Physical Properties of Hydrocarbons

Part 24—C_1-C_4 Aldehydes

From charts, you can get these properties for C_1-C_4 aldehydes:

- Vapor Pressure
- Heat Capacity
- Thermal Conductivity
- Viscosity
- Density

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ALTHOUGH WELL-KNOWN for many years, the C_1-C_4 aldehydes (formaldehyde, acetaldehyde, propionaldehyde, and butyraldehyde) continue to enjoy a high growth rate. Already a billion-pounds-per-year commodity, formaldehyde usage is increasing 10 percent a year. In 1966, about 1.2 billion pounds of 100 percent formaldehyde was used. Commercially, formaldehyde is sold as a 37 percent aqueous solution. On this basis, 3.3 billion pounds of solution was consumed in 1966 and over 4.5 billion pounds will be used in 1970. Half of this will be used in phenolic, urea, and melamine resins. Another 25 percent will go into producing glycols, alcohols, and pentaerythritol. Good reactivity, low price and important end use markets have combined to give formaldehyde its growth impetus. Most of the 15 producers make the formaldehyde by vapor phase oxidation of methanol. The advent of big single-train methane oxidation plants should mean cheaper methanol but a tight balance between sales and production will keep the price firm.

Acetaldehyde production probably topped 1.3 billion pounds in 1966. Almost 100 percent of it was converted on the plantsite to another product. Acetic acid alone claimed 50 percent of the acetaldehyde produced. Alcohols, glycols, and acetic anhydride accounted for most of the rest. Like many large volume chemicals, acetaldehyde production is yielding to new, more economical processes. Oxidation of ethylene is bidding to replace oxidation of ethyl alcohol as the favorite route.

Propionaldehyde and butyraldehyde have never achieved the importance of the other two aldehydes. They are used chiefly as intermediates in production of synthetic resins, solvents, plasticizers, and rubber accelerators. Propionaldehyde will become increasingly available as a by-product if oxidation of propylene to propylene oxide goes commercial. Butyraldehyde is produced from crotonaldehyde or butyl alcohol.

Critical Properties and Vapor Pressure. Because the aldehydes tend to polymerize at higher temperatures, their critical properties and vapor pressures above the boiling points have not been experimentally measured. The criti-

TABLE 24-1—Physical Properties of C_1 - C_4 Aldehydes

	Boiling Point °C	Freezing Point °C	Molecular Weight	Critical Properties °C t_c	Critical Properties PSIA P_c	Critical Properties g/ml d_c
Formaldehyde	−19.2	− 92	30.02	137*	984*	0.266*
Acetaldehyde	20.2	−123	44.05	188	803*	0.263*
Propionaldehyde	48.0	− 80	58.08	220*	674*	0.261*
Butyraldehyde	74.8	− 96	72.11	248*	580*	0.259*

* Estimated.

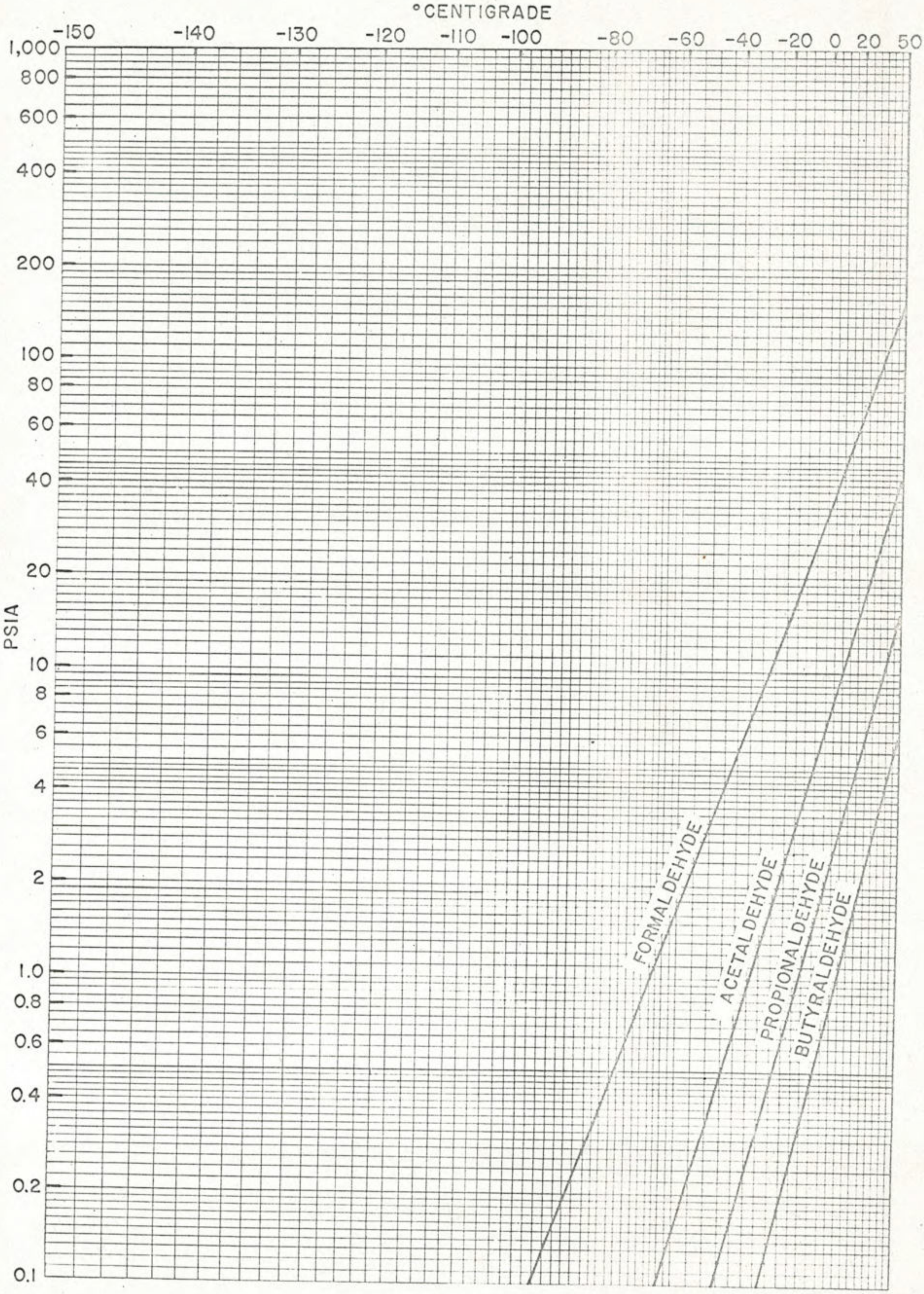


Fig. 24-1—Vapor pressure of C_1-C_4 aldehydes from —150°C to +50°C.

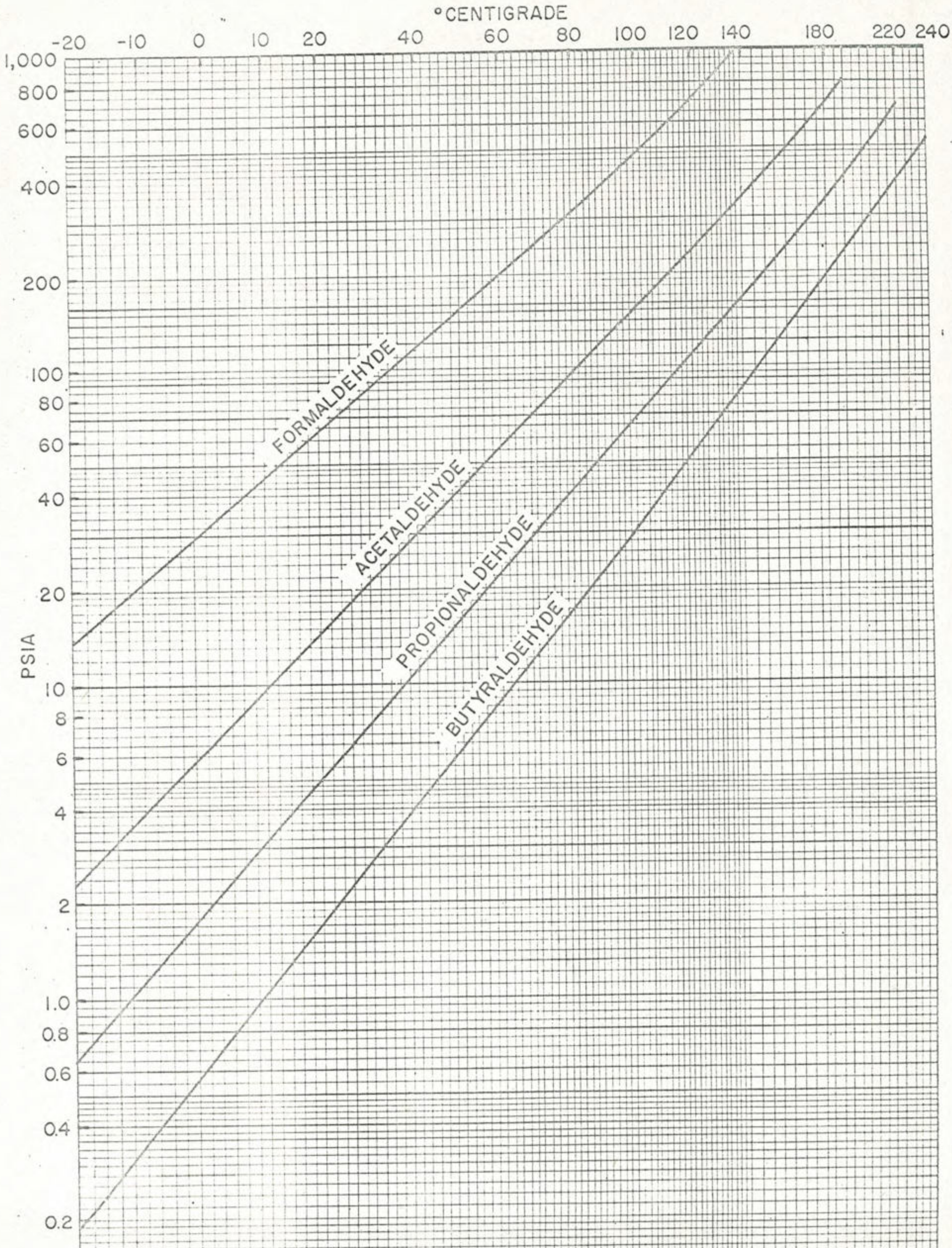


Fig. 24-2—Vapor pressure of C_1-C_4 aldehydes from −20°C to +240°C.

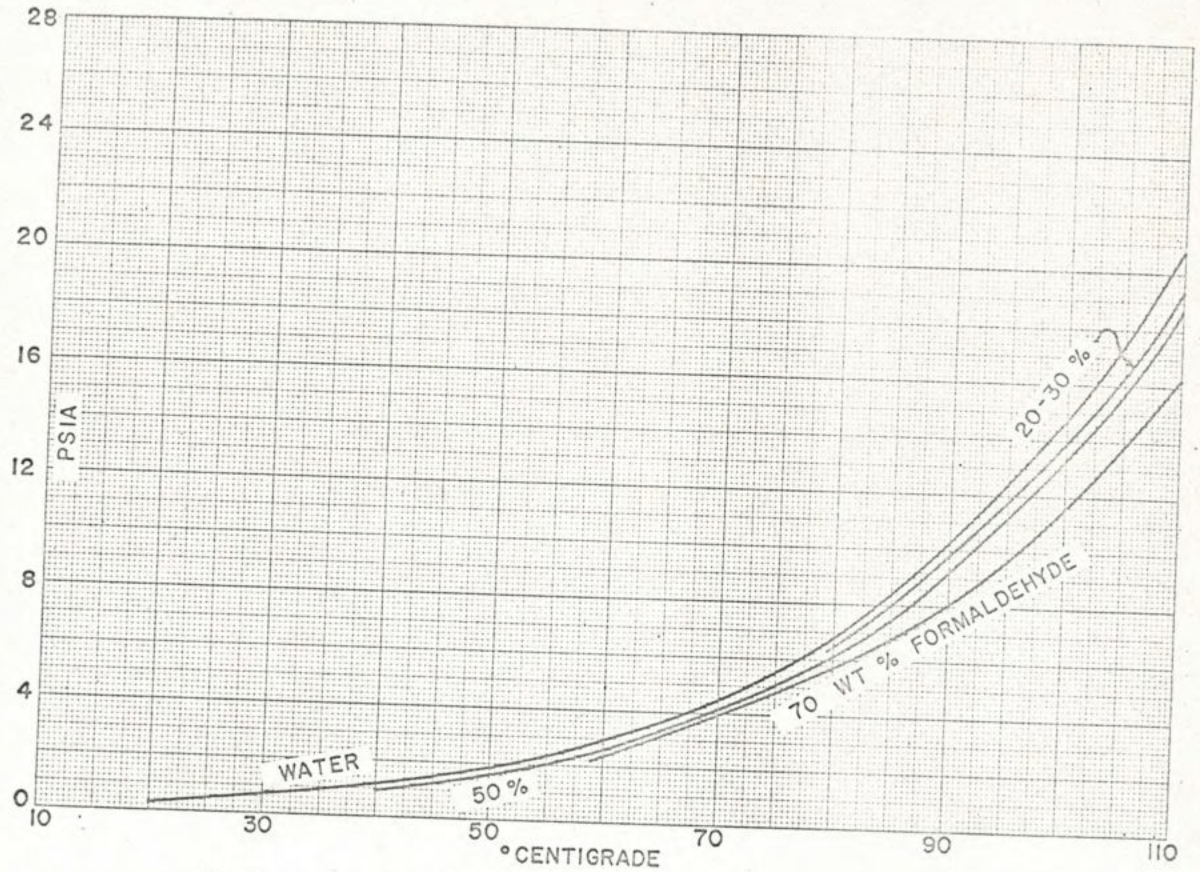


Fig. 24-3—Vapor pressure of aqueous formaldehyde from 20°C to 110°C.

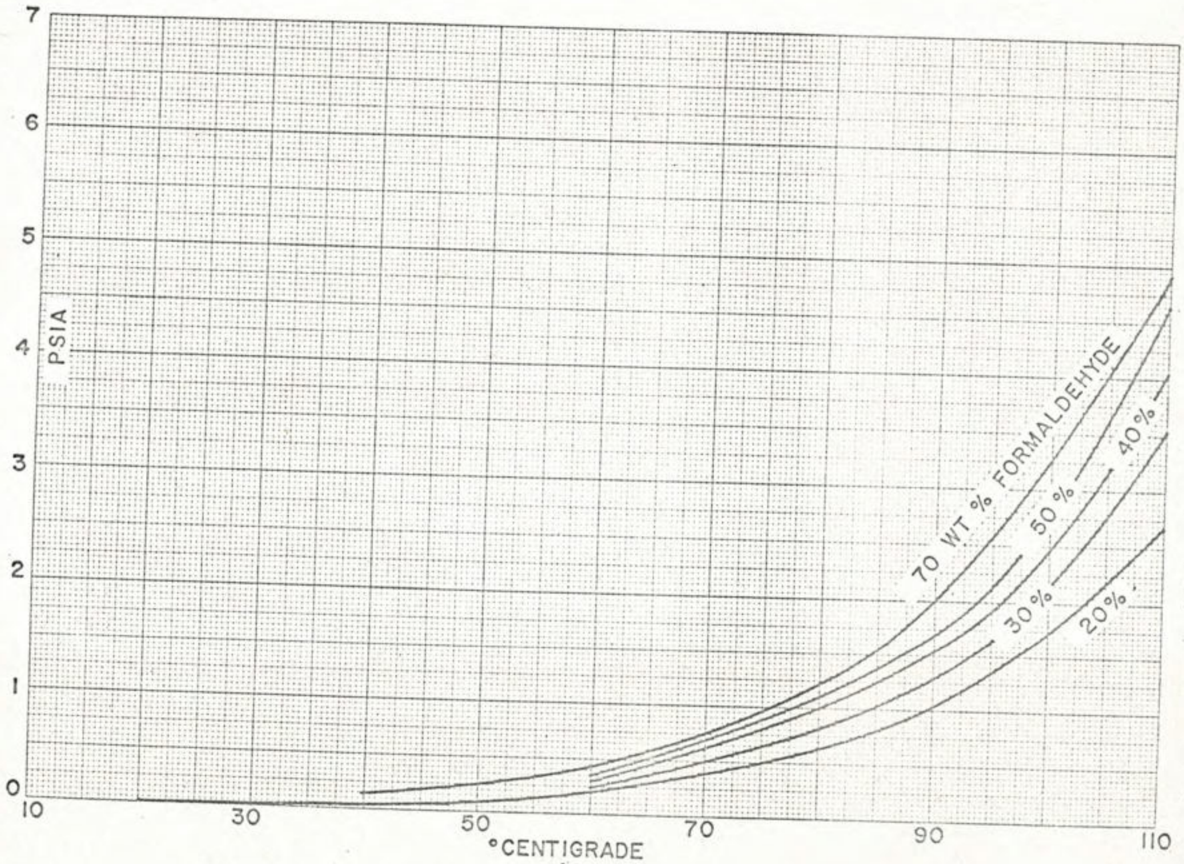


Fig. 24-4—Partial pressure of aqueous formaldehyde from 20°C to 110°C.

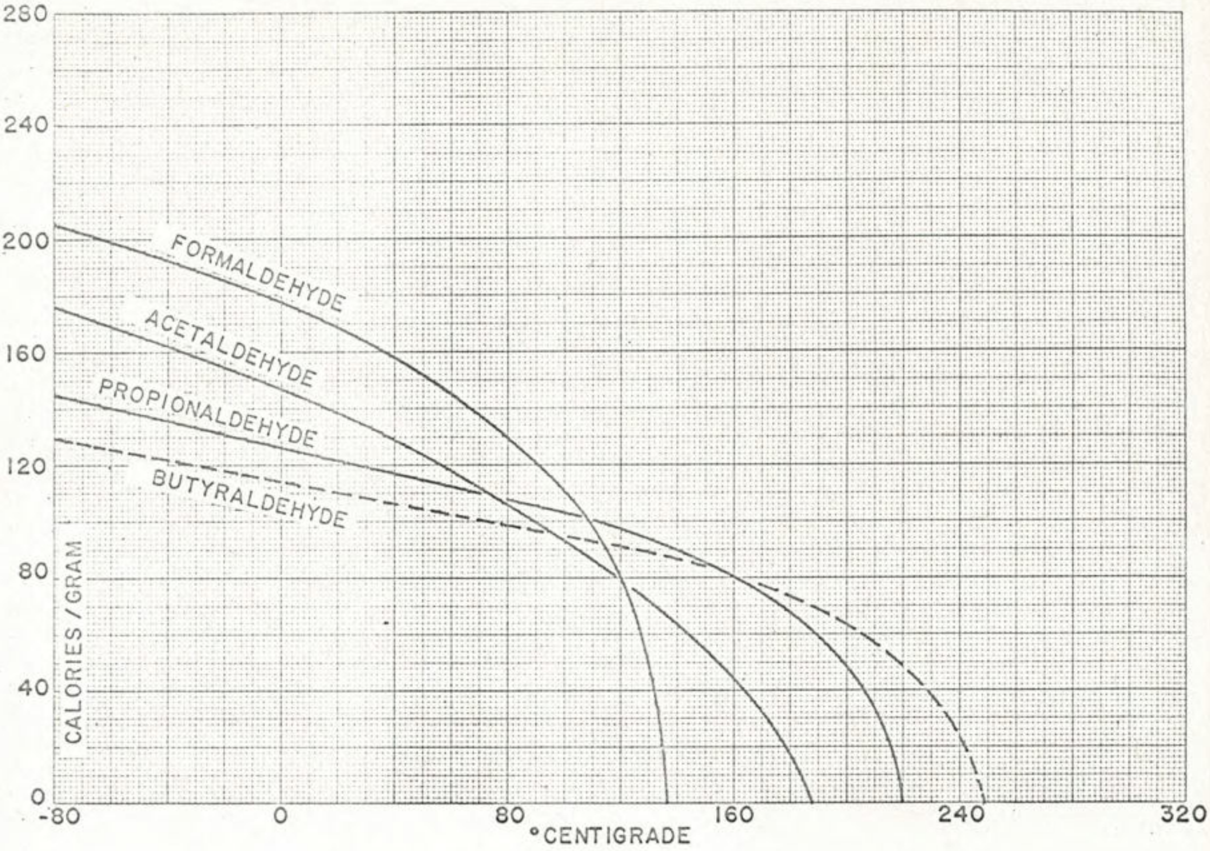


Fig. 24-5—Heat of vaporization of C_1-C_4 aldehydes from —80°C to +240°C.

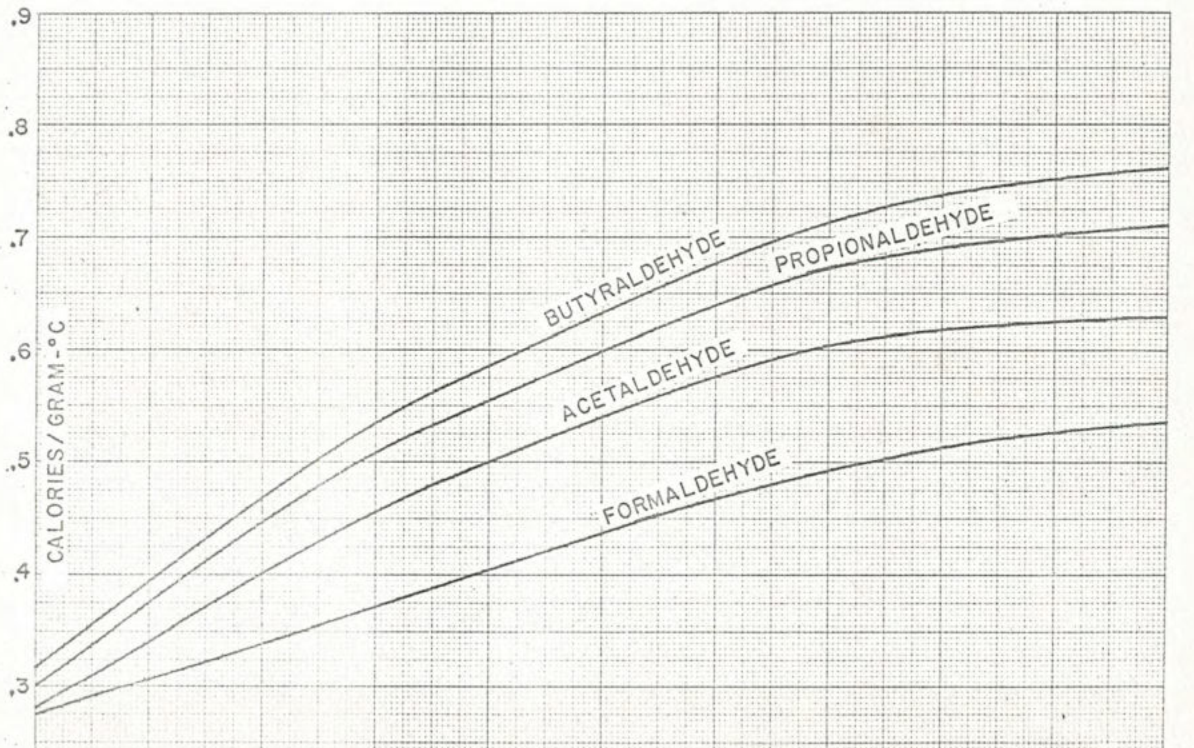


Fig. 24-6—Vapor heat capacity of C_1-C_4 aldehydes from 0°C to 1,000°C.

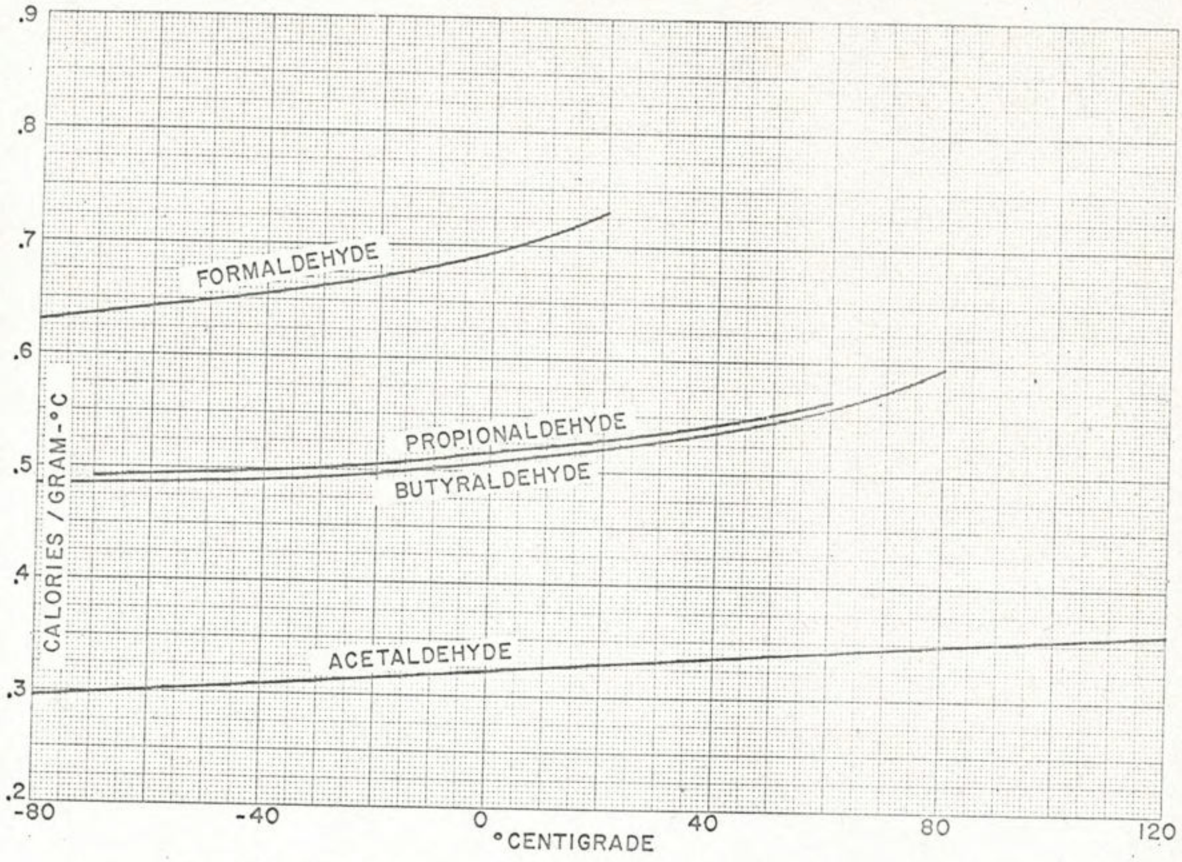


Fig. 24-7—Liquid heat capacity of C_1-C_4 aldehydes from −80 C to +120 C.

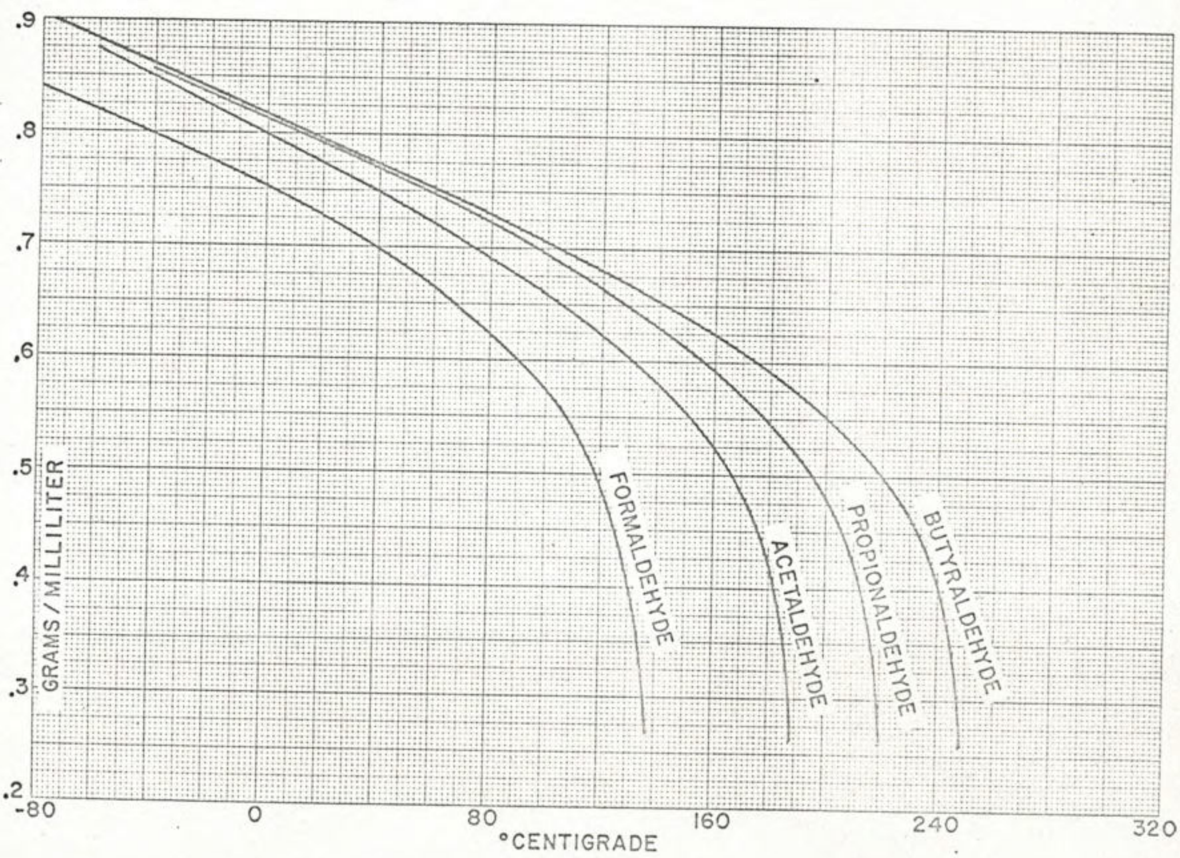


Fig. 24-8—Liquid density of C_1-C_4 aldehydes from −80°C to +240°C.

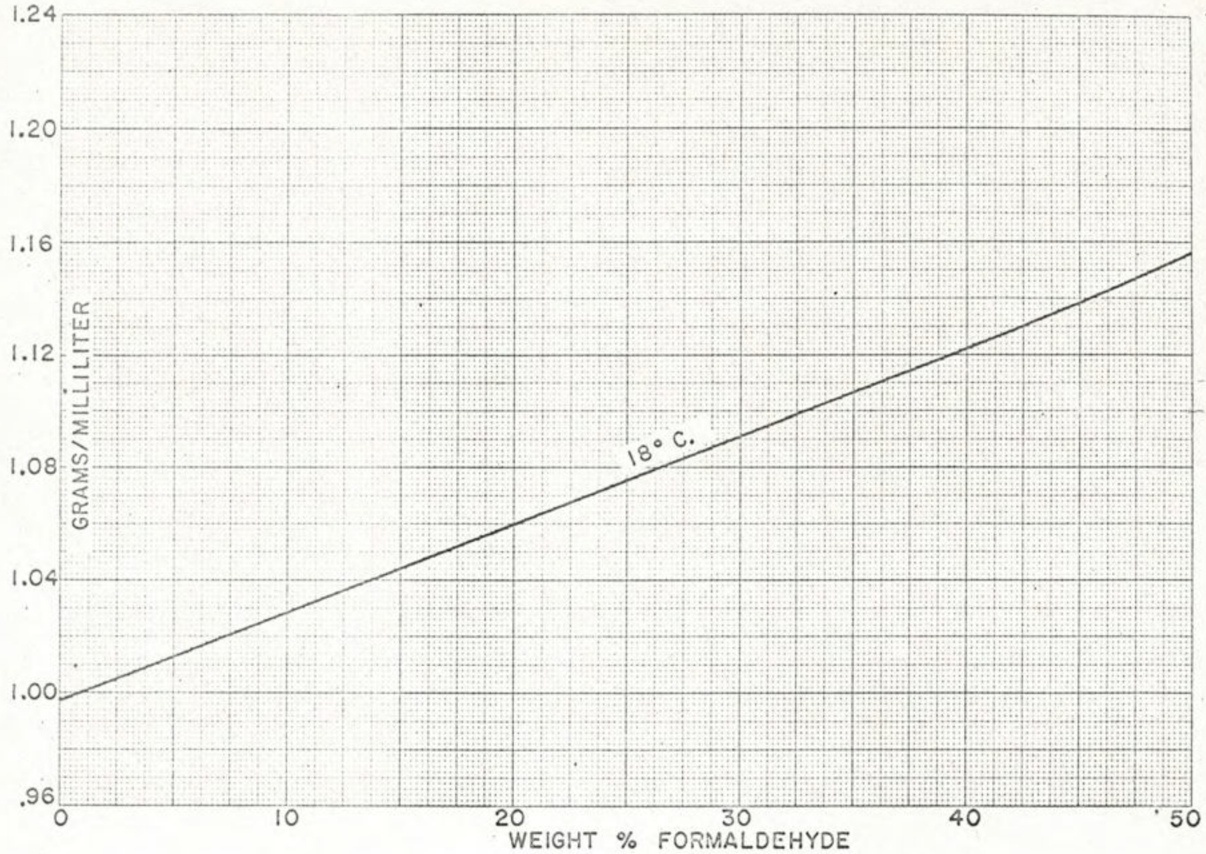


Fig. 24-9—Liquid density of aqueous formaldehyde at 18°C.

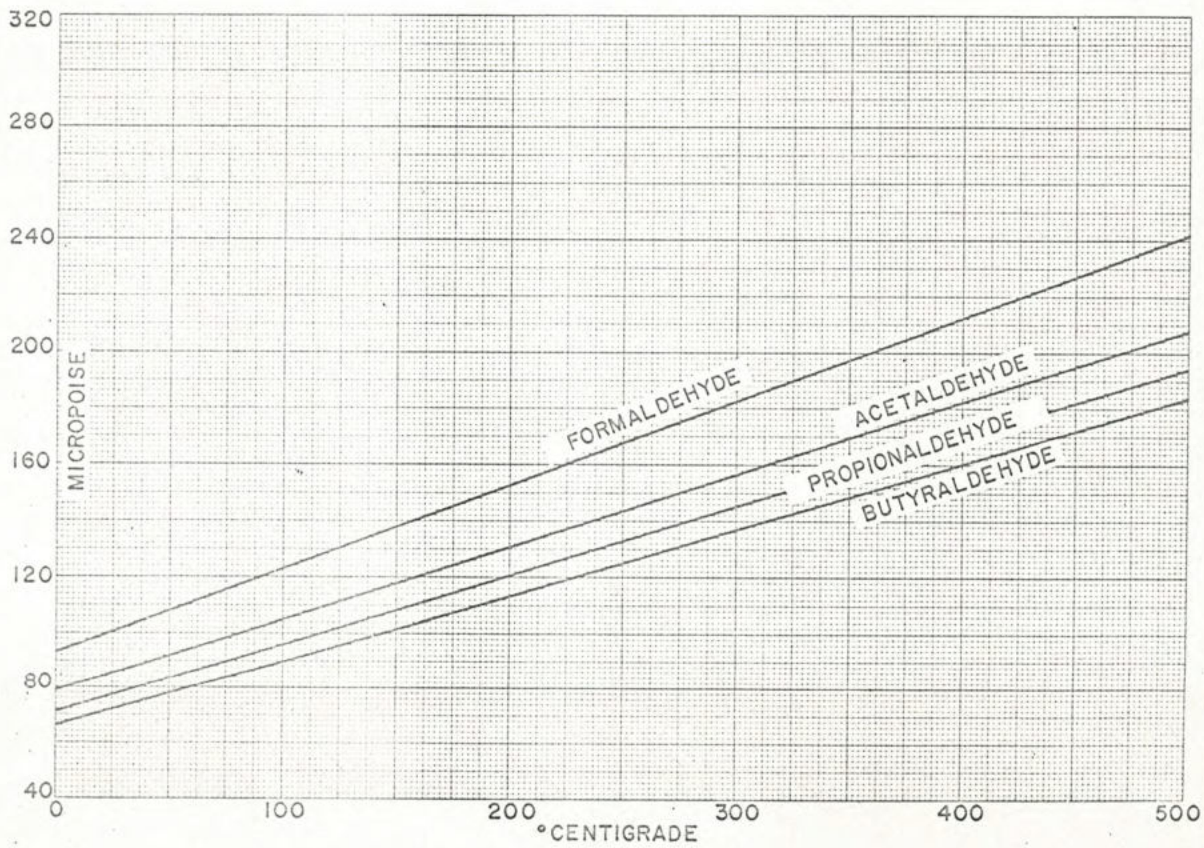


Fig. 24-10—Vapor viscosity of C_1-C_4 aldehydes from 0°C to +500°C.

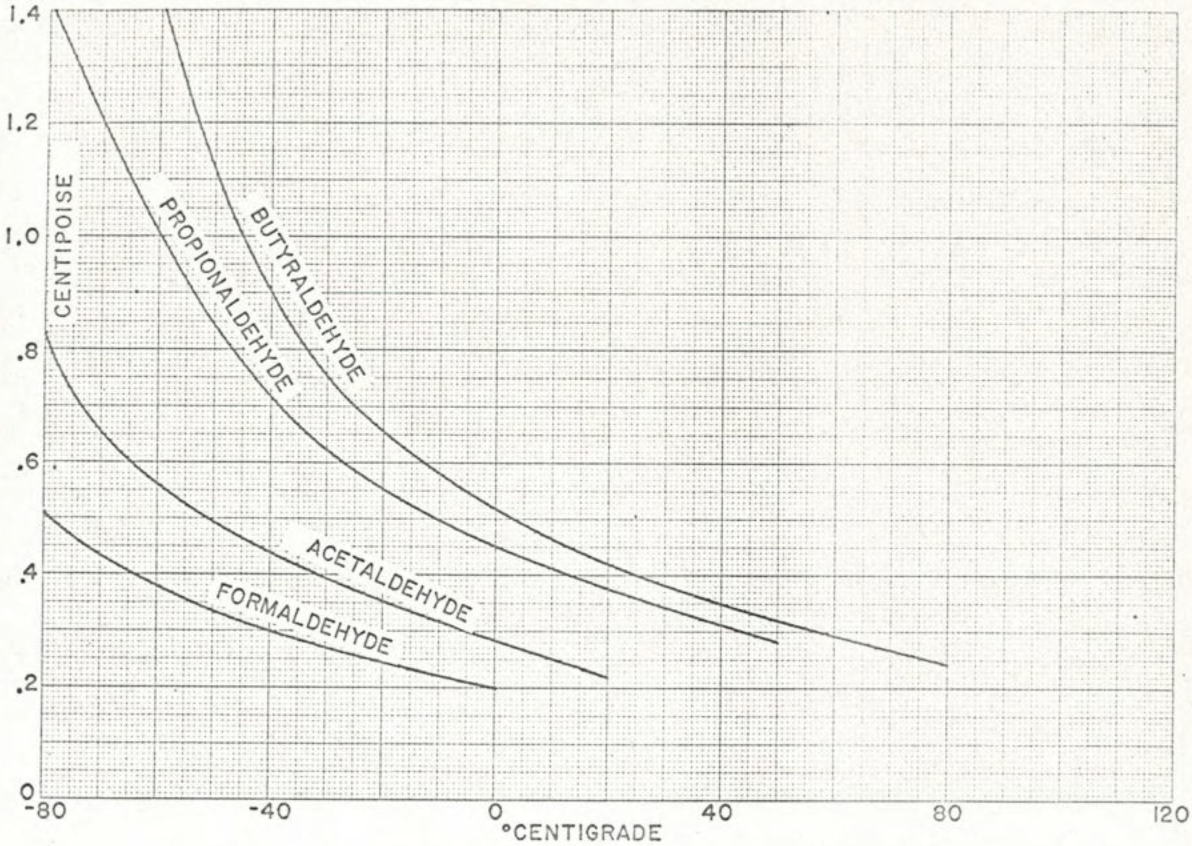


Fig. 24-11—Liquid viscosity of C_1-C_4 aldehydes from −80°C to +80°C.

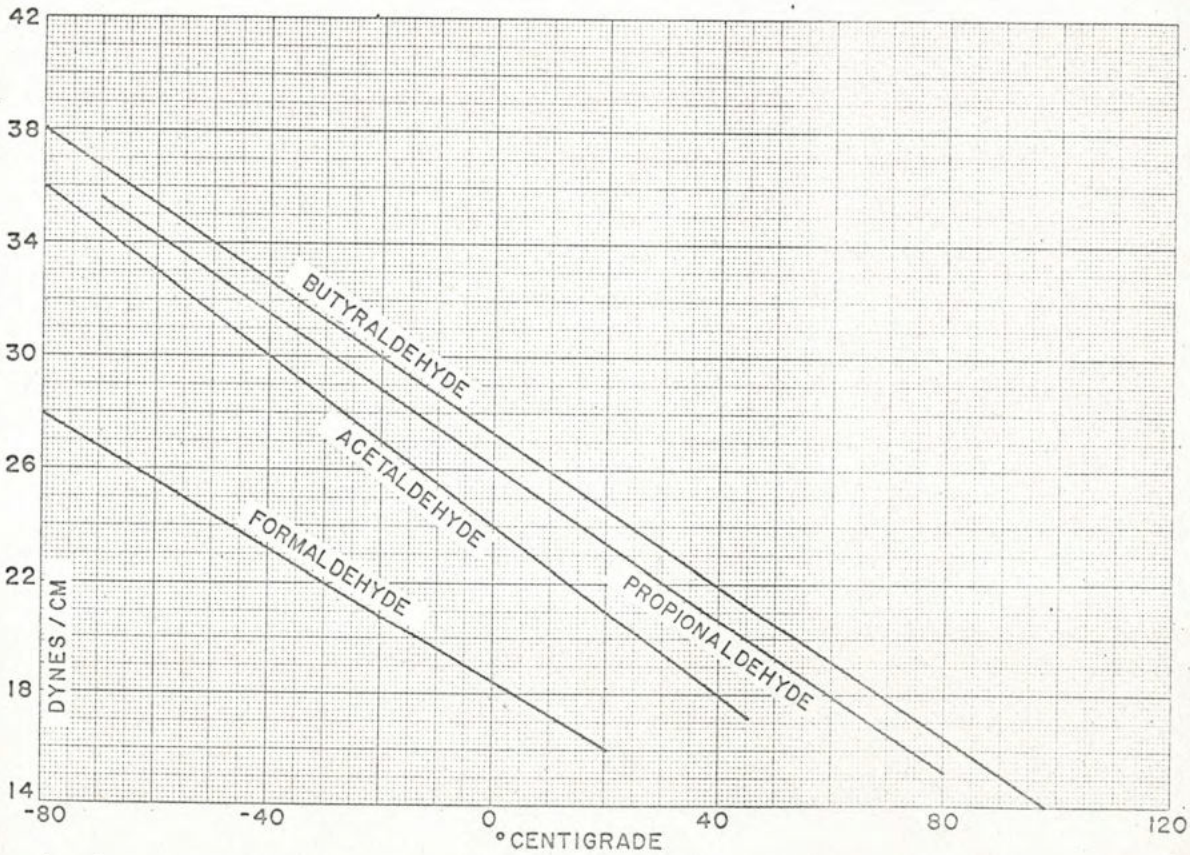


Fig. 24-12—Surface tension of C_1-C_4 aldehydes from −80°C to +100°C.

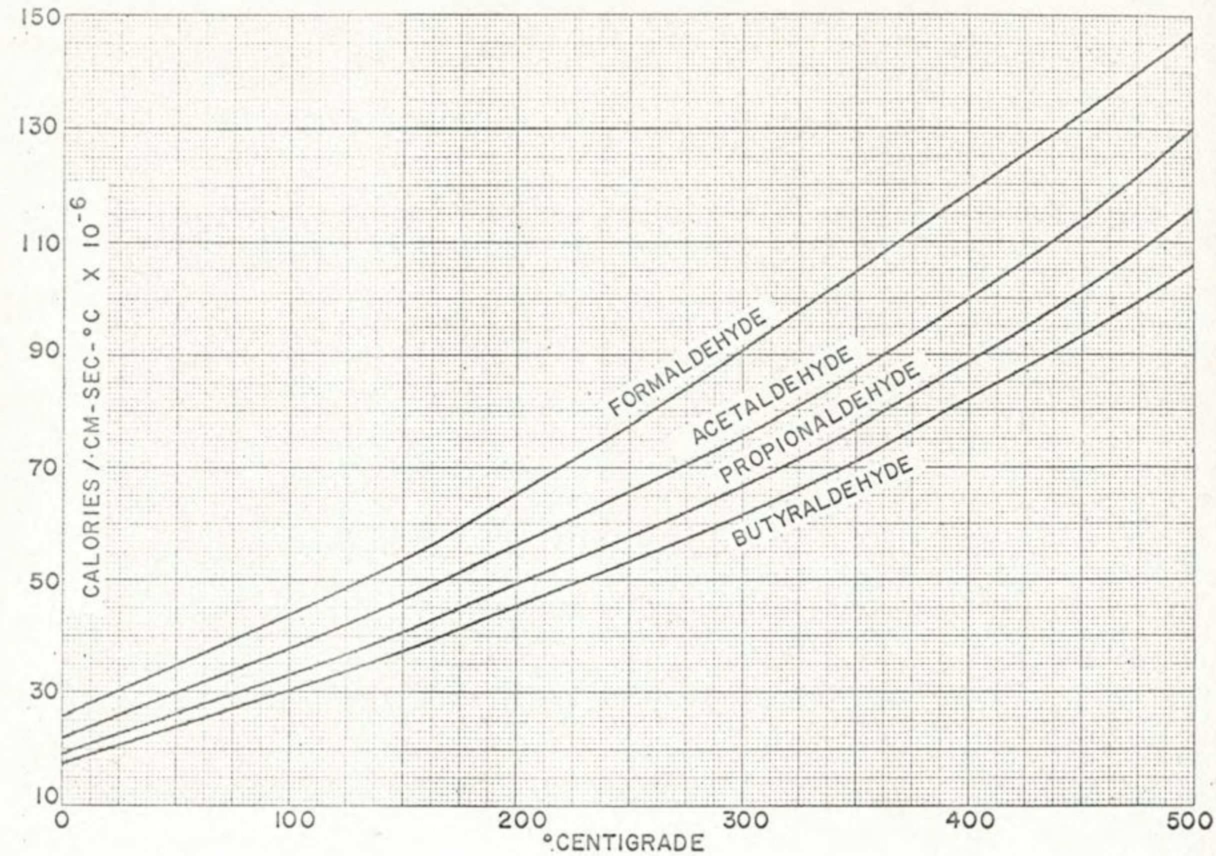


Fig. 24-13—Vapor thermal conductivity of C_1-C_4 aldehydes from 0°C to 500°C.

cal temperatures were estimated by the method of Riedel,[1] with a probable error of only a few degrees centigrade. The critical pressures and densities were determined by the method proposed by Lydersen et al.[1]

The vapor pressures of all four compounds have been measured up to the boiling point.[2,3,4,5] Christensen and Smith[6] have determined the vapor pressure of acetaldehyde up to 150° C. The vapor pressures from the boiling point up to the critical point have been calculated by the method described in previous articles.[7] When compared with the experimental data on acetaldehyde, the error averaged 5 percent.

Figs. 24-3 and 24-4 present data on the pressures of aqueous formaldehyde solutions.[3] Fig. 24-3 shows the total pressure of the system. Fig. 24-4 gives the partial pressure of the formaldehyde in the solution.

Heat of Vaporization. The heat of vaporization at the boiling point has been measured for the four compounds.[2,8,9,10] Data over a wide temperature range are available on acetaldehyde.[6] The nomograph of Kharbanda has been used to extend the data to the critical point.[11]

Heat Capacity. The vapor heat capacities of formaldehyde and acetaldehyde are available from the literature.[9,12,13] The data for propionaldehyde and butyraldehyde have been estimated by the method proposed by Khani and Doraiswamy.[14] This method gave an error of less than one percent when compared to experimental acetaldehyde data.

Coleman and De Vries[9] have measured the liquid heat capacity of acetaldehyde from the boiling point to 150° C. Parks and coworkers[10] have done the same for butyraldehyde over the temperature range of −93° C to +27° C. Only the heat capacity at 0° C is available for propionaldehyde.[15] The heat capacity at 20° C has been estimated for formaldehyde by the method of Johnson and Huang.[1] The data for all four compounds have been extended by the equation: density times heat capacity is equal to a constant. The constant is calculated from experimental data. The average error for six experimental points was 5.1 percent.

Density. Only the room temperature densities of the four aldehydes have been measured.[7,4,9] Consequently, the previously described method of Lydersen, Greenkorn, and Hougen[1] has been used to estimate the liquid densities up to the critical point, with a probable error of one percent.

Viscosity. The vapor viscosities have been estimated by the method of Bromley and Wilke.[16]

There is a limited amount of data on the liquid viscosities of acetaldehyde,[2,15] propionaldehyde,[15] and butyraldehyde.[15,17] The method of Thomas[1] has been used to estimate the liquid viscosities of all four compounds. The error averaged 10 percent when estimated values were compared with experimental data.

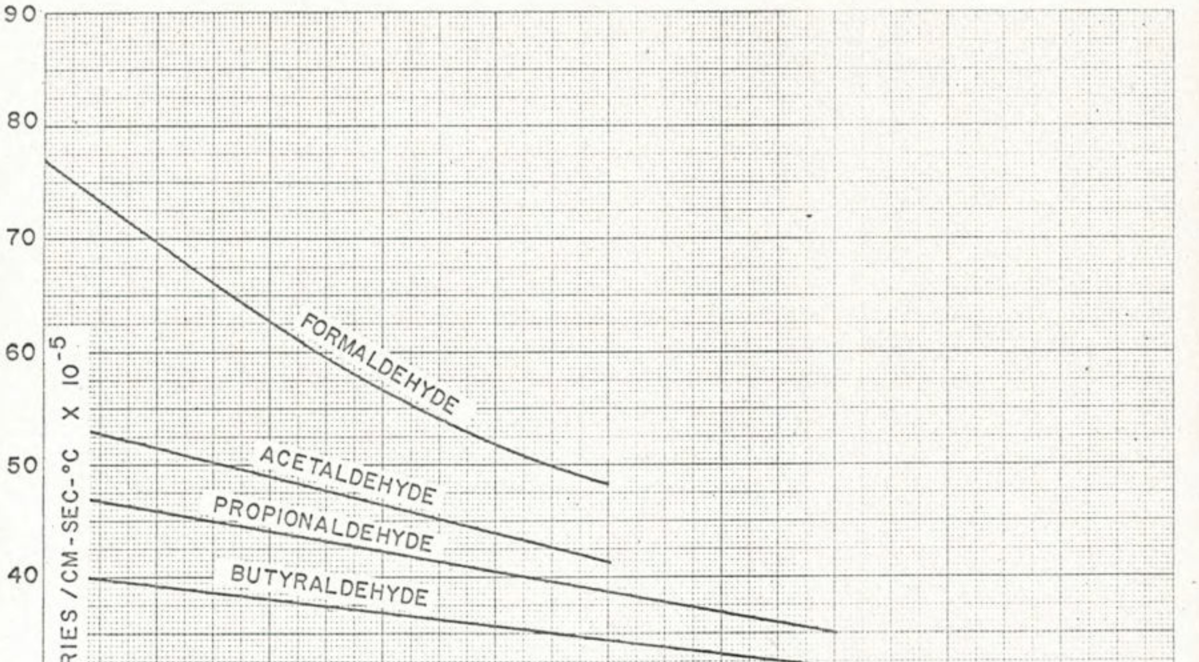
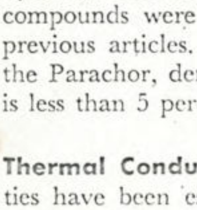


Fig. 24-14—Liquid thermal conductivity of C_1-C_4 aldehydes from −80°C to +80°C.

Surface Tension. Only the surface tension of acetaldehyde has been measured.[15] The surface tensions of all four compounds were estimated by the method described in previous articles. This method relates surface tension to the Parachor, density, and molecular weight.[18] The error is less than 5 percent.

Thermal Conductivity. The vapor thermal conductivities have been estimated by the method of Owens and Thodos.[19] The data of Vines[20] were used to calculate the quasicritical thermal conductivity of acetaldehyde and propionaldehyde.

Jobst has carried out an extensive series of liquid thermal conductivity measurements over a wide temperature range on a variety of compounds.[21] Jobst's apparatus appears to have solved the problem of inconsistency that has plagued most investigators. His data on acetaldehyde, propionaldehyde and butyraldehyde are presented in Fig. 24-14. The data for formaldehyde were estimated by the method of Robbins and Kingrea.[22]



About the author

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Indexing Terms: Acetaldehyde-9, Butyraldehyde-9, Computations-4, Formaldehyde-9, Heat-7, Liquid Phase-5, Physical Properties-7, Pressure-6, Properties/Characteristics-7, Propionaldehyde-9, Temperature-6, Vapor Phase-5.

Part 25, C_1-C_4 Acids, will appear in an early issue.