Physical Properties of Hydrocarbons

Part 11—Miscellaneous Alcohols

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THE PHYSICAL PROPERTIES of the C_1-C_4 aliphatic alcohols have been presented in two previous articles. This final article on the alcohol compounds includes one unsaturated compound (allyl alcohol), and three higher aliphatic alcohols (amyl alcohol, hexyl alcohol, and heptyl alcohol). Although all four of these compounds have reached commercial status in specialized uses, none of them compare with the alcohols covered in the earlier articles in volume production.

Allyl alcohol, with its highly reactive double-bond and alcohol functional group, has always intrigued chemical engineers. The Shell Oil Co. pioneered allyl alcohol production in its search for a synthetic route to glycerine in the early 1940s. Today, about 17 million pounds per year of allyl alcohol is produced for specialty uses.

The three aliphatic alcohols are used mainly as solvents in specialized solvent systems.

Critical Properties and Vapor Pressure. Only the critical temperatures of the compounds have been experimentally determined.[1,2,3,4,5] The critical temperature of heptyl alcohol and the critical pressure and density of all four compounds have been calculated by the method of Lydersen, which relates the critical properties to the molecular structure. The error is normally ±5° in the critical temperature; ±20 psi in the pressure; and, ±0.01 grams/ml in the density.

The vapor pressure up to the boiling point has been experimentally determined for all four compounds.[2] Higher pressure data are available on allyl alcohol[3] and hexyl alcohol.[6] The data were extrapolated over the wide temperature range by a Cox chart plot.

Heat of Vaporization. The heat of vaporization is available only at the boiling points for allyl alcohol,[1] amyl alcohol,[7] and hexyl alcohol.[6] The heat of vaporization was estimated for heptyl alcohol at its boiling point by the method of Riedel. On the other three compounds, this method gave errors of less than 2 percent. The reduced temperature method of Watson was used to extrapolate this value over the wider temperature range.

TABLE 11-1—Miscellaneous Alcohols

Alcohols	Boiling Point (°C)	Freezing Point (°C)	Molecular Weight	CRITICAL PROPERTIES °C T_c	psia P_c	g/ml d_c
Allyl	96.9	−129	58.08	272	831*	0.286*
1-Amyl	138.1	− 79	88.1	310.7	557*	.265*
1-Hexyl	157.5	− 46.7	102.2	313.5	490*	.264*
1-Heptyl	175.8	....	116.2	333*	436*	.262*

* Estimated

Heat Capacity. The vapor heat capacity is available only for allyl alcohol.[8] The data for the other three compounds have been estimated by the recently proposed method of Richani and Doraiswamy.[9] In this method,

$$Cp = a + bT + cT^2 + dT^3$$

where

Cp = vapor heat capacity, cal/mole — ° C

T = temperature, ° K

and a, b, c, d = constants calculated from the molecular structure

The method gives excellent results for temperature above 200° C. However, in the 0-100° C range, errors as high as 20 percent were found for some alcohols. Since these are high boiling alcohols, the vapor will seldom be encountered below 200° C. Above 200° C, the error is only 1-3 percent.

Data for liquid heat capacity are almost nonexistent. Thus, the value at 20° C was calculated by the molecular structure method of Johnson and Huang. The error was

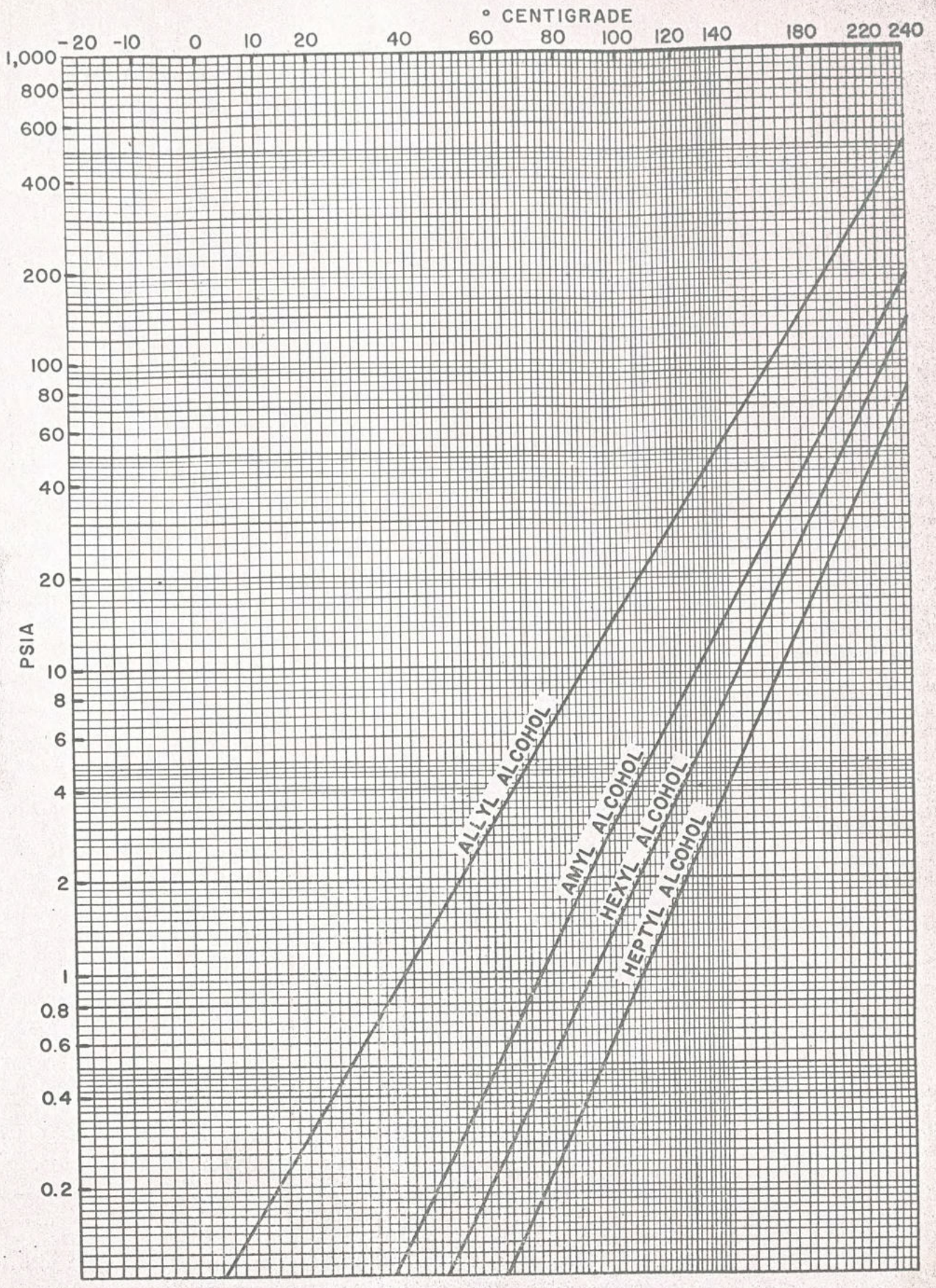

Fig. 11-1—Gives vapor pressure of miscellaneous alcohols.

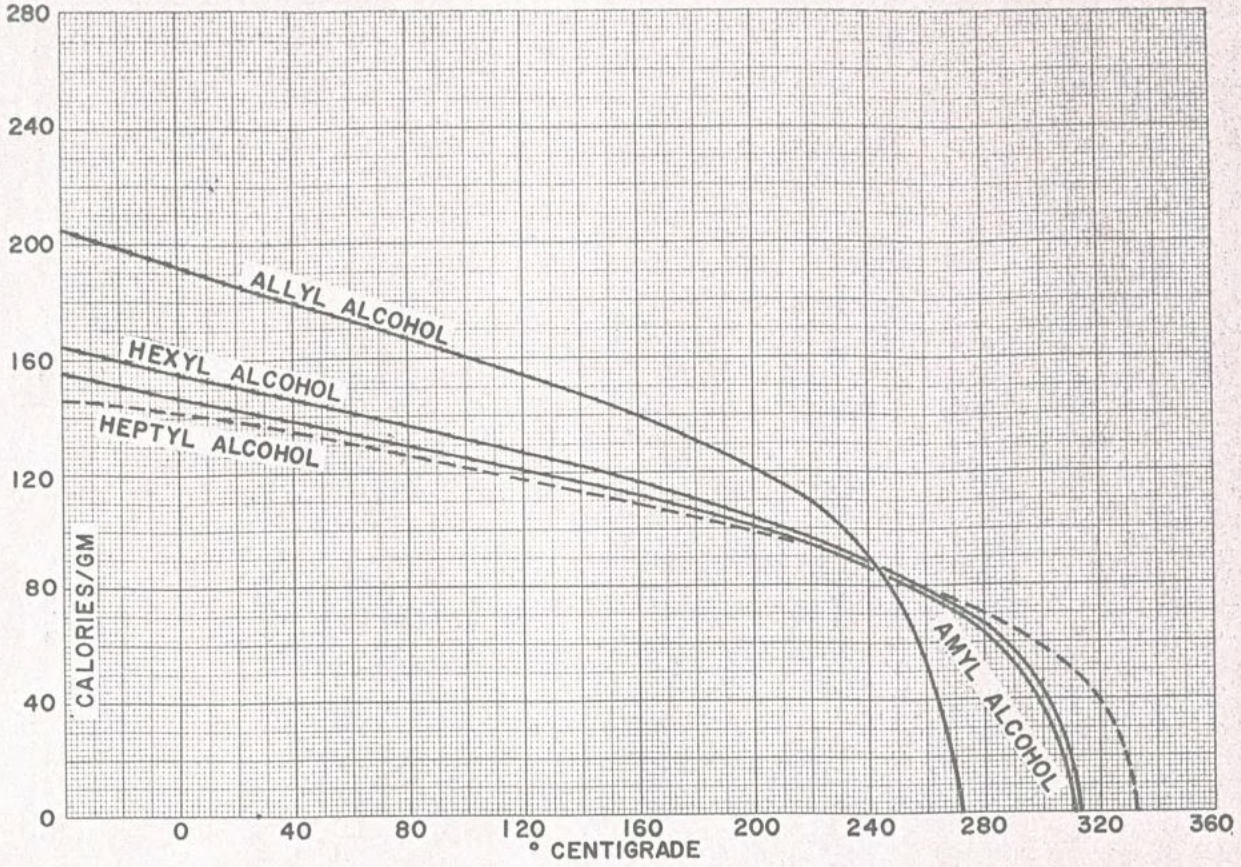

Fig. 11-2—Shows heat of vaporization for miscellaneous alcohols.

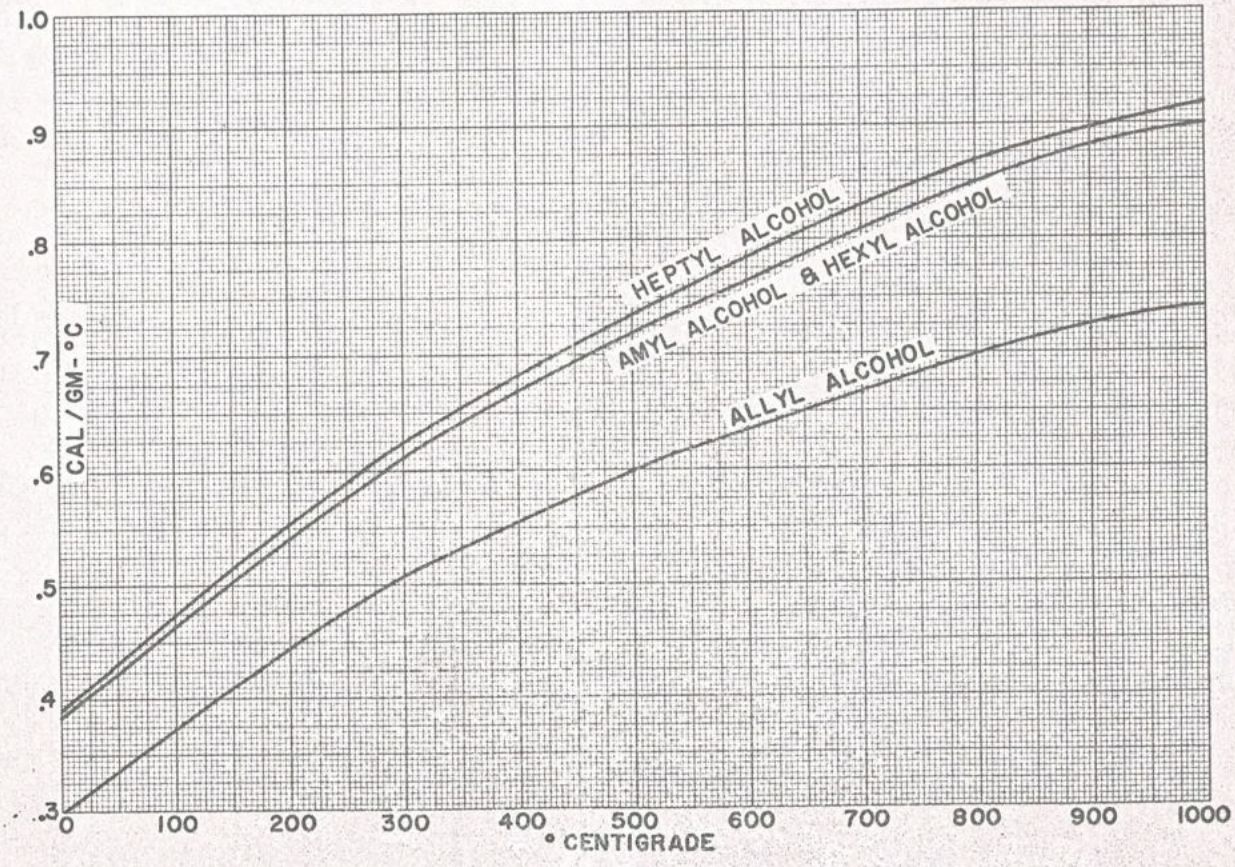

Fig. 11-3—Shows vapor heat capacity for miscellaneous alcohols.

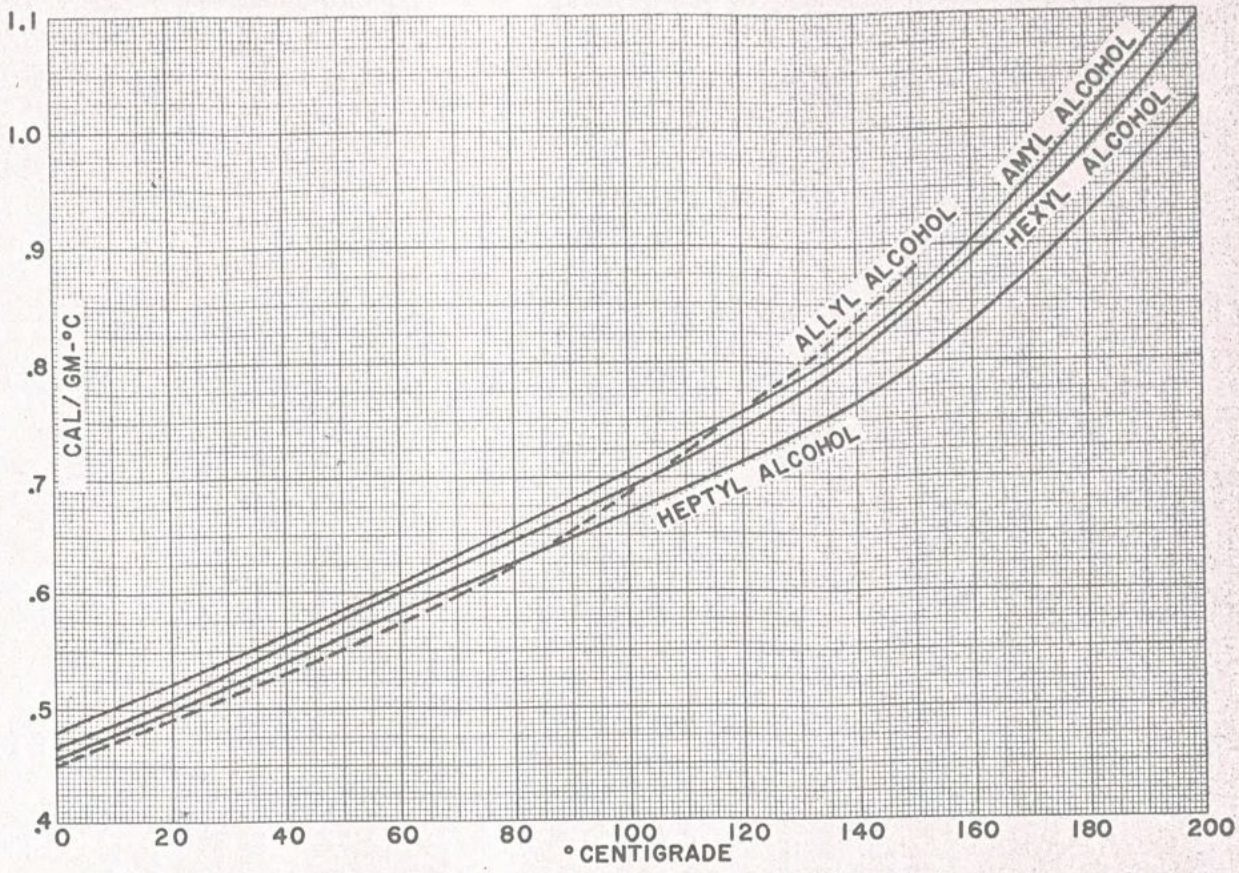

Fig. 11-4—Shows liquid heat capacity for miscellaneous alcohols.

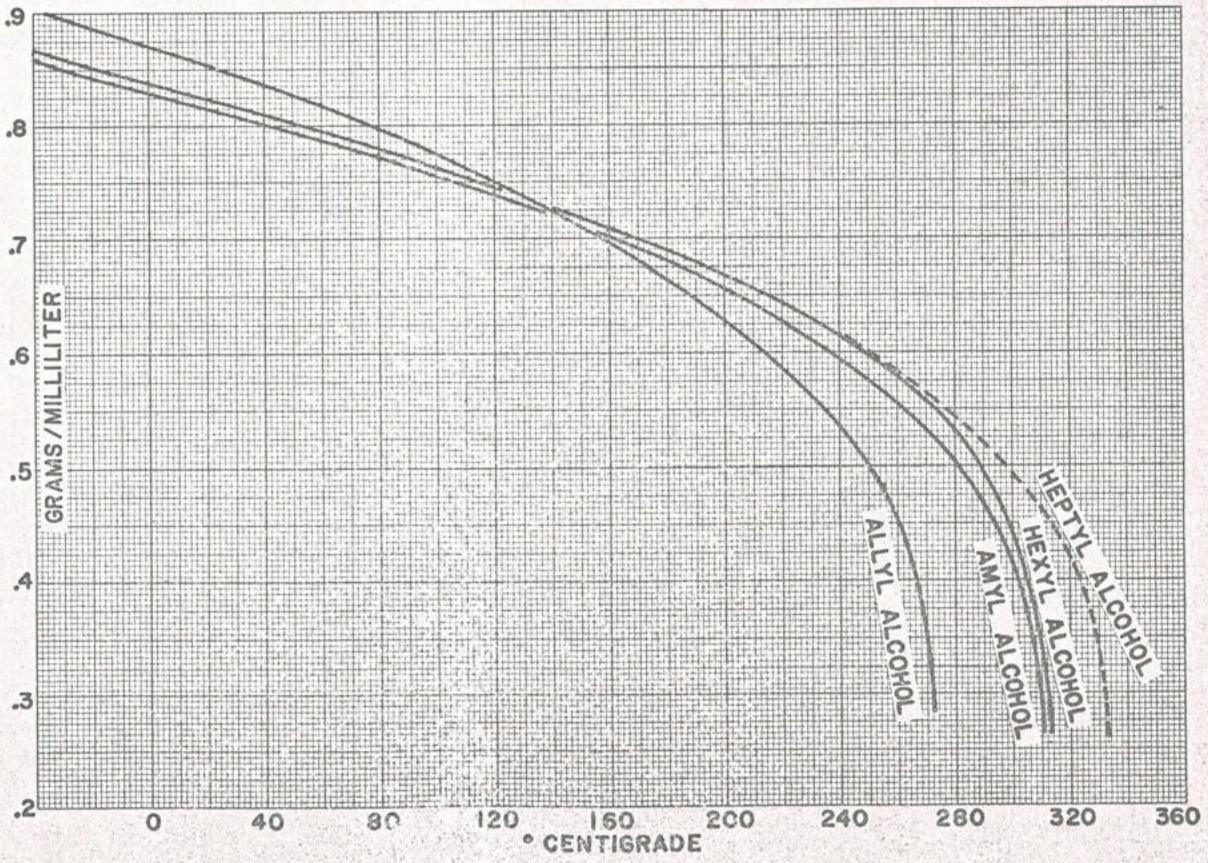

Fig. 11-5—Shows liquid density for miscellaneous alcohols.

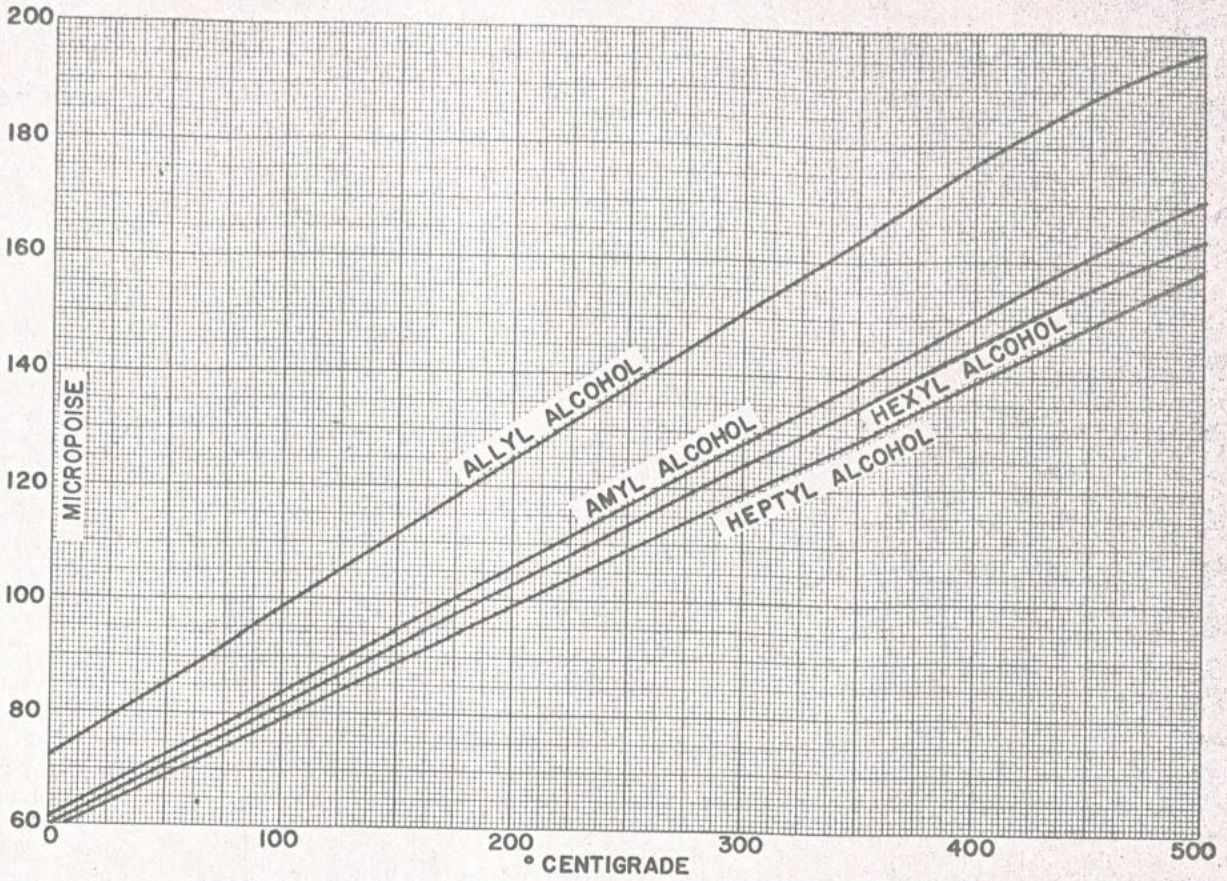

Fig. 11-6—Shows vapor viscosity for miscellaneous alcohols.

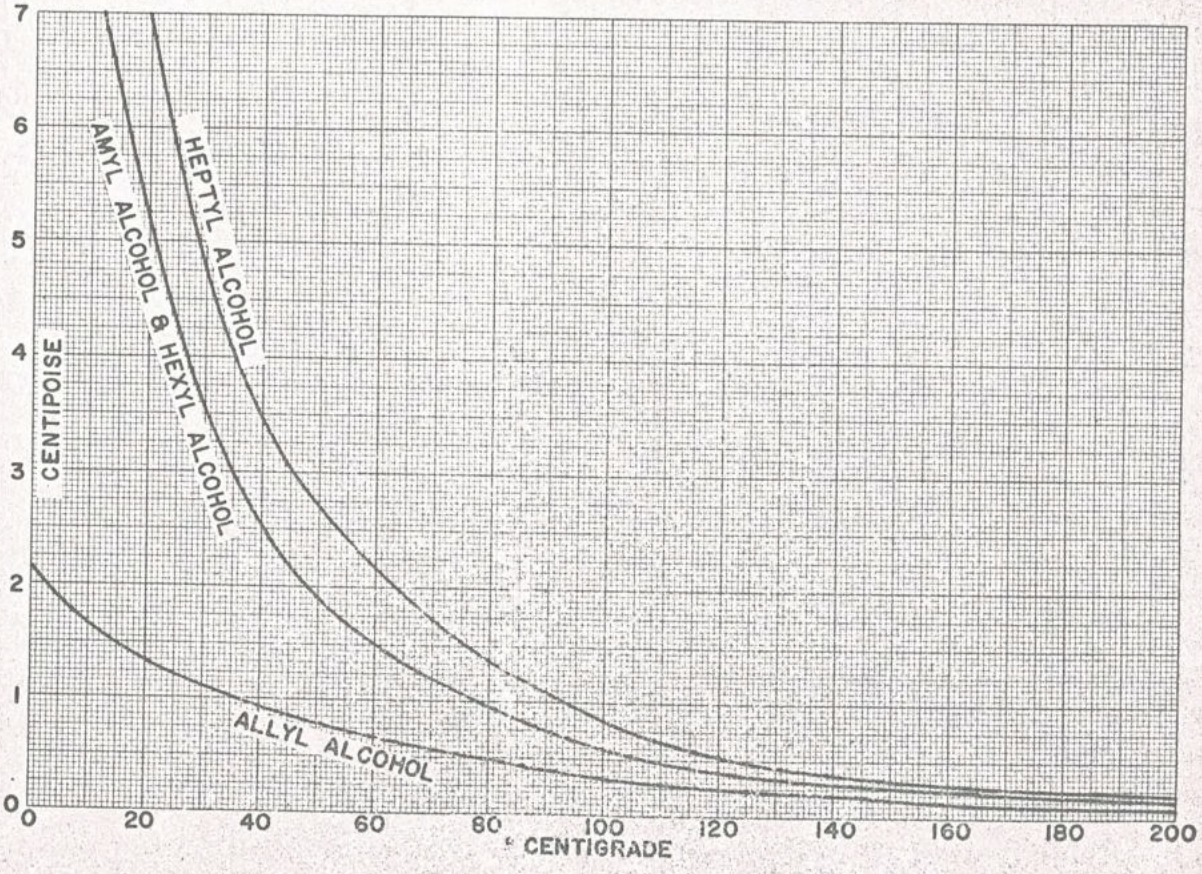

Fig. 11-7—Shows liquid viscosity for miscellaneous alcohols.

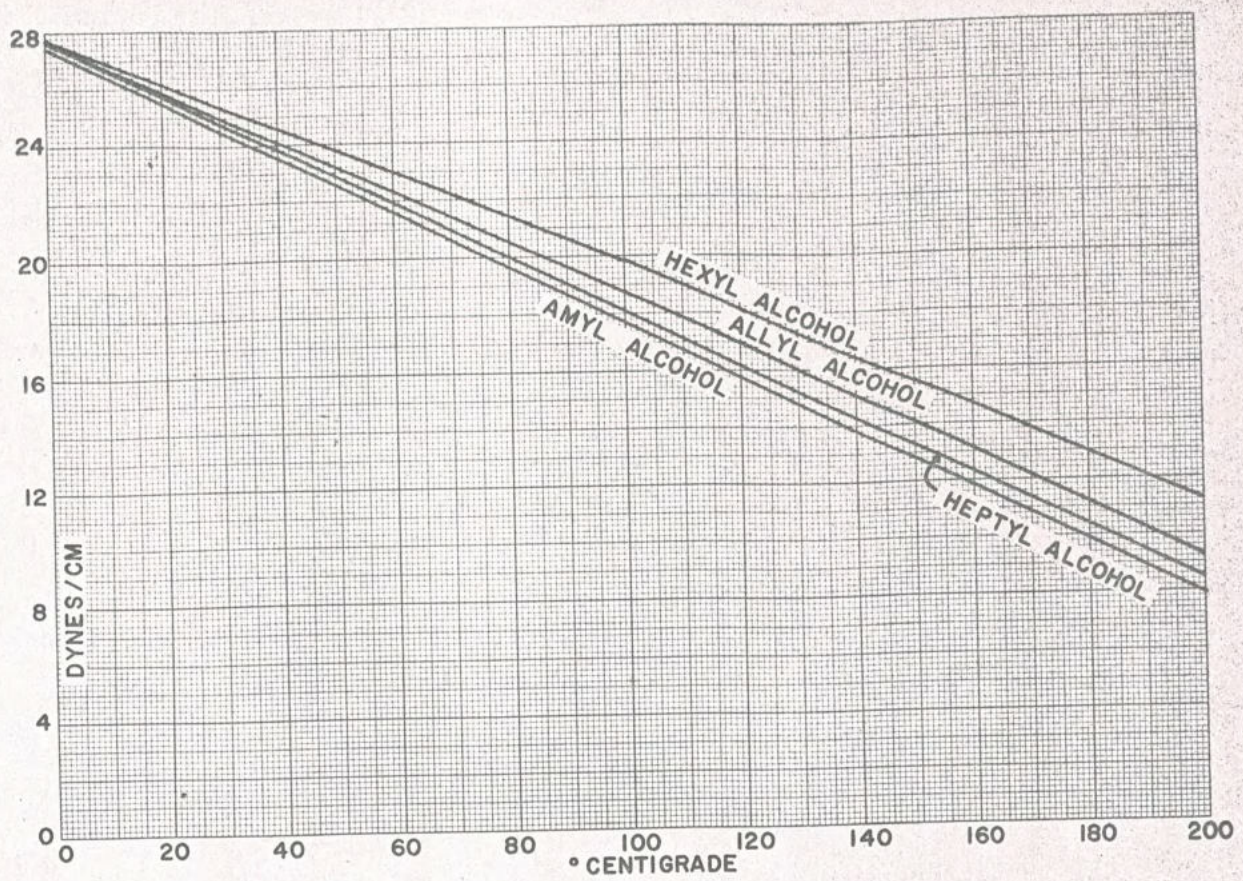

Fig. 11-8—Shows surface tension for miscellaneous alcohols.

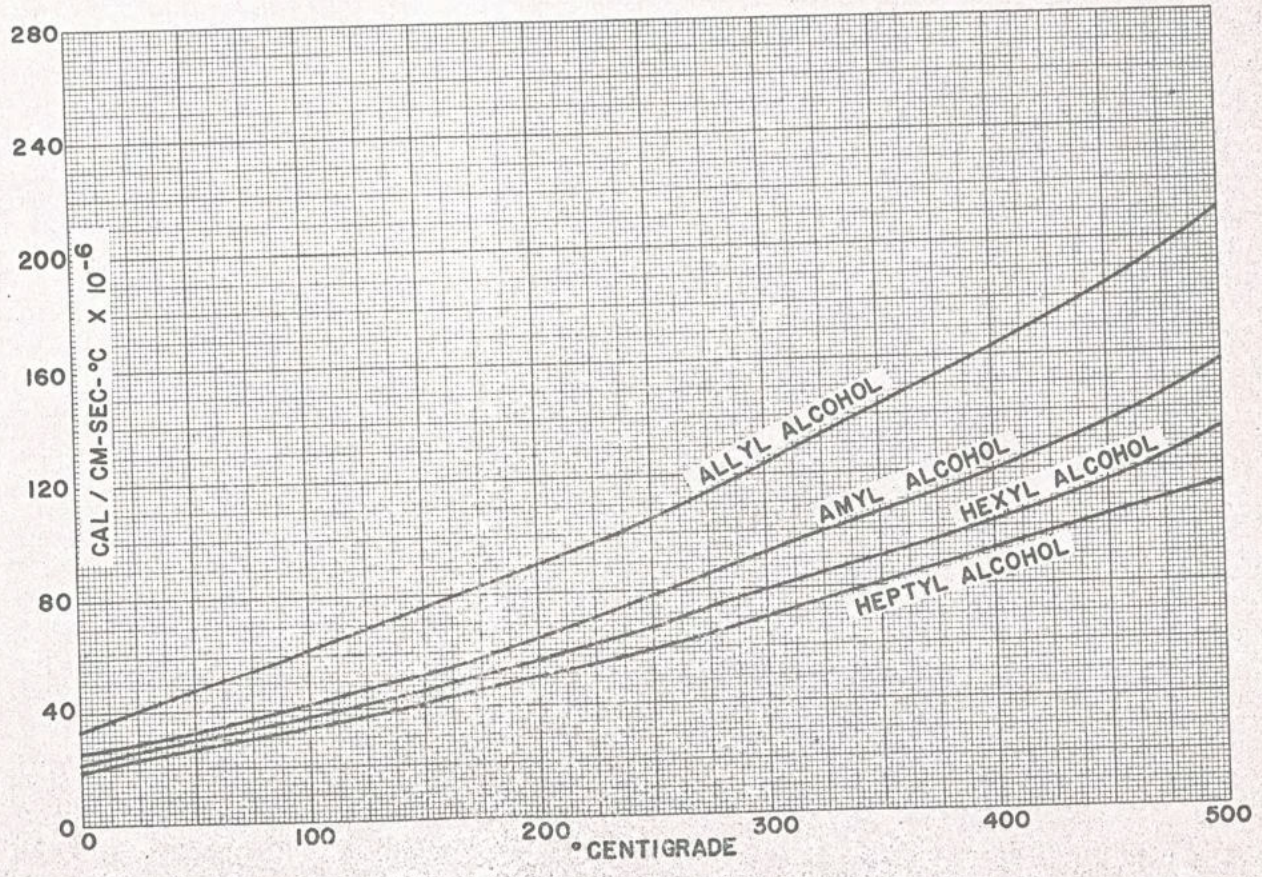

Fig. 11-9—Shows vapor thermal conductivity for miscellaneous alcohols.

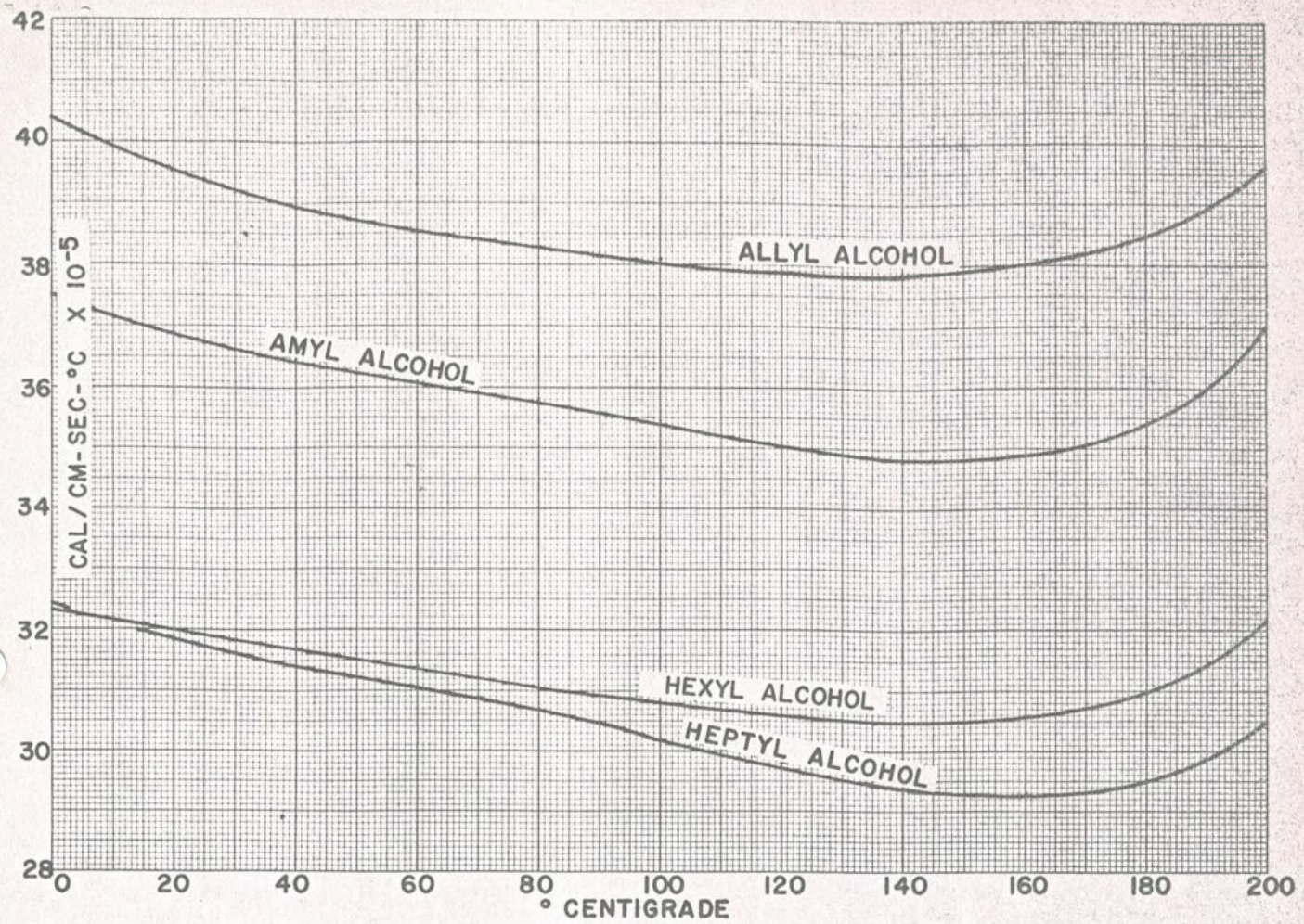

Fig. 11-10—Shows liquid thermal conductivity for miscellaneous alcohols.

less than 2 percent when compared to experimental data for amyl alcohol and hexyl alcohol. The 20° C value was extrapolated over the temperature range by the method of Chow and Bright. The error is generally 5-10 percent.

Density. The densities for allyl alcohol[1,3] and heptyl alcohol[10] have been experimentally determined only in the 0-30° C range. Costello and Bowden[5] have determined the density for amyl alcohol from −60 to +180° C and for hexyl alcohol from −20 to +240° C. Additional data on hexyl alcohol are also available from the experimental work of Hovorka.[6] The data have been extended over the entire temperature range by the method of Lyderson, Greenkorn, and Hougen which relates the change in density to the critical properties, compressibility factor, and reduced temperature. Comparison of seven experimental points with calculated values gave an average error of 2.4 percent and a maximum error of 4.7 percent.

Viscosity. There are no vapor viscosity data on any of the four compounds. Consequently, the estimation method of Bromley and Wilke has been used. The error should be less than 2 percent.

The liquid viscosity has been experimentally determined for all four compounds.[4,6]

Surface Tension. Surface tension data for allyl alcohol are available in the 0-100° C range.[4,7] Hovorka[6] determined the surface tension for hexyl alcohol up to 160° C. Data for hexyl alcohol and heptyl alcohol are reported at 20°C by Muller.[11] The data have been extrapolated over the temperature range by use of the nomograph of Kharbanda and a plot of the log of the surface tension against the log of the critical temperature minus the temperature of the desired point.

Thermal Conductivity. As in the previous article, the thermal conductivities have been estimated by the method of Thodos and Owens for the vapors and the method of Robbins and Kingrea for the liquids.

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Indexing Terms: Alcohols-9, Allyl Alcohol-9, Amyl Alcohol-9, Computations-4, Heat-7, Heptyl Alcohol-9, Hexyl Alcohol-9, Liquid Phase-5, Physical Properties-7, Pressure-6, Properties/Characteristics/-7, Temperature-6, Vapor Phase-5.

Part 12 will appear in an early issue.