Physical Properties of Hydrocarbons

Part 25–C_1–C_4 Acids

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FEW CHEMICALS have experienced as long and successful a career as acetic acid. A major commodity for many years, acetic acid continuous to enjoy a steady 5 percent per year growth, buoyed largely by its use as an intermediate for producing cellulose acetate via acetic anhydride. The other 50 percent of the acetic acid market goes largely to vinyl acetate and acetic esters. Over 1.2 billion pounds will be produced in 1967 by either oxidation of acetaldehyde, ethanol and hydrocarbons or by reaction of methanol and carbon monoxide.

The other hydrocarbon acids are not faring so well. In many potential markets, the lower price of acetic acid keeps them blocked out. New products are eroding away some of their present markets. Formic acid is holding onto a stable 20 million pound/year market in textile drying and leather treatment. About 40 million pounds of propionic acid will be consumed this year in producing propionates, plasticizers and herbicides. Butyric acid finds a variety of specialty uses in producing plasticizers and esters.

The physical properties of the $C_1 - C_4$ acids have been extensively studied over the years. Because they are often used as water solutions, their aqueous properties are also included in this article.

Vapor Pressure and Critical Properties. The critical properties have been determined for all but formic acid.[1,2,3,4] The method of Riedel has been used to estimate the critical temperature and pressure of formic acid.[5] The critical density was calculated by Vowles' method.[5]

Stull[1] provides vapor pressure data up to the critical point for acetic acid and propionic acid. Data on all four compounds are available up to the boiling point.[1,2,6] The vapor pressures up to the critical point were calculated by the method recommended by Miller[7] and described in previous articles. For acetic and propionic acid, this method gave an average error of 3.4 percent.

Heat of Vaporization. The heat of vaporization of acetic acid has been measured over the entire temperature range.[3] Only the boiling point data are available on the other three compounds,[2,3,6] and there is a difference of up to 10 percent in the values reported. The data which the author considered to be the most reliable have been extrapolated over the temperature range by the nomograph of Kharbanda.[8]

Heat Capacity. The vapor heat capacities of formic acid[9] and acetic acid[10] have been reported in the literature. The method of Rihani and Doraiswamy[11] has been used to calculate the vapor heat capacities of phopionic acid and butyric acid, with a probable error of less than 1 percent.

There is quite a wide variation in liquid heat capacity data in the literature. Acetic acid data are available up to 80° C.[3] The heat capacities up to 40° C have been measured on the other three acids.[2,3,6] The data have been extended to 200° C by the equation,

density × heat capacity = a constant evaluated from known data

For acetic and butyric acid, this method gave an average error of 2.8 percent for six experimental points.

Density. Timmermans has measured the density of acetic acid up to its critical point.[2] Data over the entire temperature range are also reported for propionic acid.[2,4] The density has been measured from 15° to 50° C for formic acid[2,12]; and from 0 to 70° C for butyric acid.[2] The density up to the critical point was calculated for these two compounds by the method proposed by Lyderson and cowarkers.[5] When compared to seven experimental values, the error averaged 0.9 percent.

TABLE 25-1—Physical Properties of C_1-C_4 Acids

	Boiling Point, °C	Freezing Point, °C	Molecular Weight	Critical Properties		
				T_c °C	P_c PSIA	d_c g/ml
Formic Acid.....	100.6	8.2	46.02	308*	1,055*	0.392*
Acetic Acid.....	118.1	16.6	60.05	321.6	840	0.351
Propionic Acid...	141.1	−20.7	74.08	339.5	778	0.315
Butyric Acid.....	163.5	− 5.2	88.11	355	764	0.302

* Estimated.

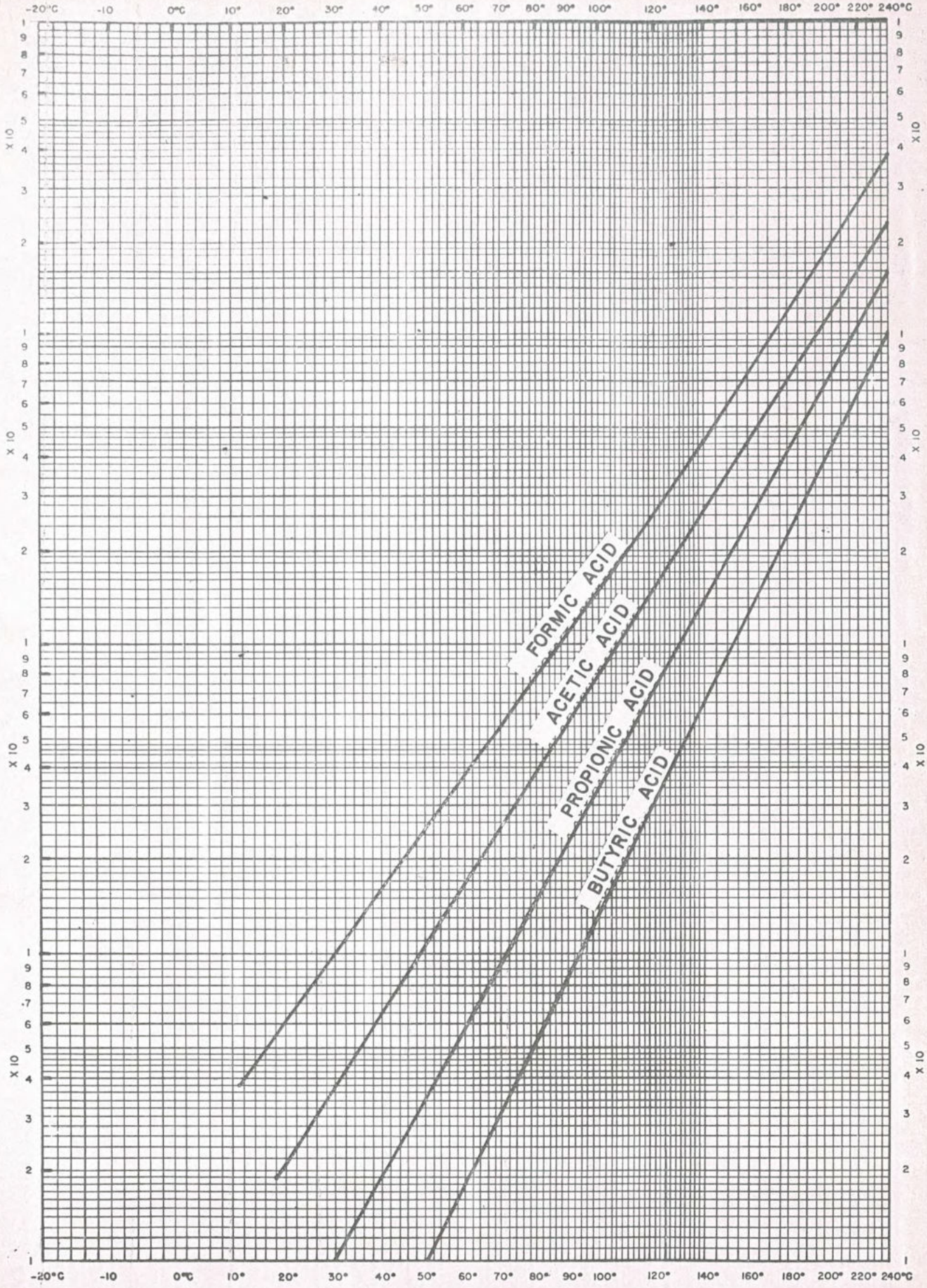

Fig. 25-1—Gives vapor pressure of C_1—C_4 acids from 10° C to 240° C.

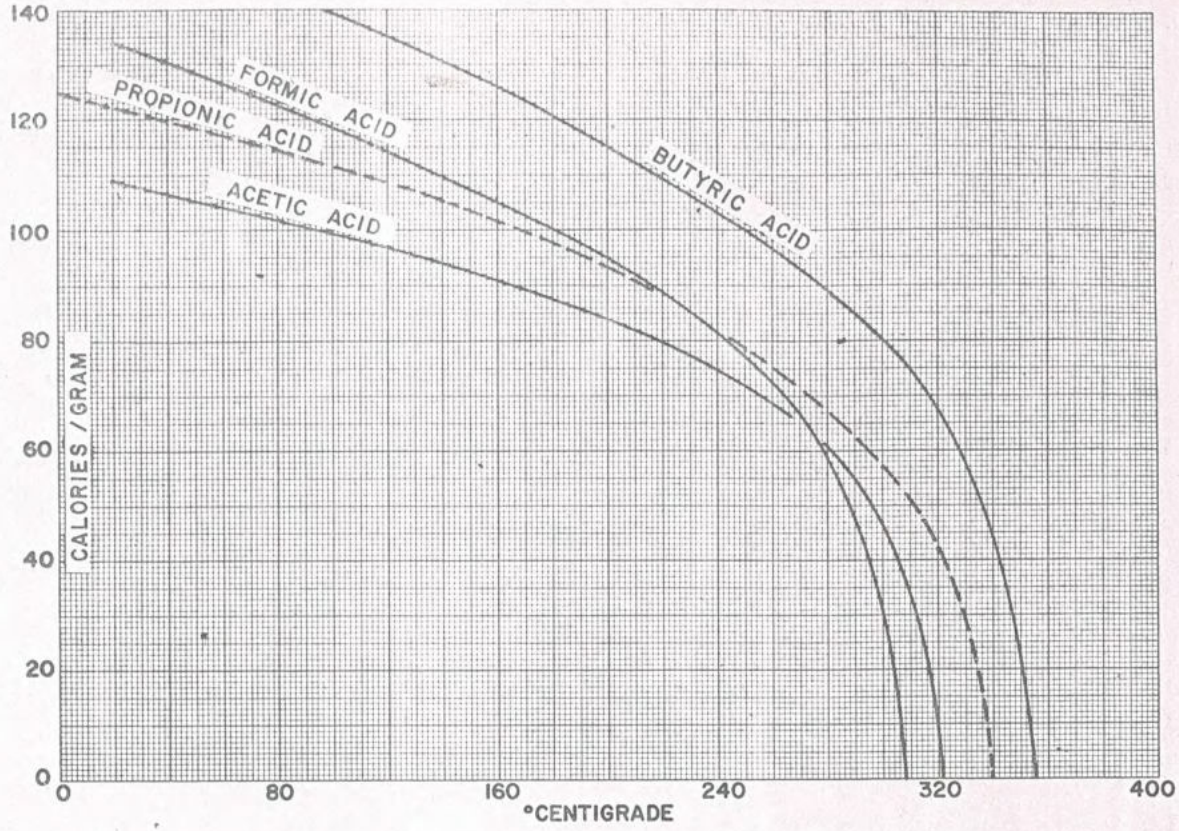

Fig. 25-2—Gives heat of vaporization of C_1—C_4 acids from 0° C to 360° C.

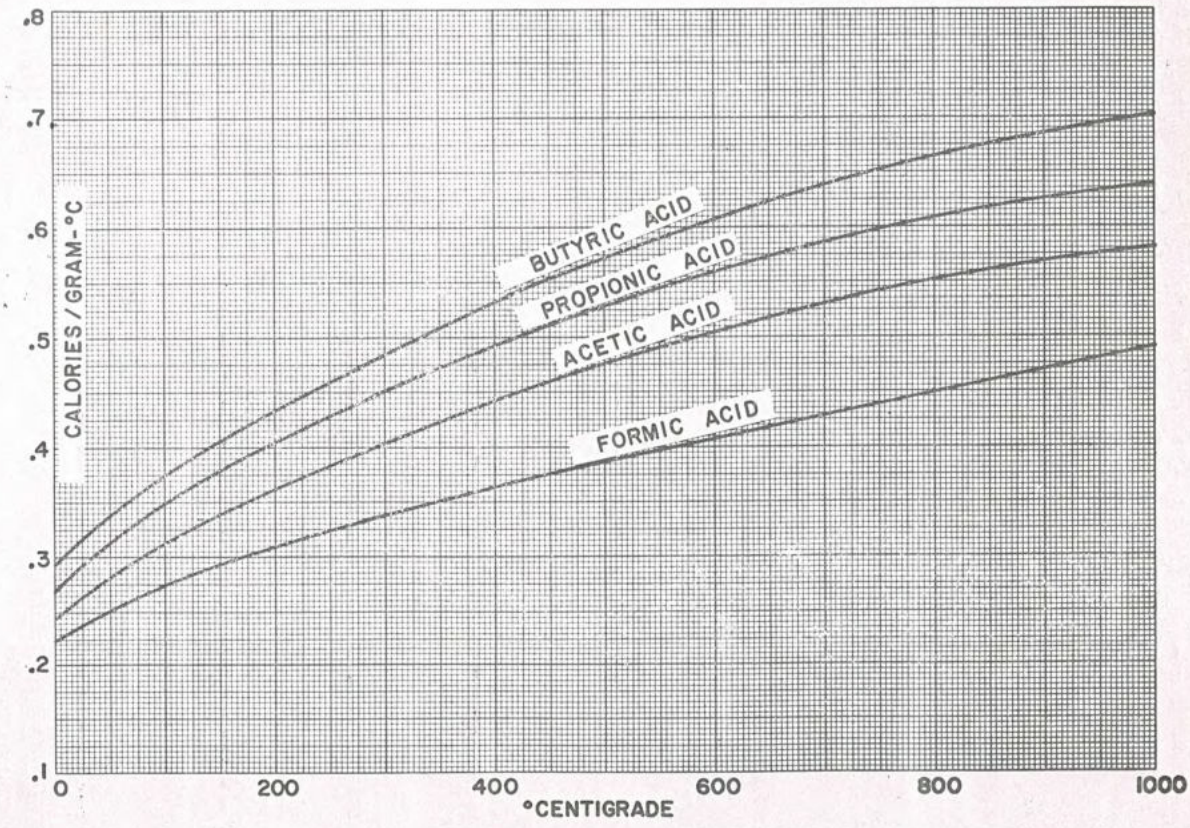

Fig. 25-3—Gives vapor heat capacity of C_1—C_4 acids from 0° C to 1000° C.

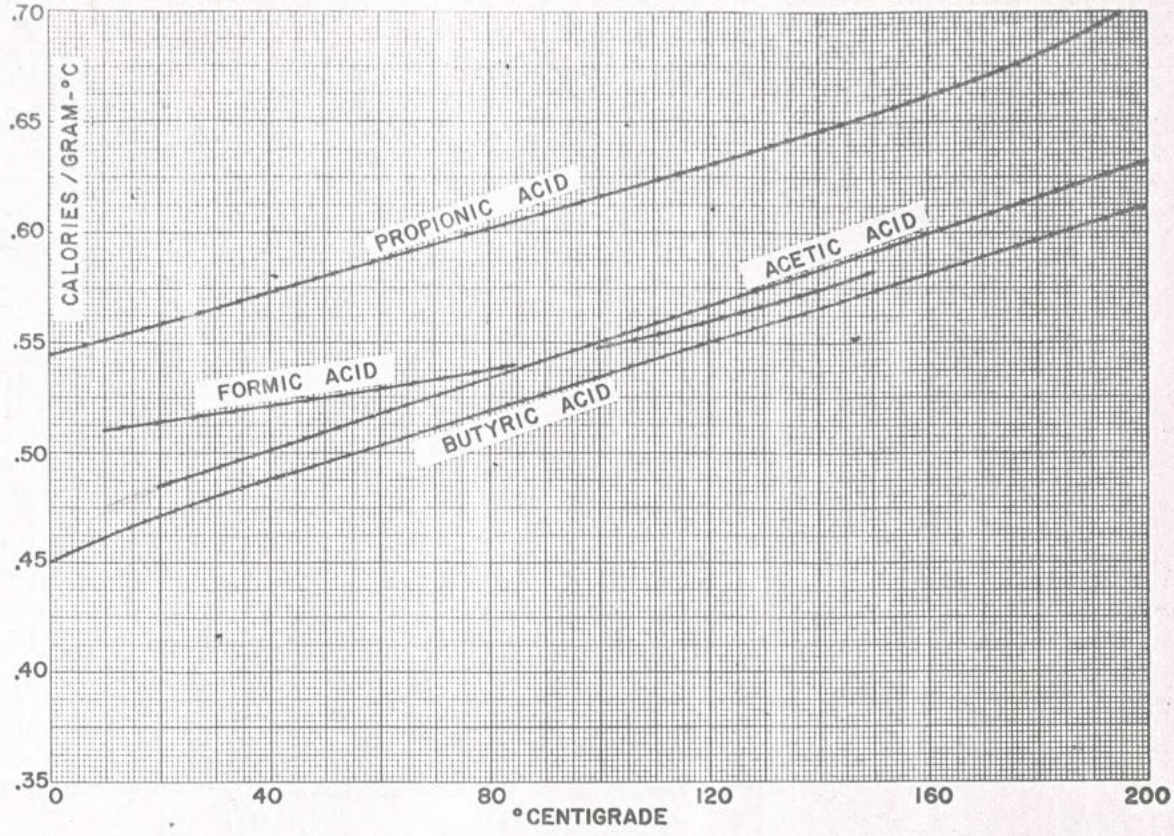

Fig. 25-4—Gives liquid heat capacity of C_1—C_4 acids from 0° C to 200° C.

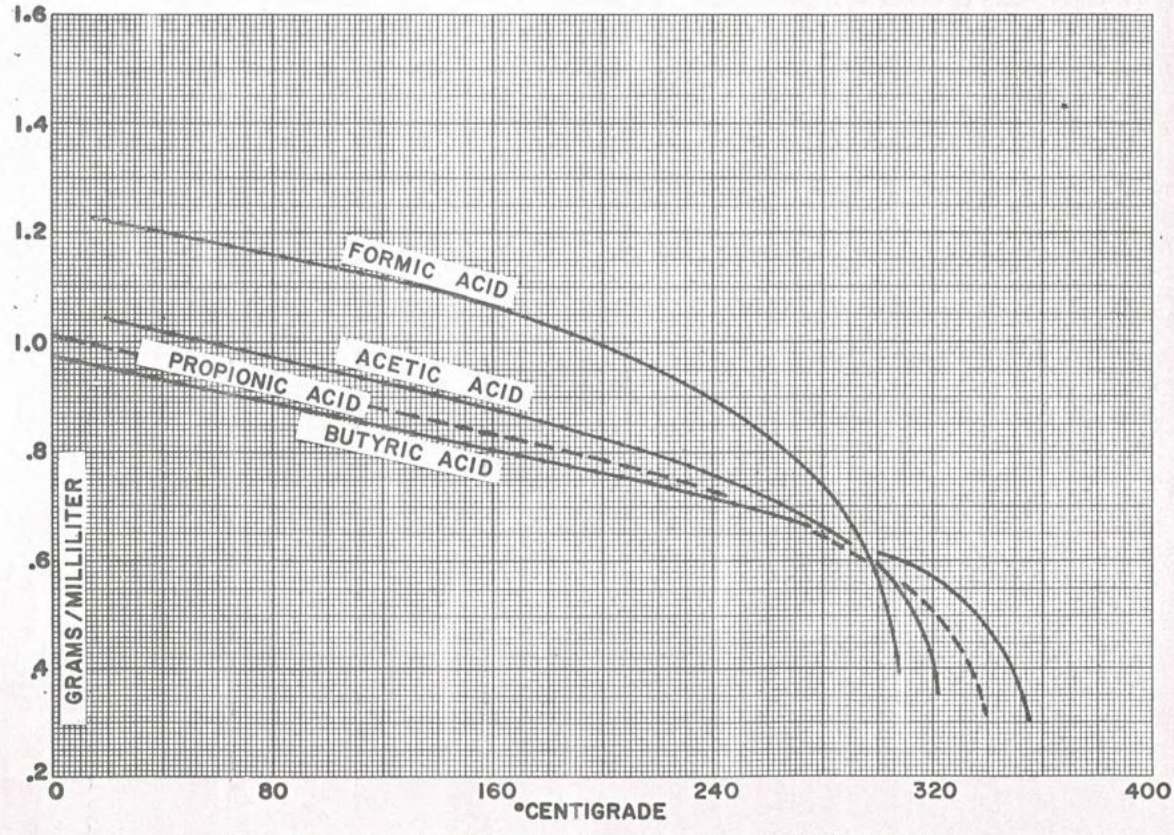

Fig. 25-5—Gives liquid density of C_1—C_4 acid from 0° C to 360° C.

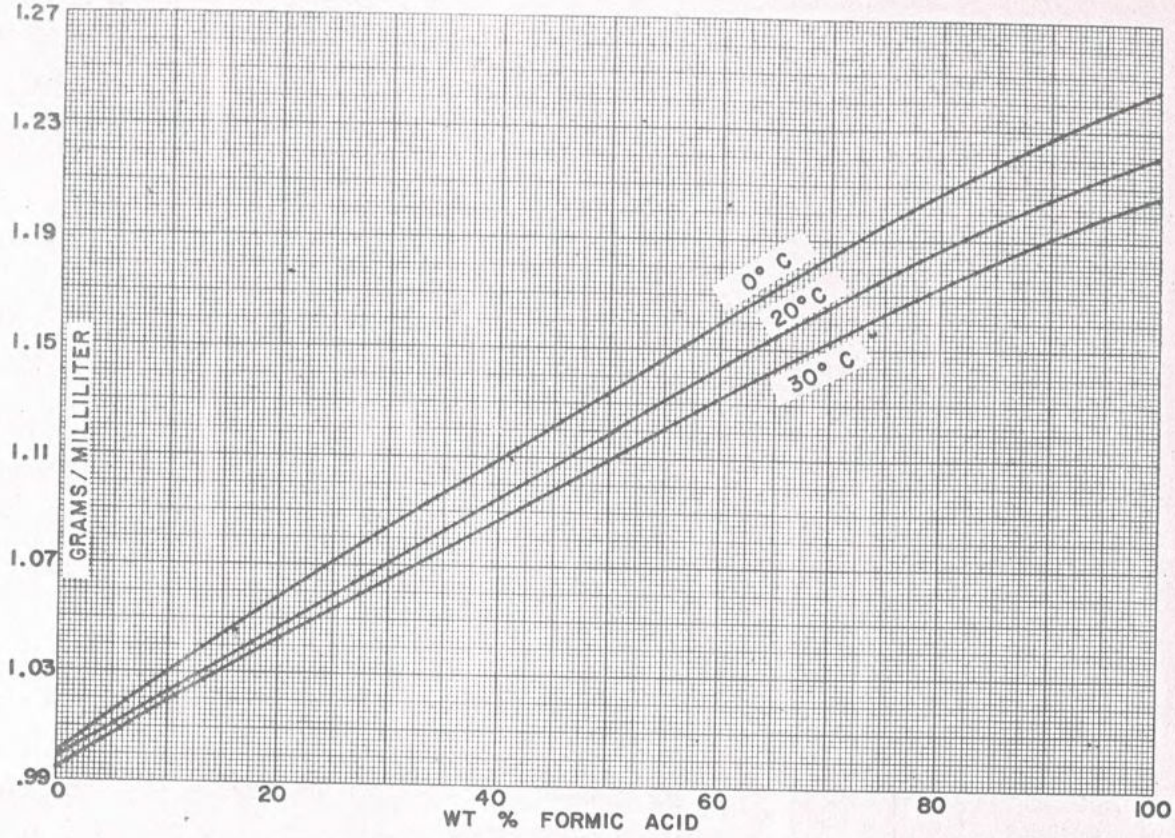

Fig. 25-6—Gives liquid density of aqueous formic acid from 0° C to 30° C.

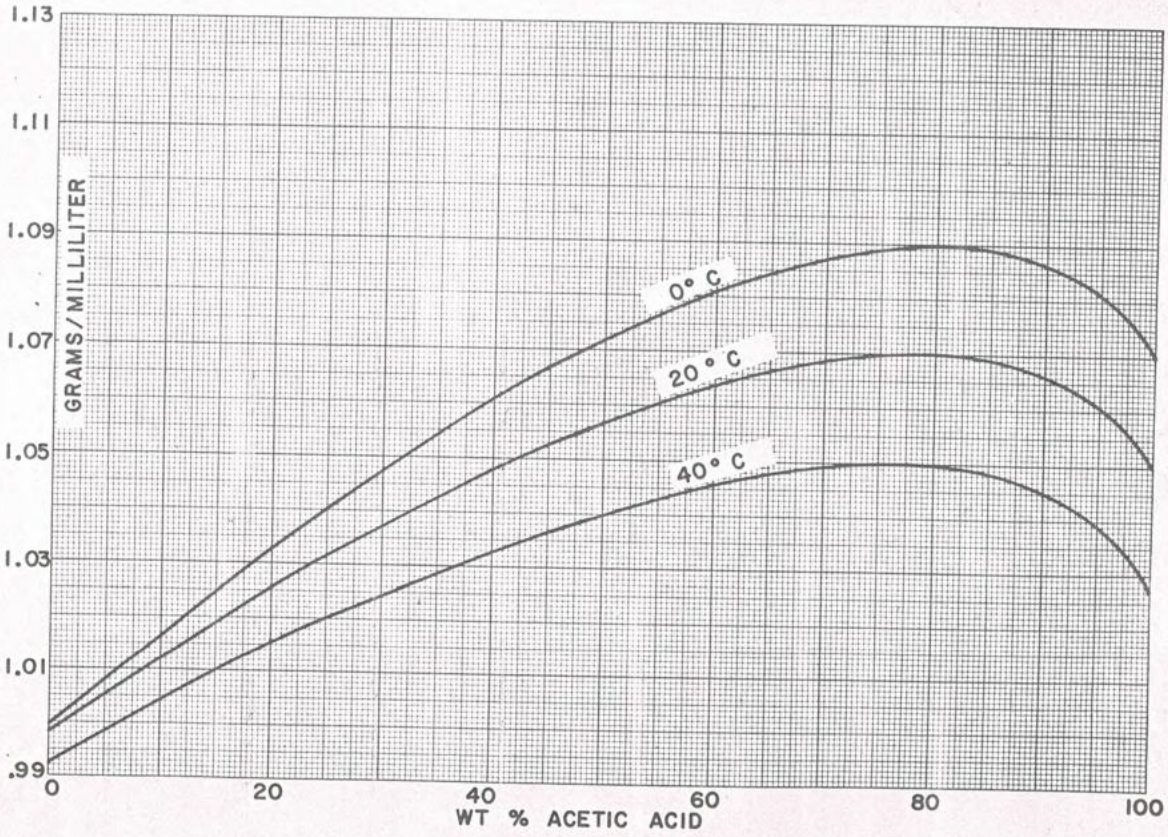

Fig. 25-7—Gives liquid density of aqueous acetic acid from 0° C to 40° C.

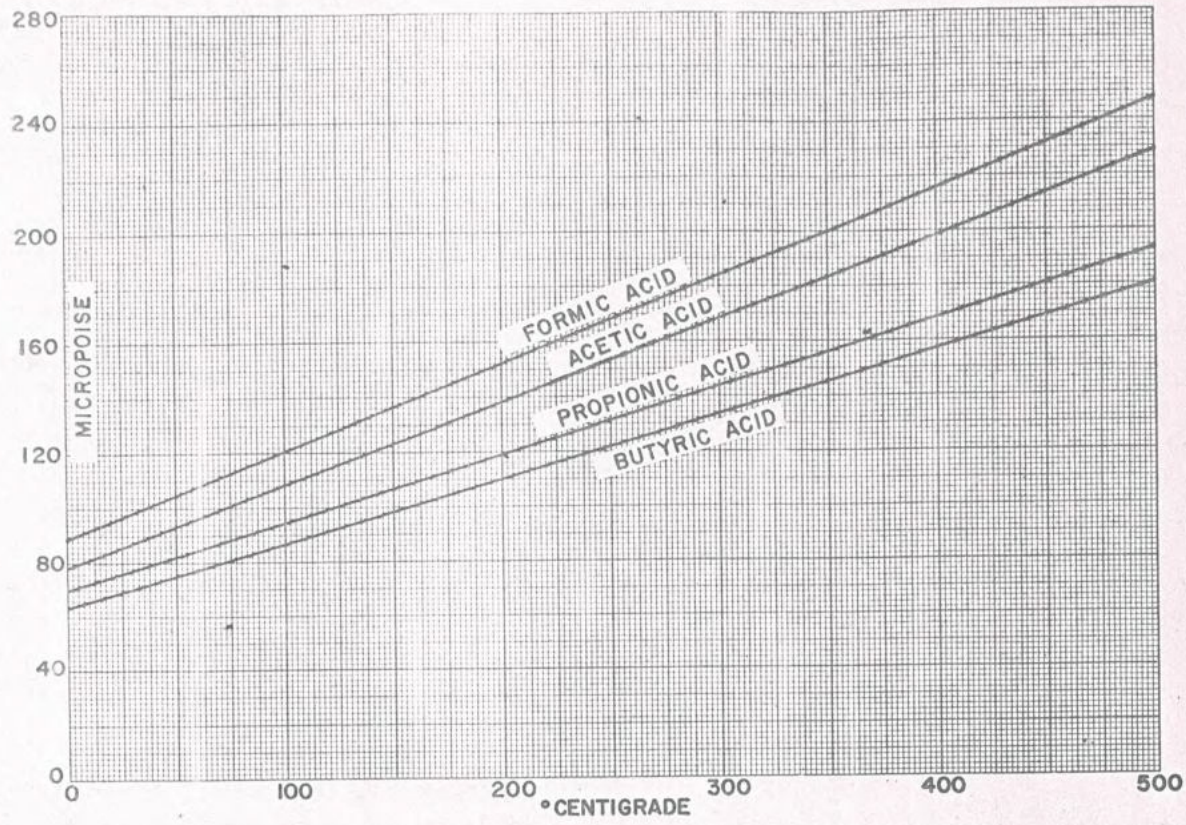

Fig. 25-8—Gives vapor viscosity of C_1—C_4 acids from 0° C to 500° C.

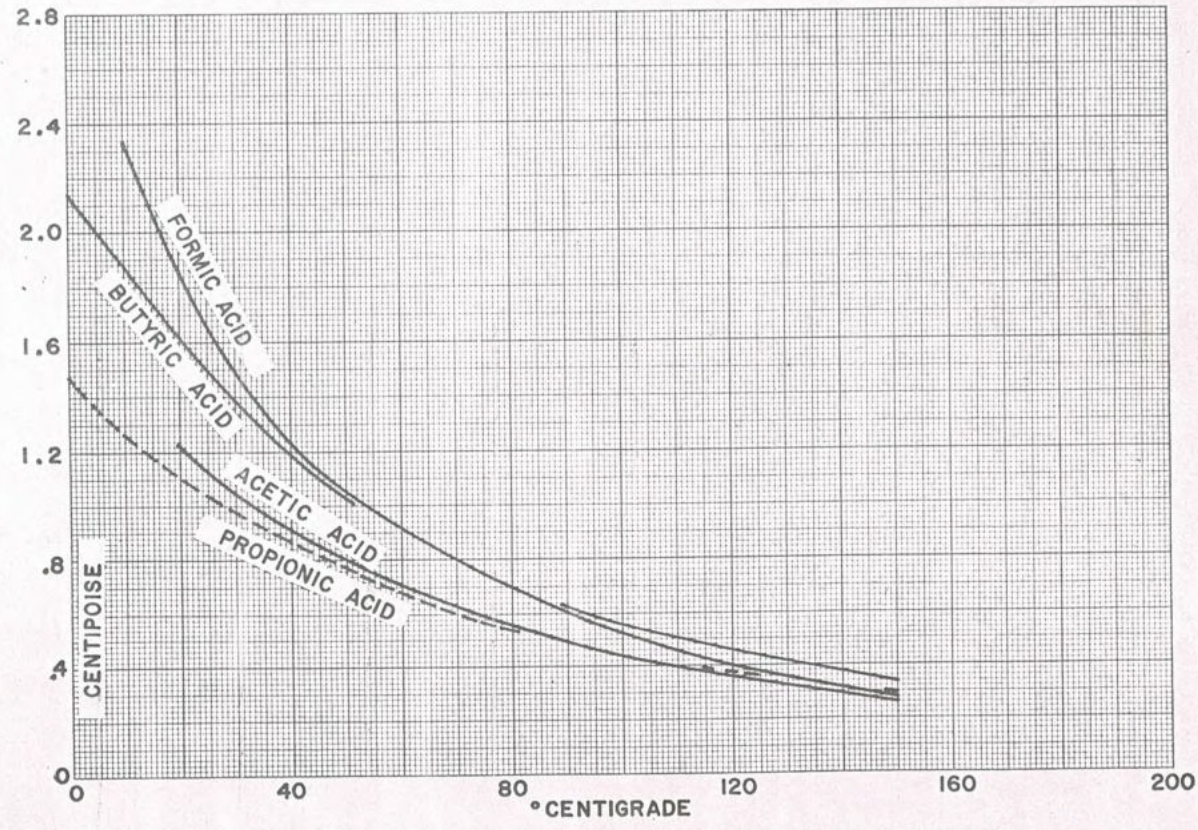

Fig. 25-9—Gives liquid viscosity of C_1—C_4 acids from 0° C to 150° C.

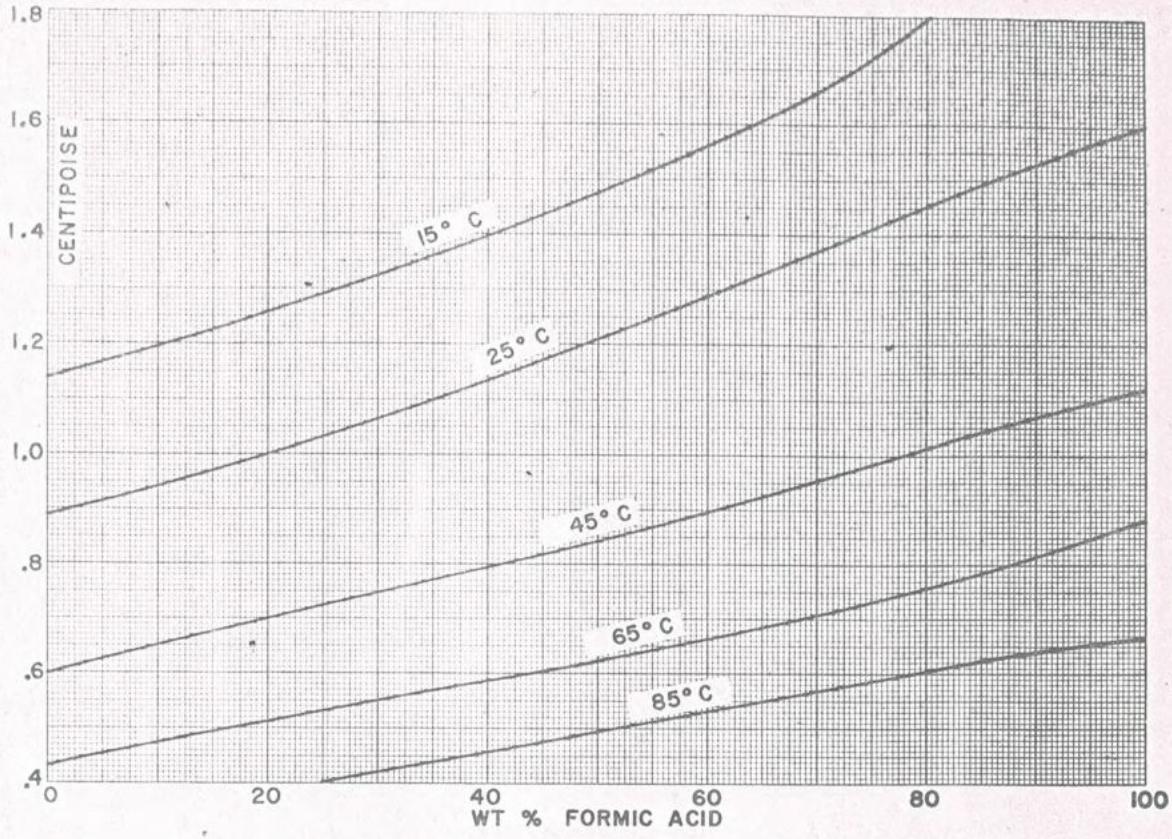

Fig. 25-10—Gives liquid viscosity of aqueous formic acid from 15° C to 85° C.

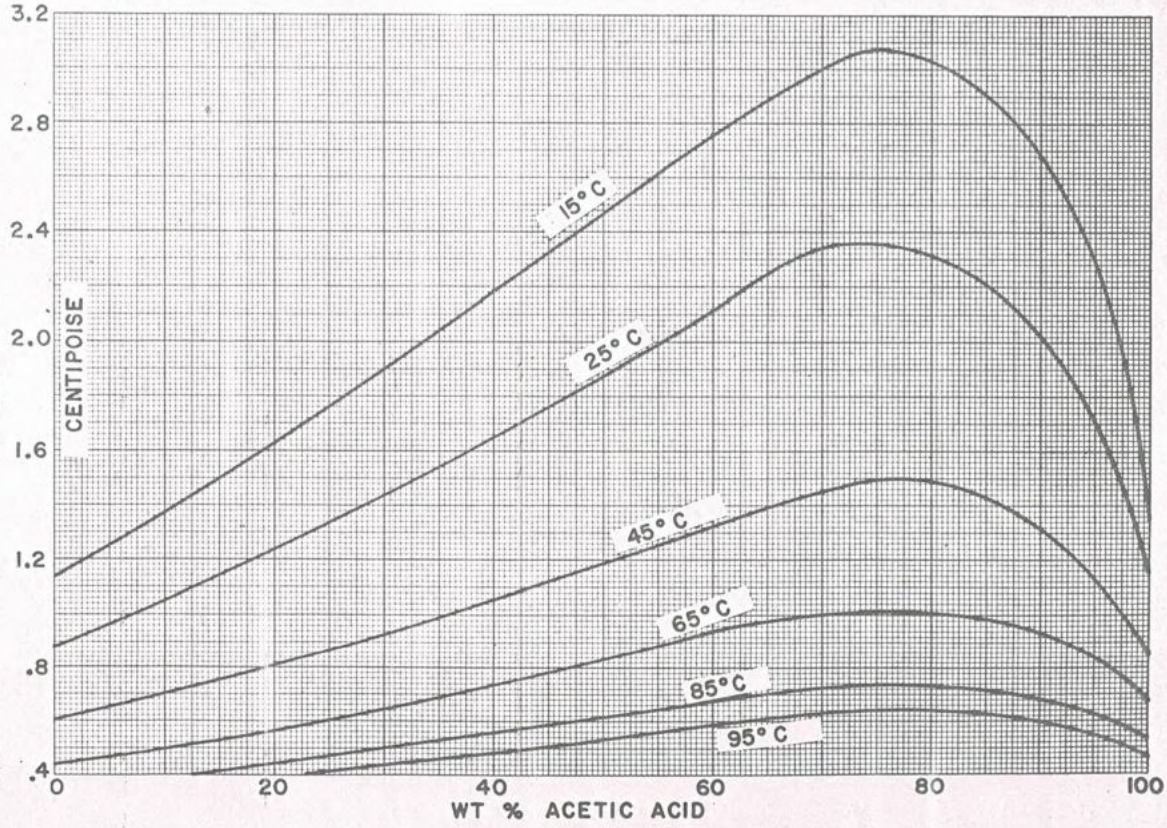

Fig. 25-11—Gives liquid viscosity of aqueous acetic acid from 15° C to 95° C.

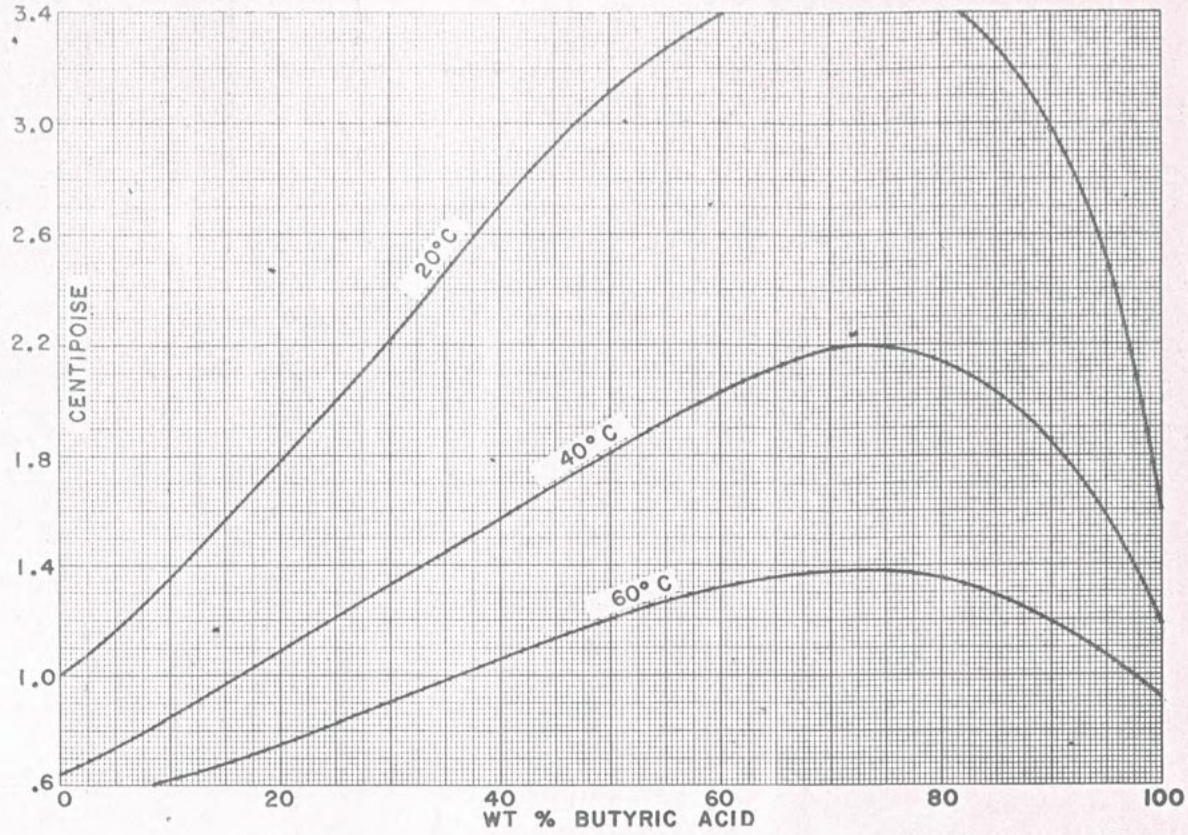

Fig. 25-12—Gives liquid viscosity of aqueous butyric acid from 20° C to 60° C.

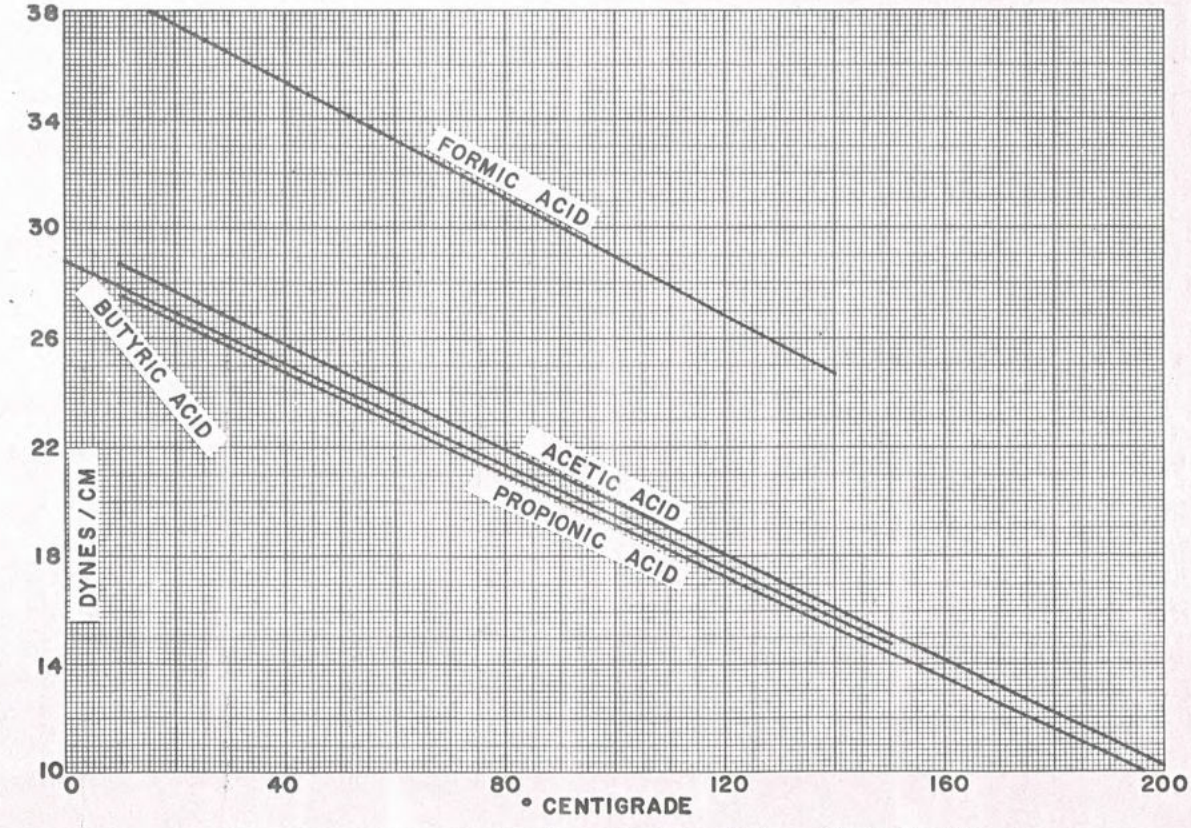

Fig. 25-13—Gives surface tension of C_1—C_4 acids from 0° C to 200° C.

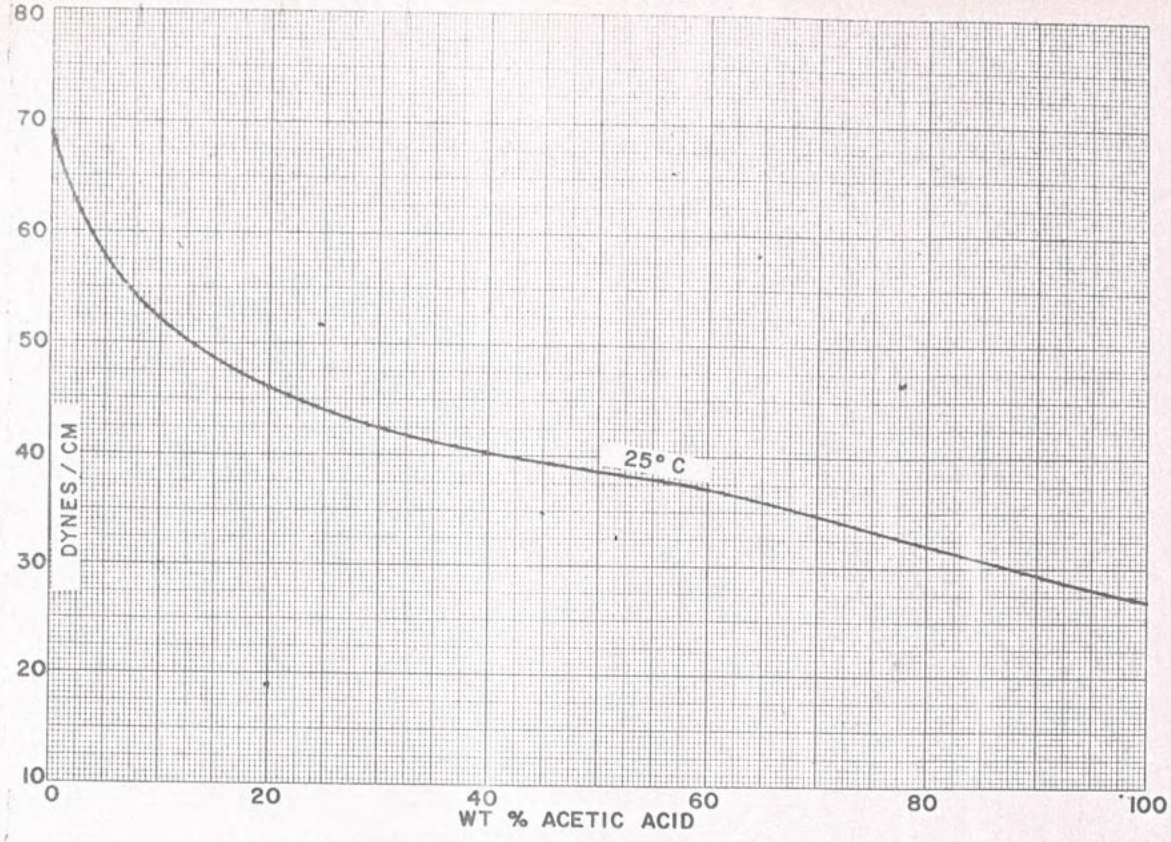

Fig. 25-14—Gives surface tension of aqueous acetic acid at 25° C.

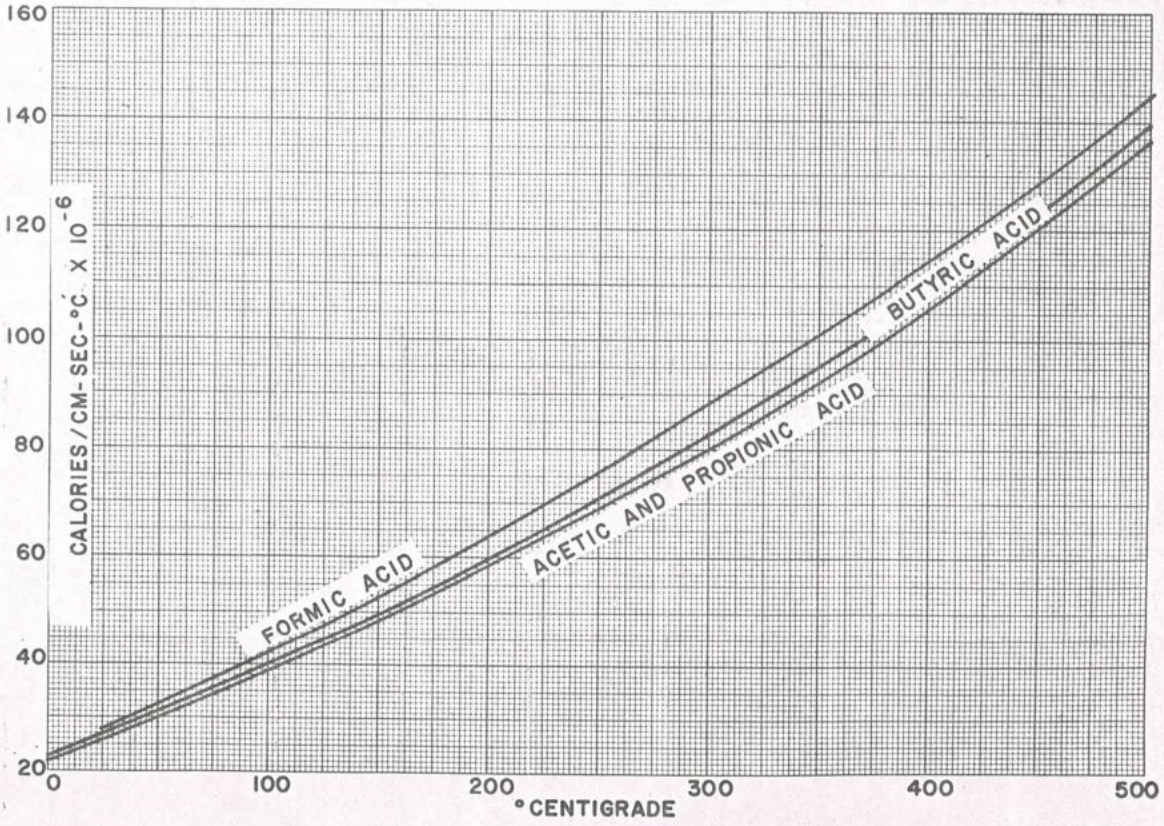

Fig. 25-15—Gives vapor thermal conductivity of C_1—C_4 acids from 0° C to 500° C.

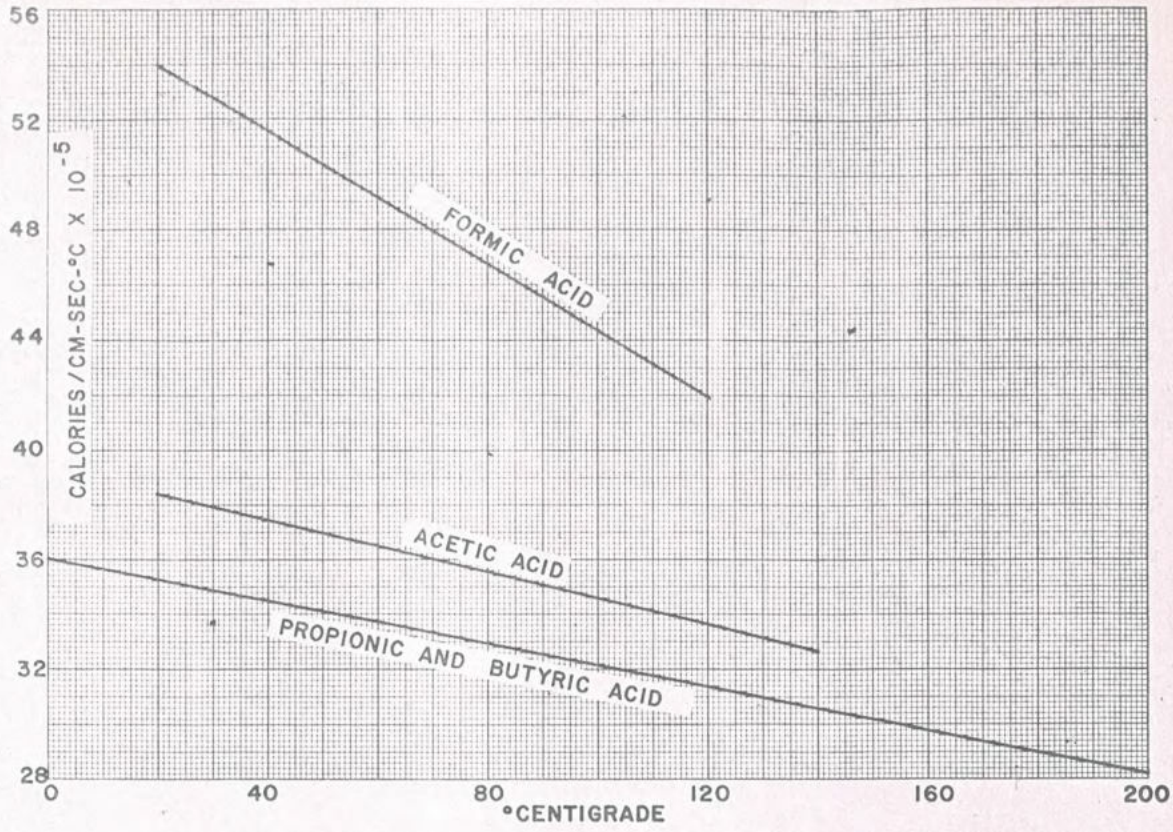

Fig. 25-16—Gives liquid thermal conductivity of C_1—C_4 acids from 0° C to 200° C.

Additionally, the aqueous densities of formic acid[3] from 0-30° C and acetic acid[3] from 0-40° C are plotted in Graphs 25-6 and 25-7.

Viscosity. Only the vapor viscosity of acetic acid has been measured.[3] The viscosities of the other three acids were calculated by the method of Bromley and Wilke,[13] with a probable error of 3 percent.

Extensive work has been done on measurng the liquid viscosities of both the pure acids[2,3,4] and the aqueous solutions. Graph 25-9 is a plot of the pure acid viscosity up to 150° C. Graphs 25-10, 25-11, and 25-12 present data from the International Critical Tables[4] for aqueous formic acid, acetic acid, and butyric acid.

Surface Tension. The International Critical Tables report experimental surface tension data for formic acid up to 100° C; acetic acid to 250° C; propionic acid to 140° C, and butyric acid to 160° C.

Graph 25-14 shows how the surface tension of aqueous acetic acid varies with concentration at 25° C.[6]

Thermal Conductivity. The vapor thermal conductivities have been estimated by the method described in previous articles.[14]

Graph 25-16 is a plot of the liquid thermal conductivity data determined by Jobst in his extensive work on oxygenated hydrocarbons.[15]

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Indexing Terms: Acetic Acid-9, Butyric Acid-9, Computations-4, Formic Acid-9, Heat-7, Liquid Phase-5, Physical Properties-7, Pressure-6, Properties/Characteristics-7, Propionic Acid-9, Temperature-6, Vapor Phase-5.

Part 26 will appear in an early issue.