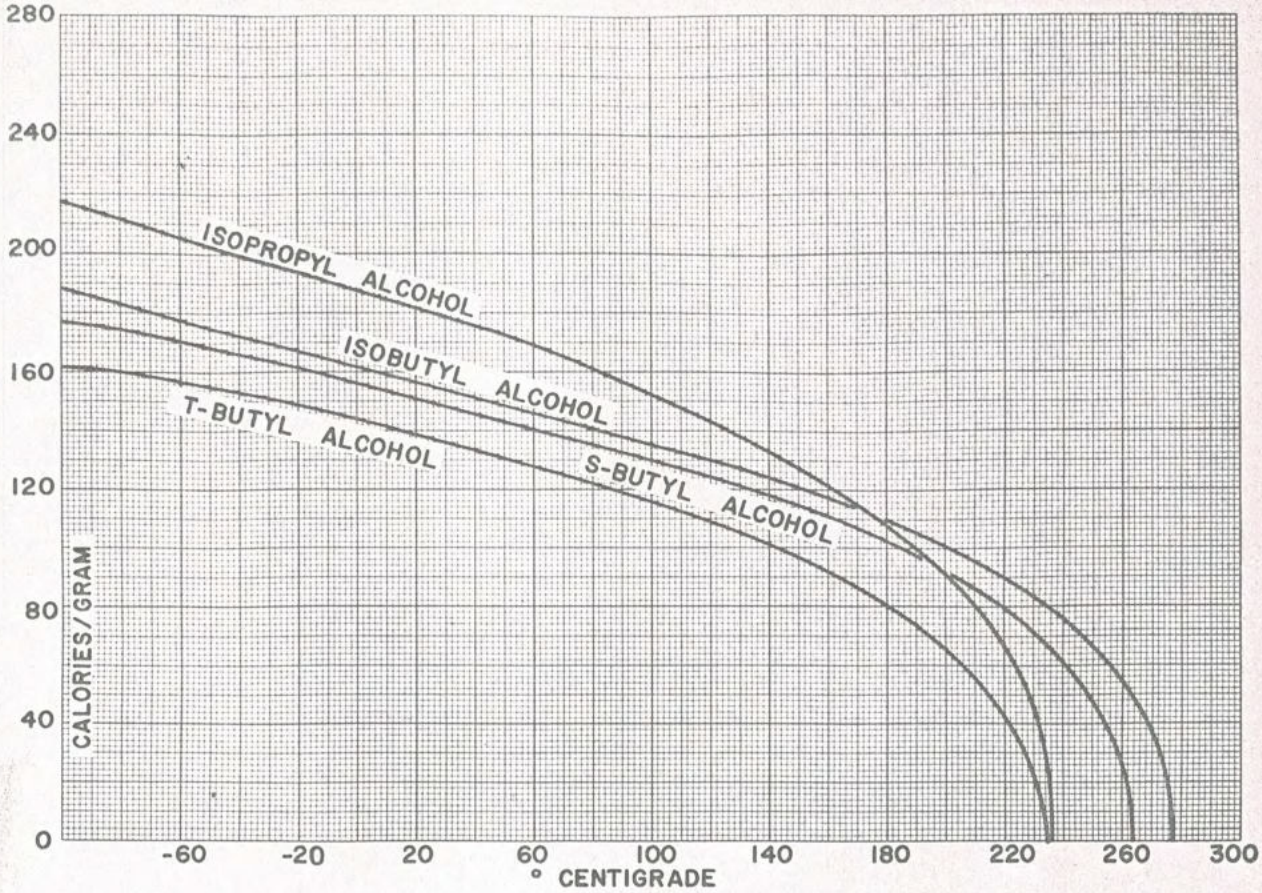

Fig. 10-2—Gives heat of vaporization over a range of — 100° C to + 260° C.

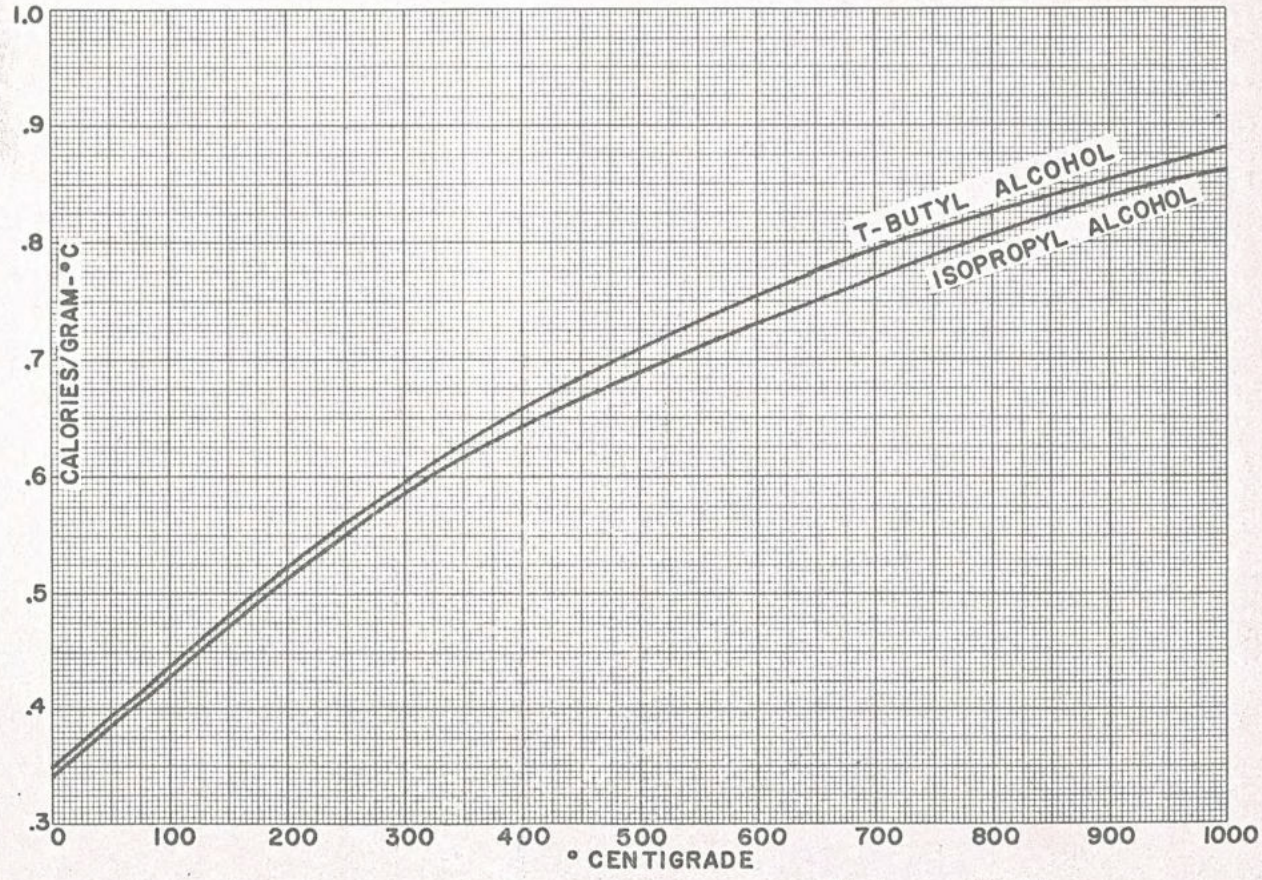

Fig. 10-3—Gives vapor heat capacity over a range of 0°C to + 1,000°C.

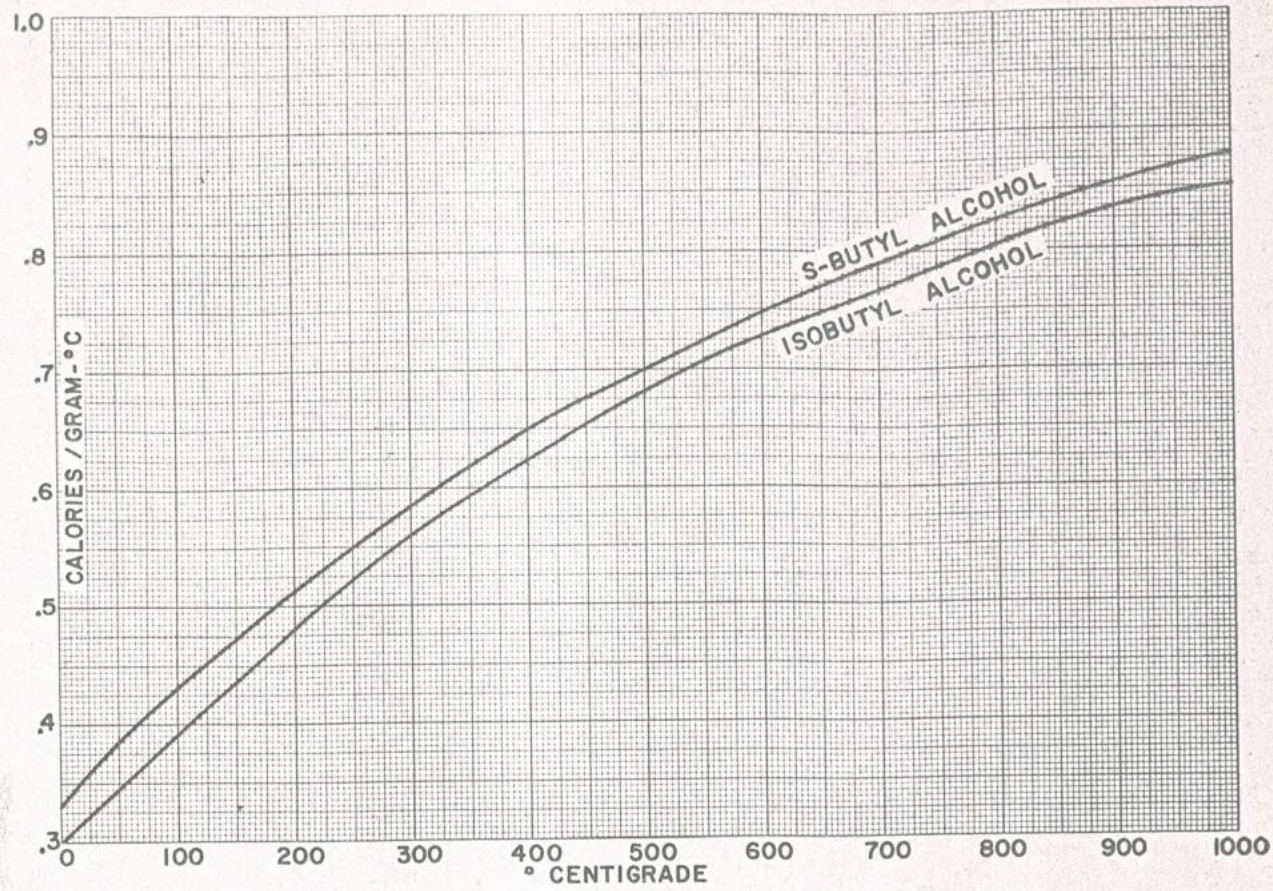

Fig. 10-3A—Gives vapor heat capacity over a range of 0°C to + 1,000°C.

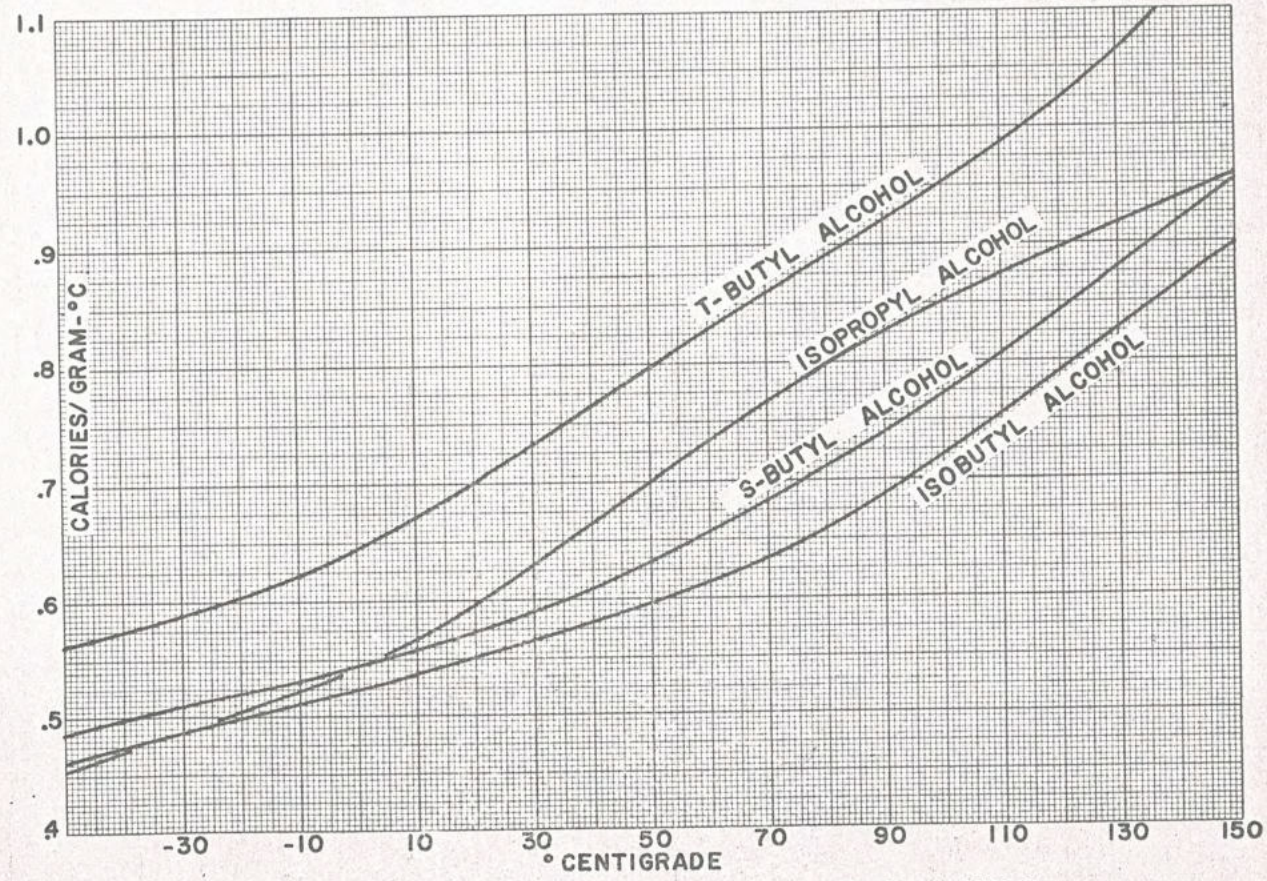

Fig. 10-4—Gives liquid heat capacity over a range of —50° C to + 150° C.

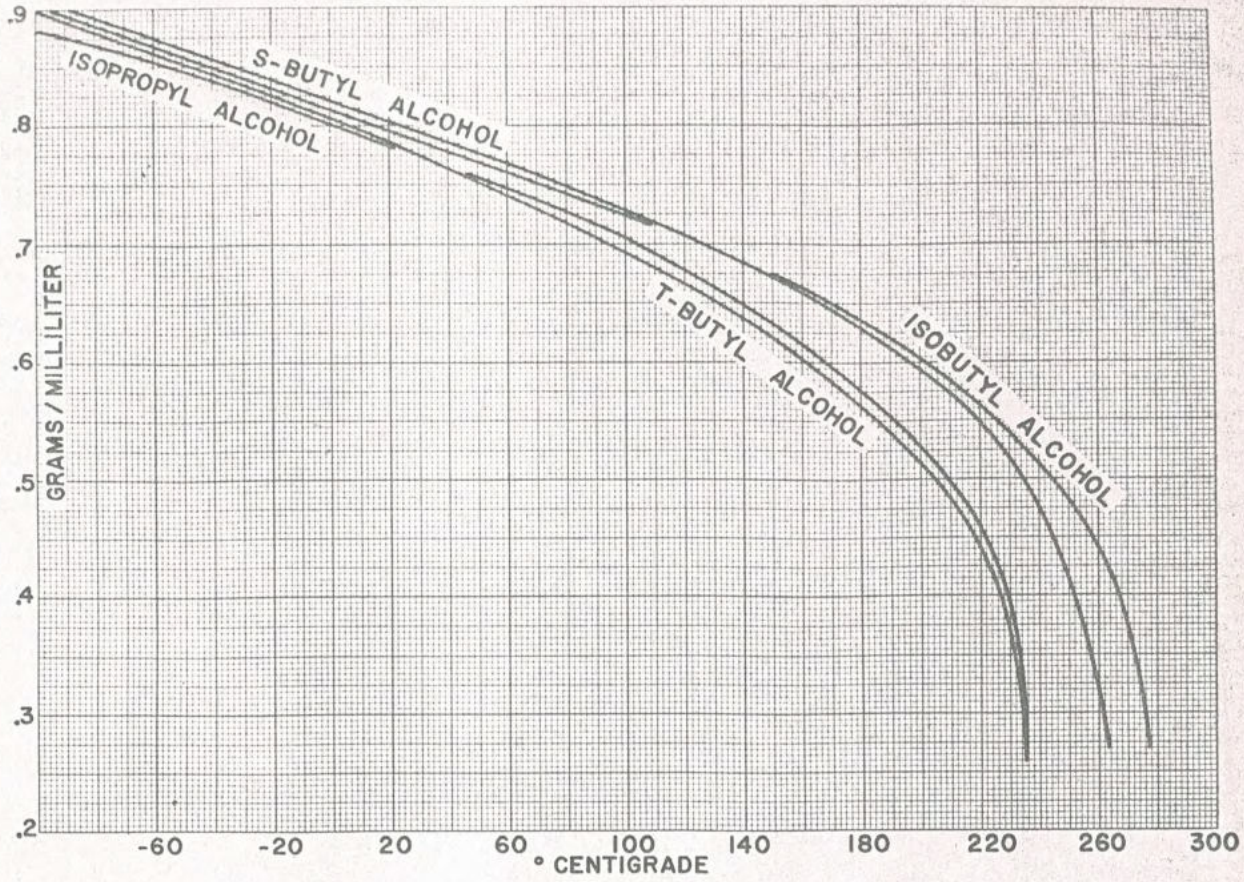

Fig. 10-5—Gives liquid density over a range of — 100° C to + 300° C.

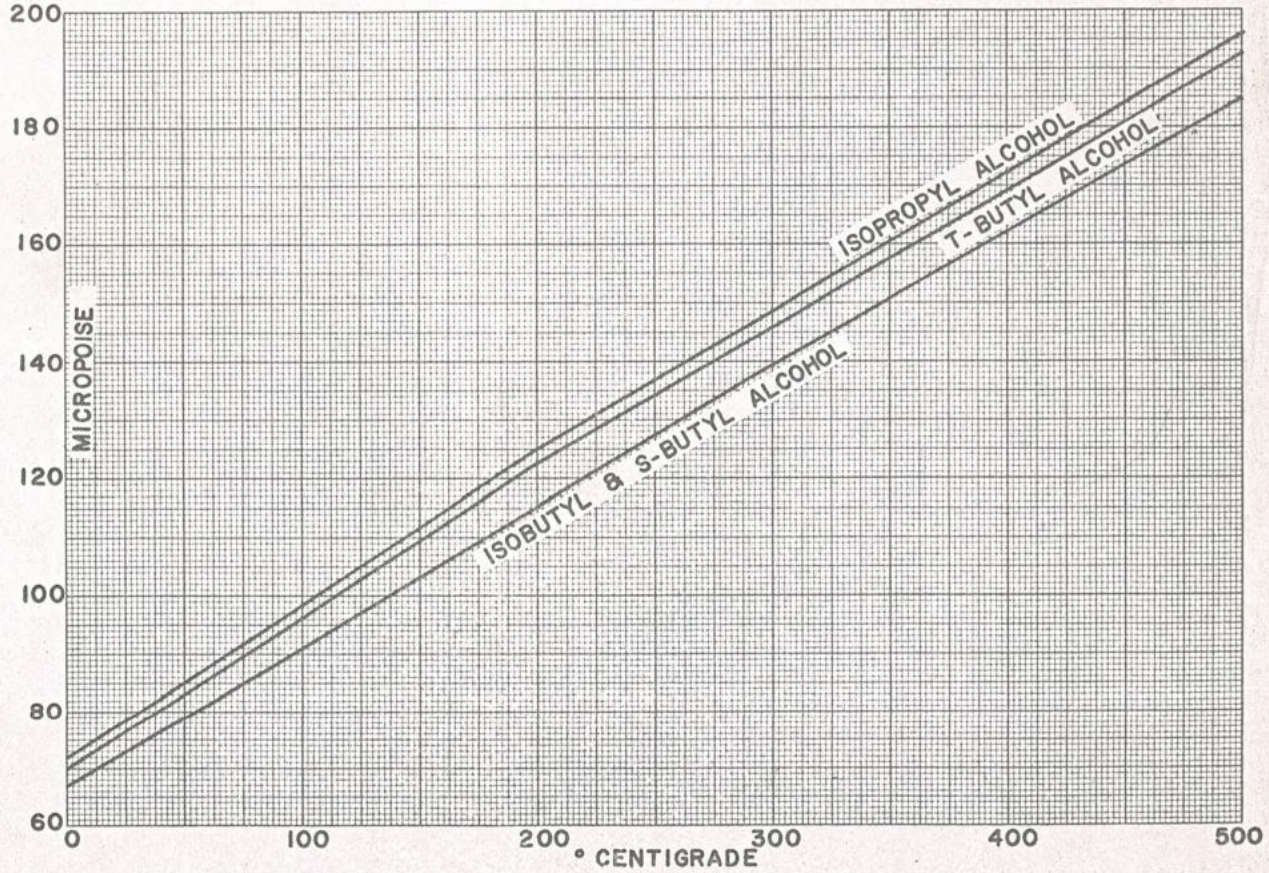

Fig. 10-6—Gives vapor viscosity over a range of 0°C to + 500°C.

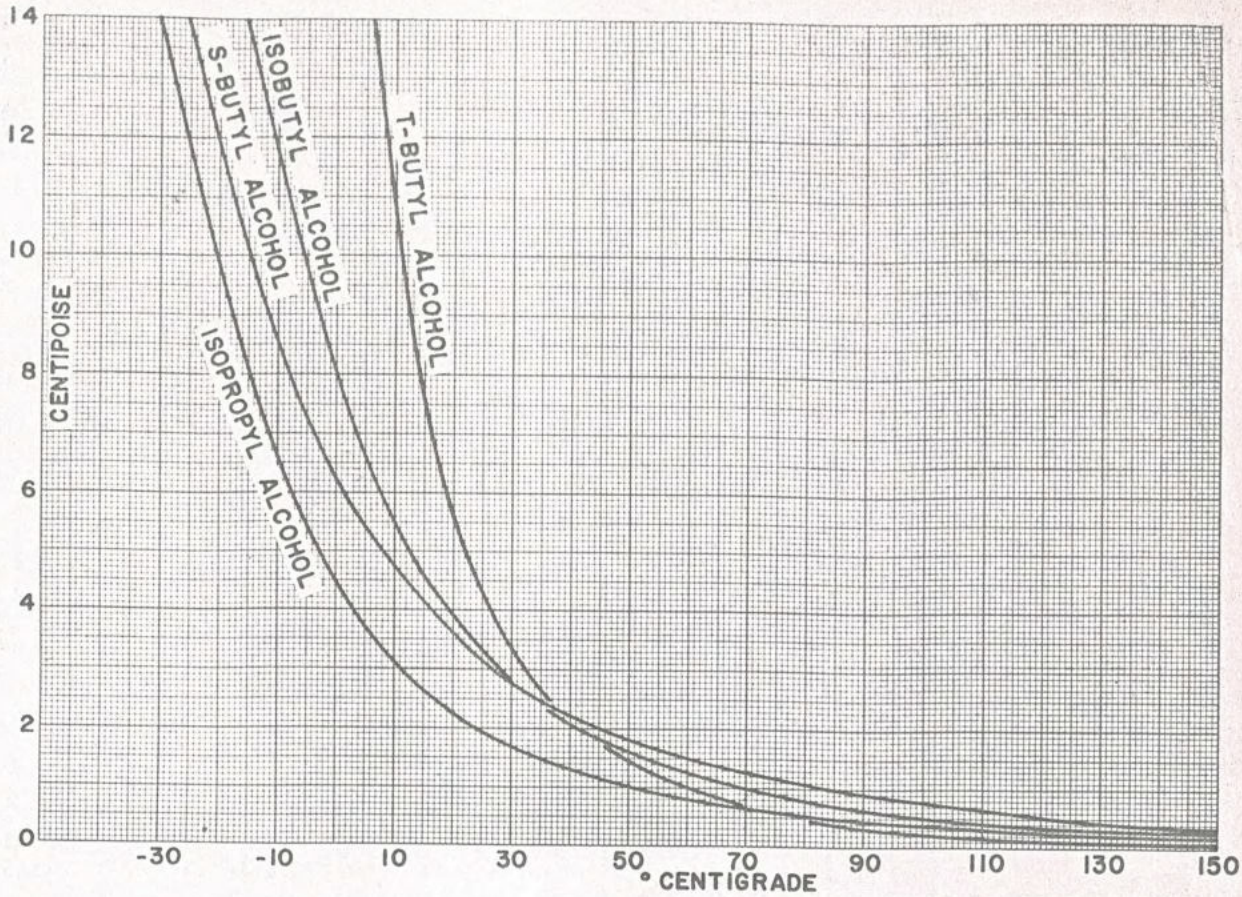

Fig. 10-7—Gives liquid velocity over range of −50° C to +150° C.

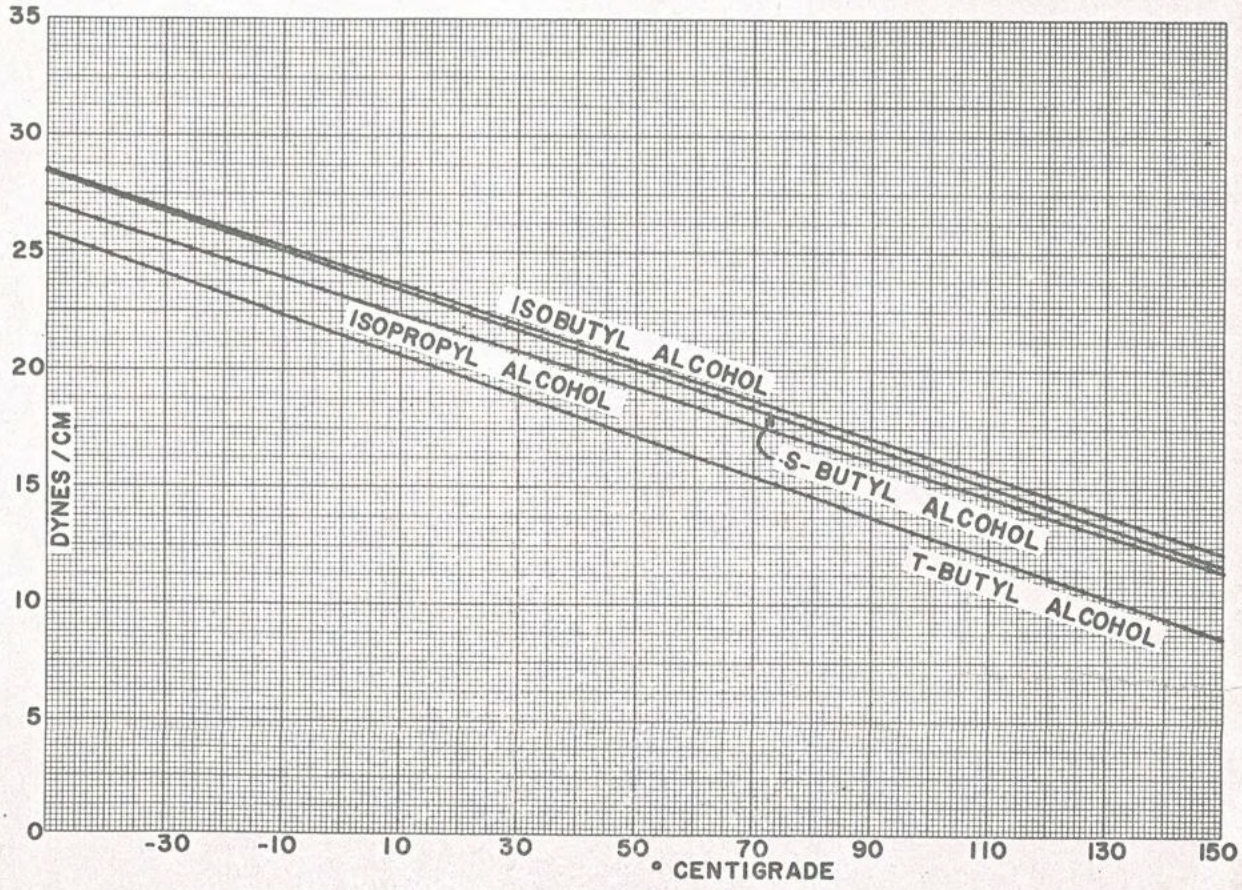

Fig. 10-8—Gives surface tension over a range of — 50° C to + 150° C.

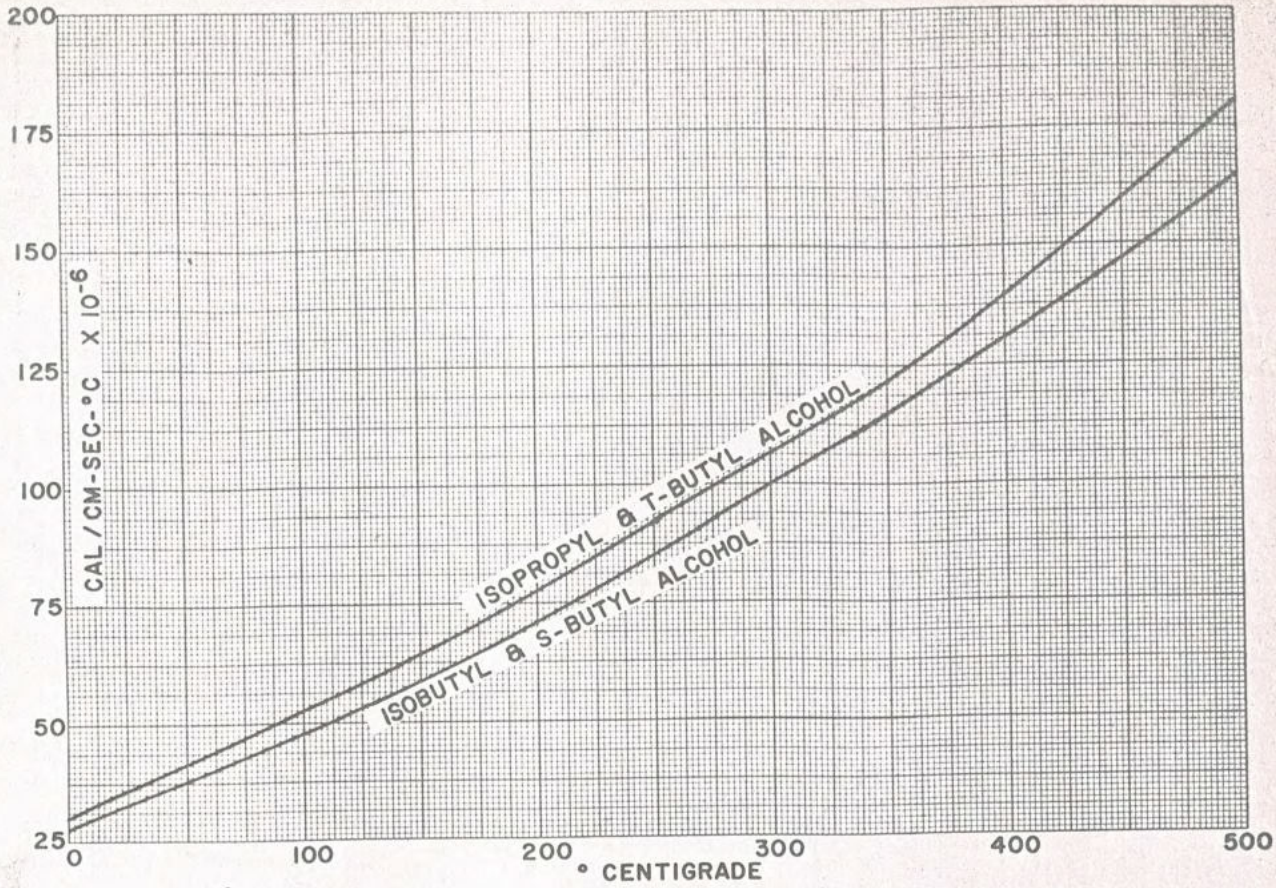

Fig. 10-9—Gives vapor thermal conductivity over a range of 0°C to + 500°C.

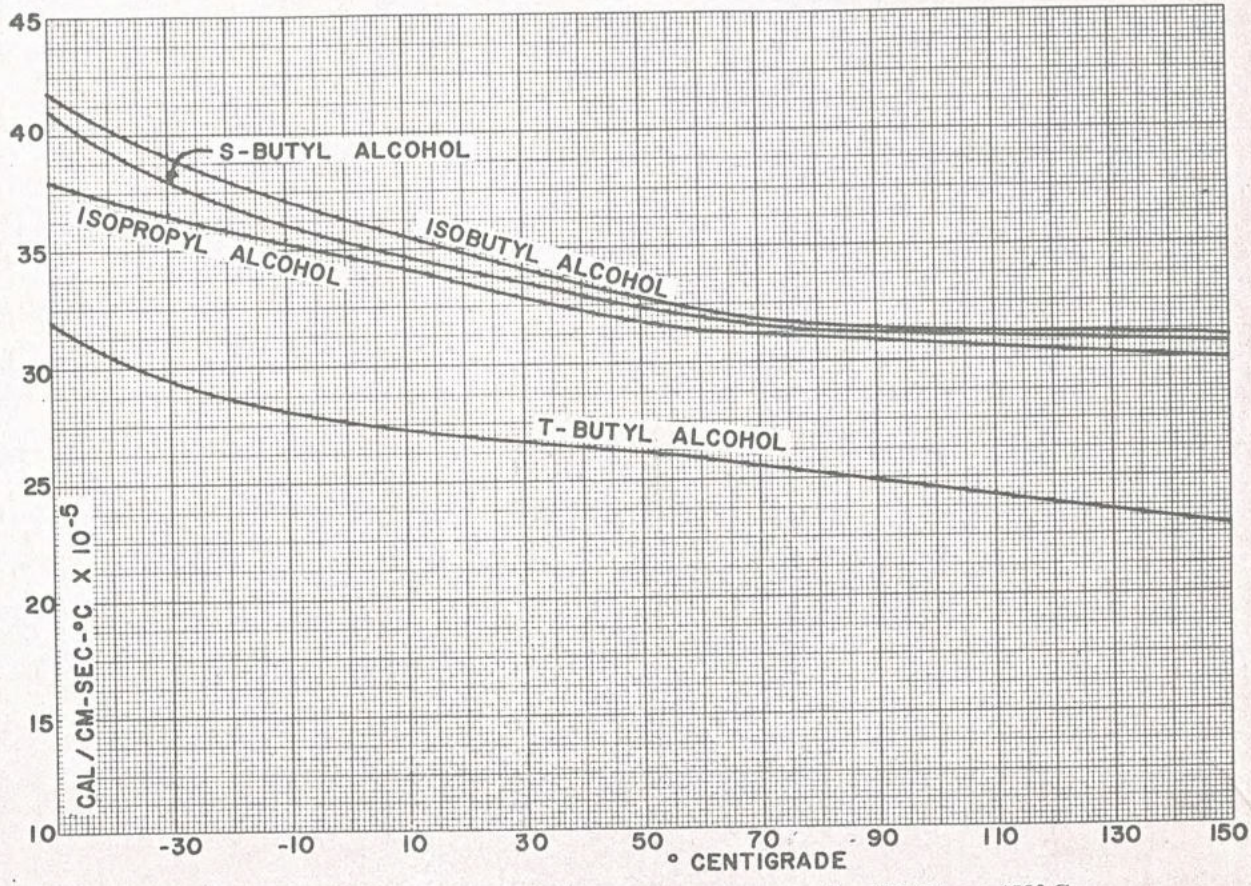

Fig. 10-10—Gives liquid thermal conductivity over range of — 50° C to + 150° C.

Part 11 will appear in an early issue.