Physical Properties of Hydrocarbons

PART 31—Esters

From charts you can get these properties for esters:

- Vapor Pressure
- Heat of Vaporization
- Heat Capacity
- Liquid Density
- Viscosity
- Surface Tension
- Thermal Conductivity

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ACETIC ANHYDRIDE is one of the most important esters, with sales in 1967 of about 1.7 billion pounds. The major market for acetic anhydride is in the production of cellulose acetate. Other important uses include production of collulosic plastics, vinyl acetate, and aspirin. Acetic anhydride is a mature commercial product enjoying a stable price situation and steady growth.

Propionic anhydride finds uses in such specialty products as perfumes, flavors, and pharmaceuticals.

Most of the 35 million pounds a year of isopropyl acetate production goes into lacquer formulations. The excellent properties that it gives to lacquers, coupled with low price, should enable it to maintain its market. Ethyl formate has no major markets but is used in production of fumigants and vitamin B_1.

Acetic anhydride is produced by three major processes: (1) dehydration of acetic acid, (2) decomposition of acetone, and (3) oxidation of acetaldehyde. The formates and acetates are prepared by reacting the appropriate alcohol and organic acid in the presence of *p*-toluenesulfonic acid.

Critical Properties and Vapor Pressure. The critical temperatures and pressures have been measured for acetic anhydride and ethyl formate.[1] The critical density is available only for ethyl formate.[2] The method of Riedel[3] was used to estimate the critical temperatures and pressures of propionic acid and isopropyl acetate. Vowles' method was used to calculate the critical densities.[3]

Stull summarizes the data available on the vapor pressures of acetic anhydride and ethyl formate from the melting point to the critical point, and for propionic anhydride and isopropyl acetate up to the boiling point.[1] The vapor

TABLE 31-1—Physical Properties of Esters

Compound	Boiling Point, °C	Freezing Point, °C	Molecular Weight	Critical Properties °C T_c	PSIA P_c	g/ml d_c
Acetic Anhydride	139.9	−73	102.09	296.0	675	0.349*
Propionic Anhydride	167.0	−45	130.15	313*	478*	0.320*
Ethyl Formate	54.2	−79	74.09	235.3	686	0.323
Isopropyl Acetate	89.0	....	102.15	243*	507*	0.297*

* Estimated.

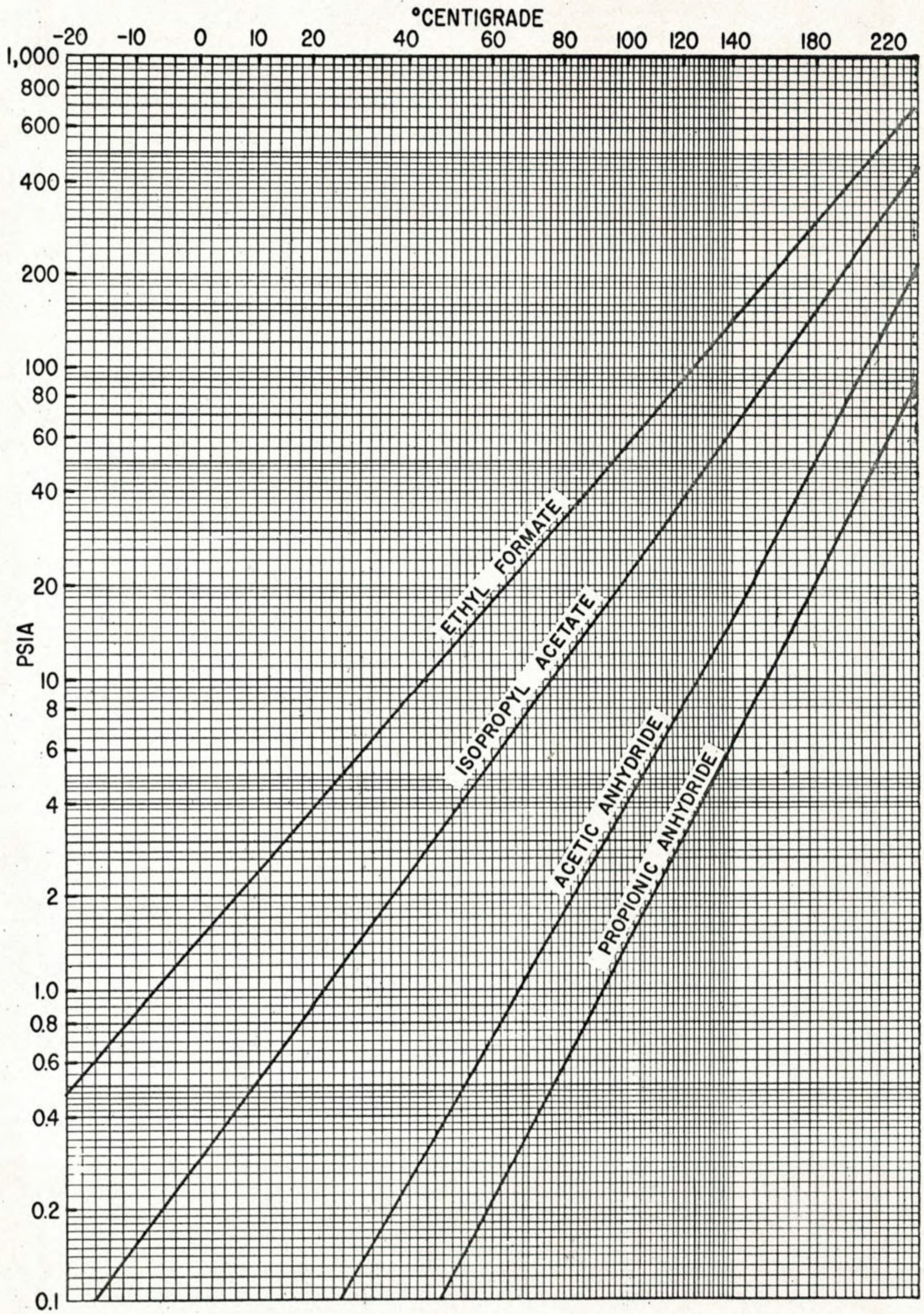

Fig. 31-1—Gives vapor pressure of esters from −20° C to +240° C.

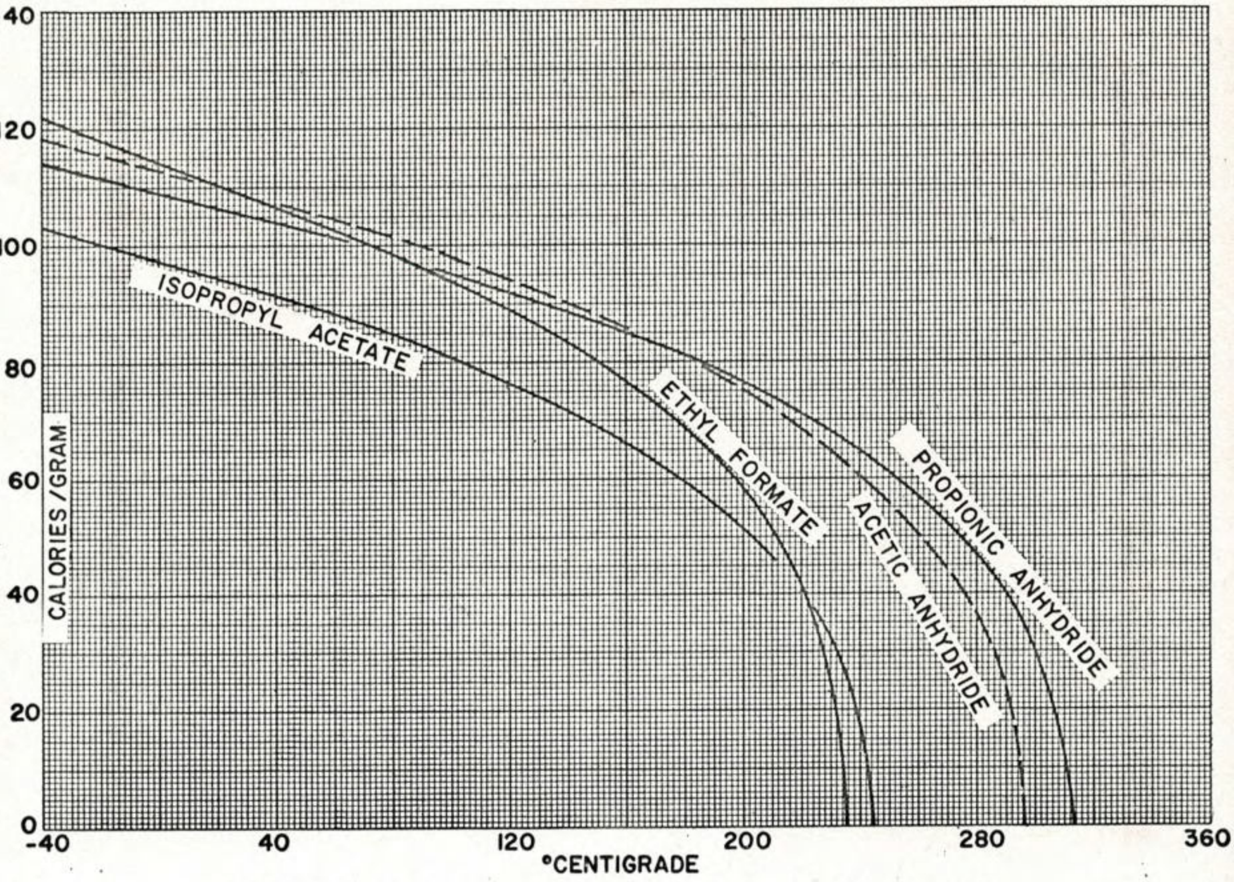

Fig. 31-2—Gives heat of vaporization of esters from —40° Cto + 310° C.

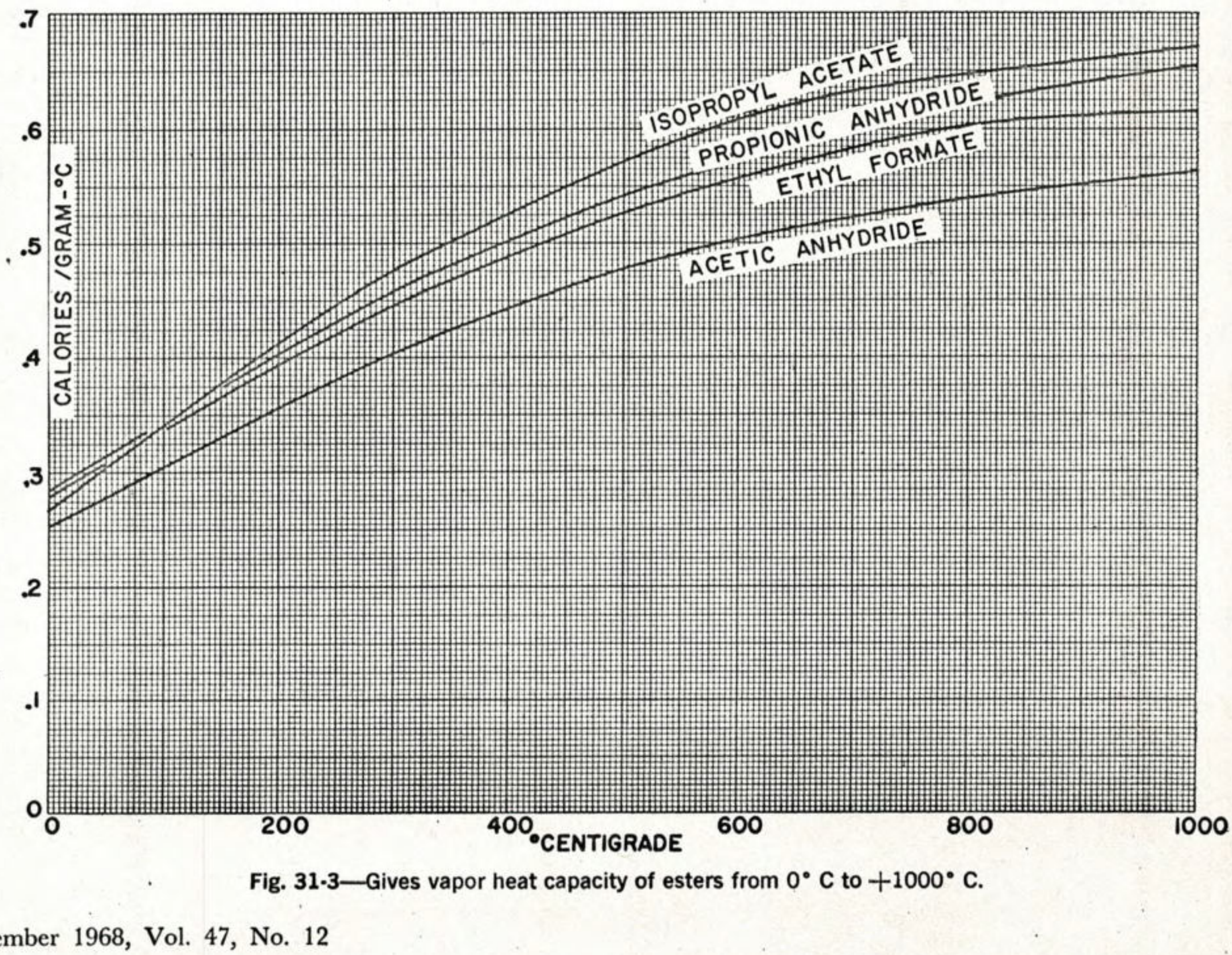

Fig. 31-3—Gives vapor heat capacity of esters from 0° C to +1000° C.

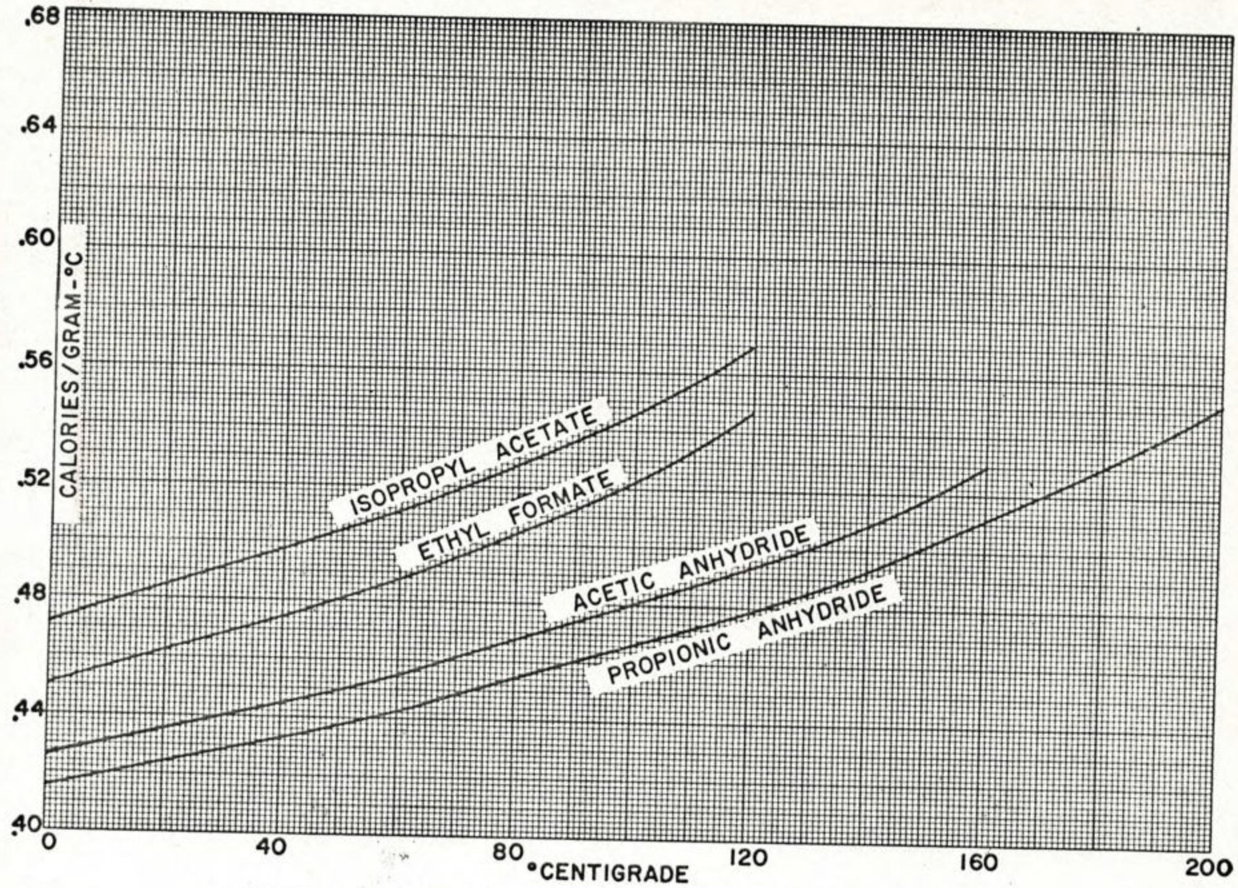

Fig. 31-4—Gives liquid heat capacity of esters from 0° C to +200° C.

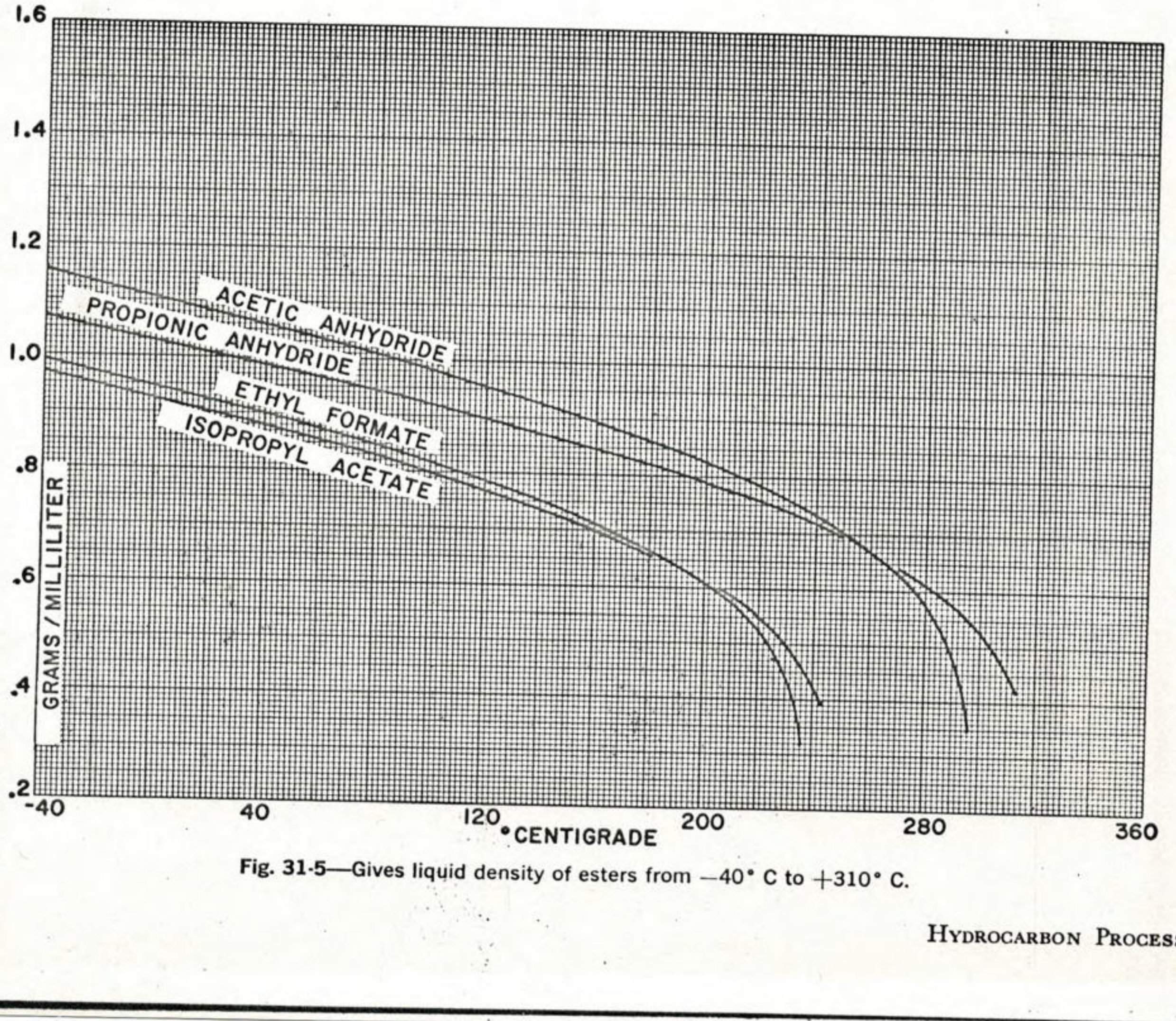

Fig. 31-5—Gives liquid density of esters from −40° C to +310° C.

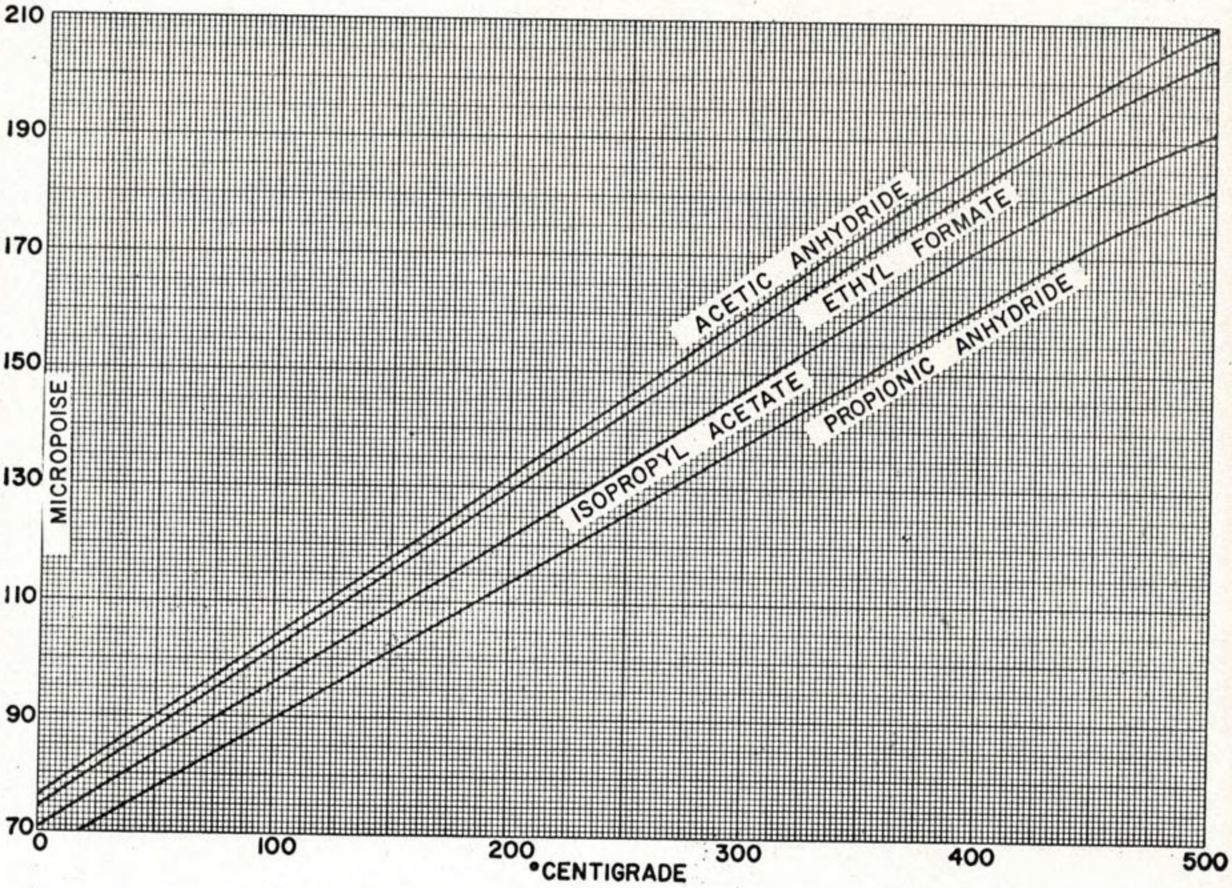

Fig. 31-6—Gives vapor viscosity of esters from 0° C to +500° C.

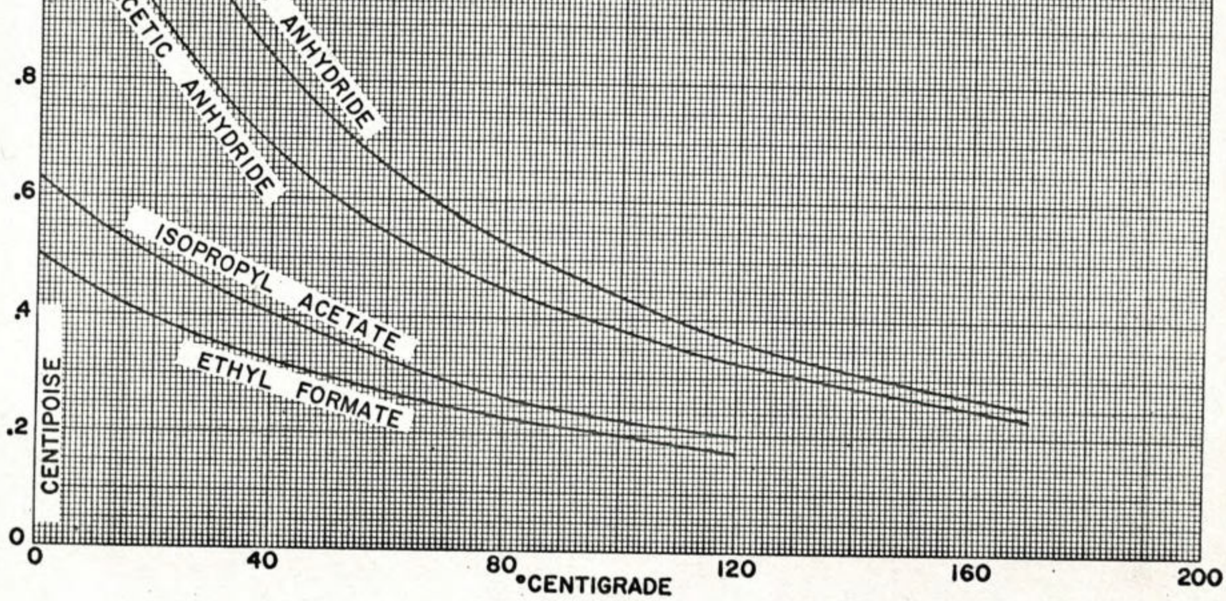

Fig. 31-7—Gives liquid viscosity of esters from 0° C to +180° C.

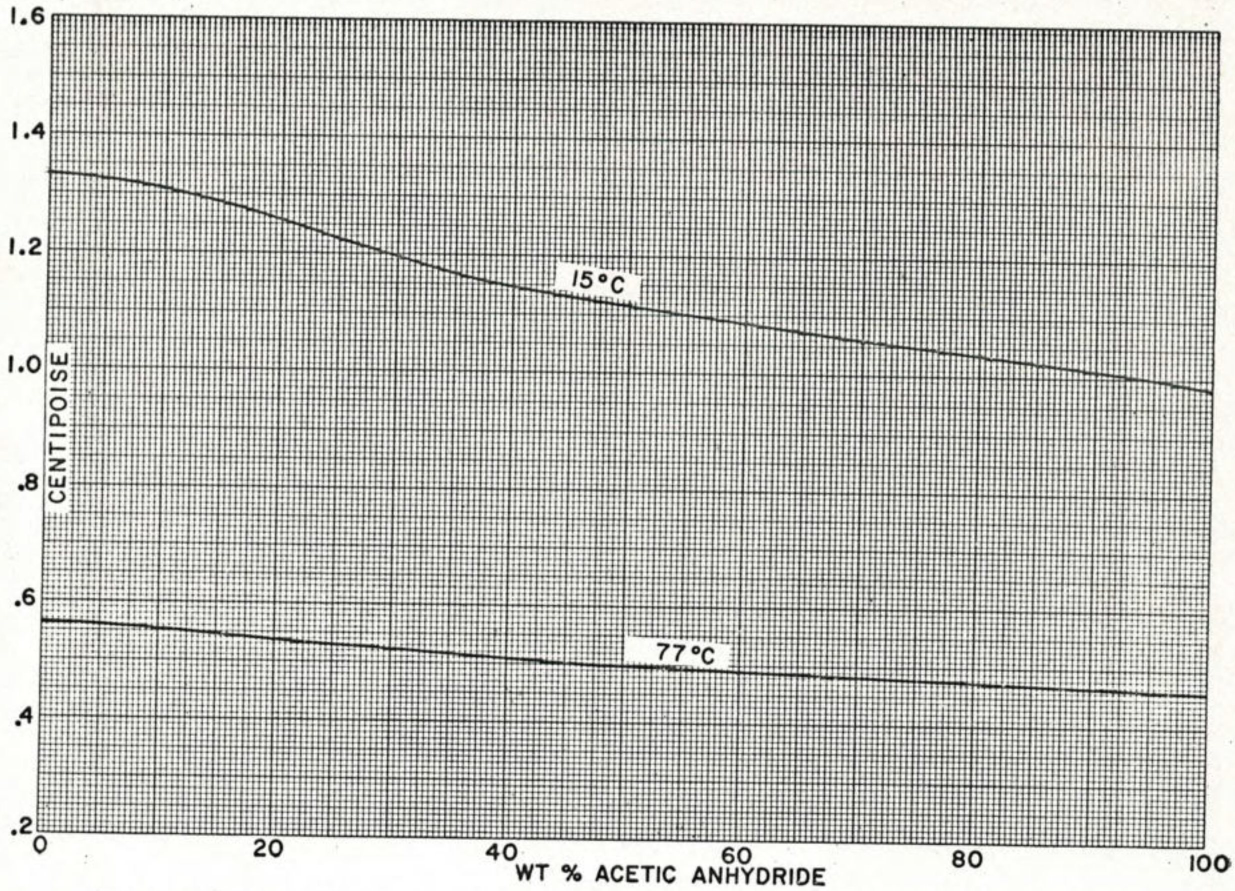

Fig. 31-8—Gives liquid viscosity of acetic acid-acetic anhydride mixtures at 15° C and 77° C.

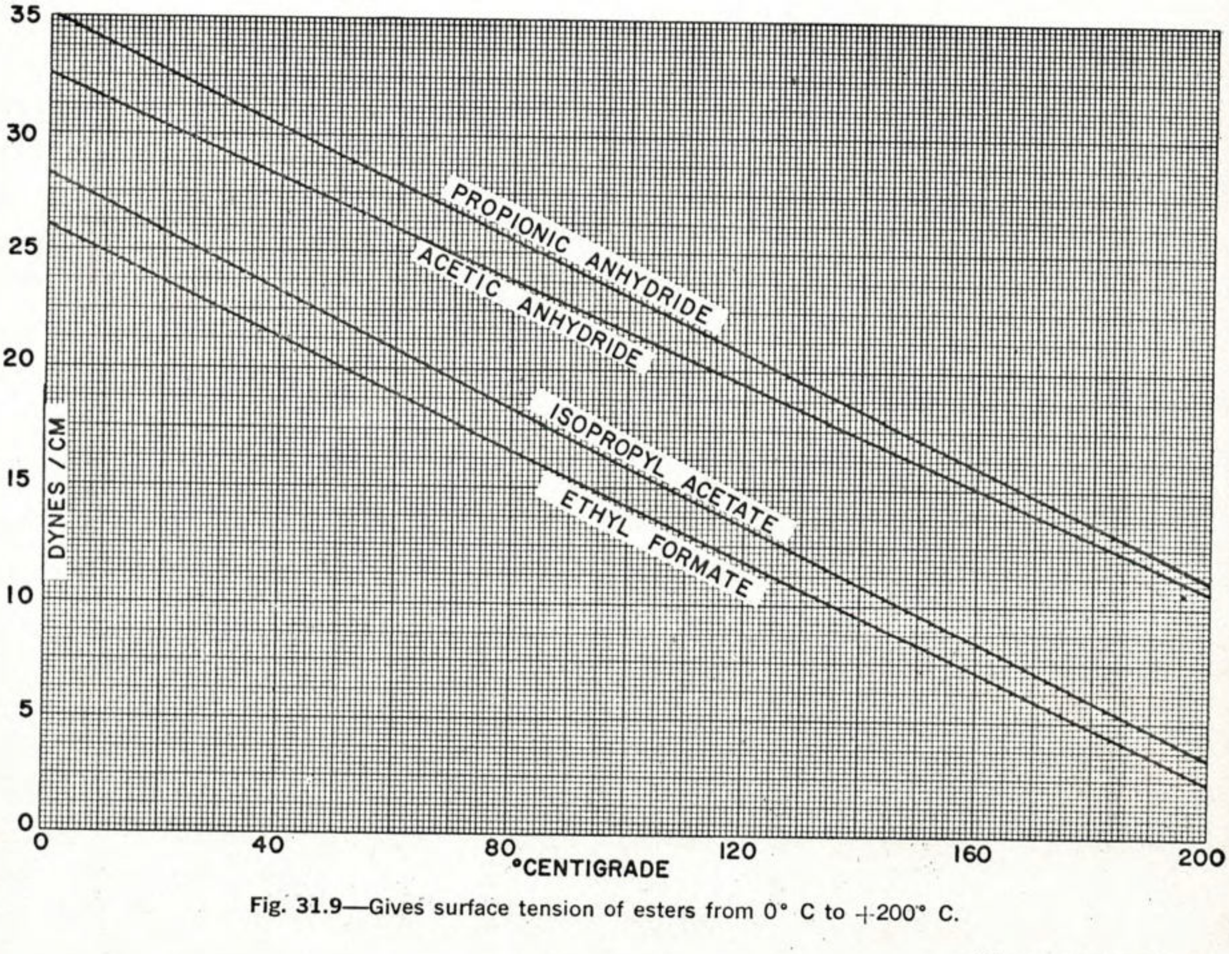

Fig. 31.9—Gives surface tension of esters from 0° C to +200° C.

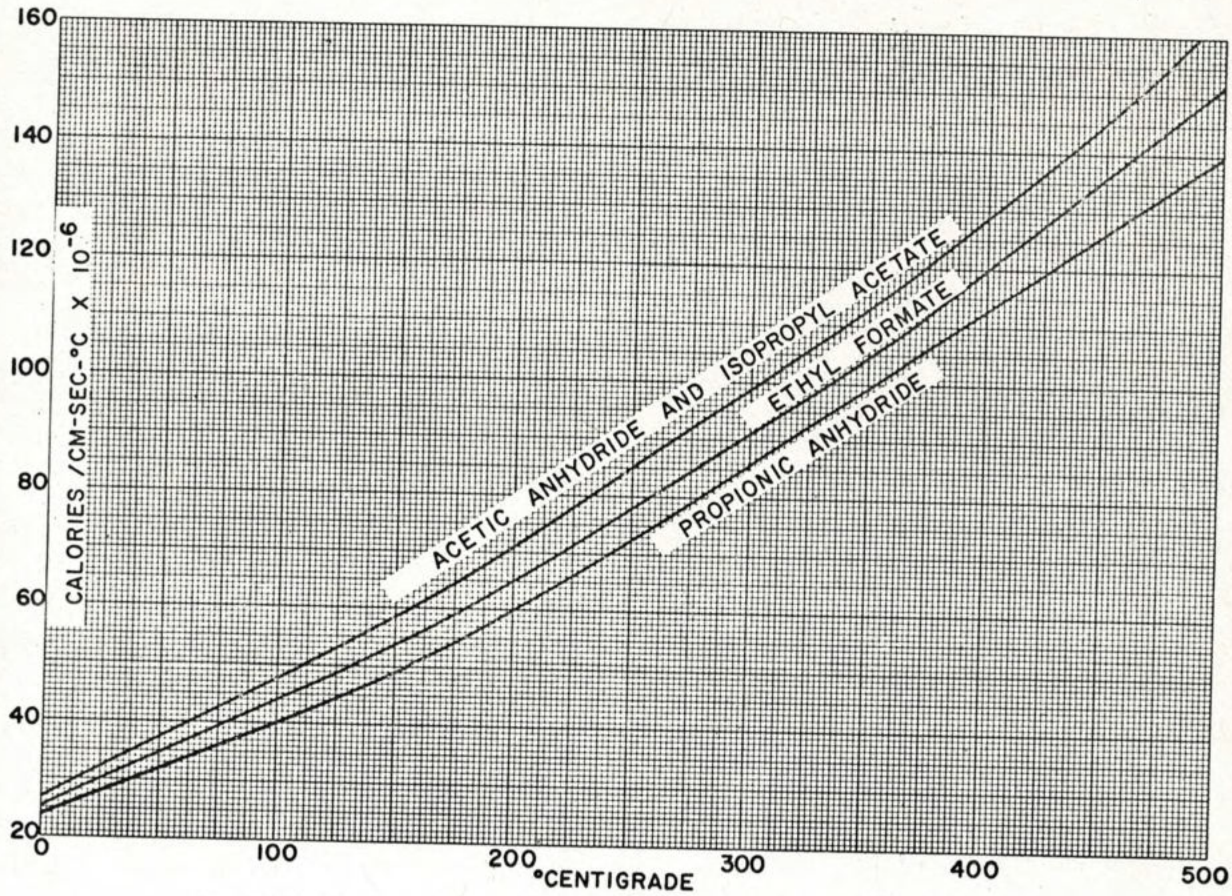

Fig. 31-10—Gives vapor thermal conductivity of esters from 0° C to +500° C.

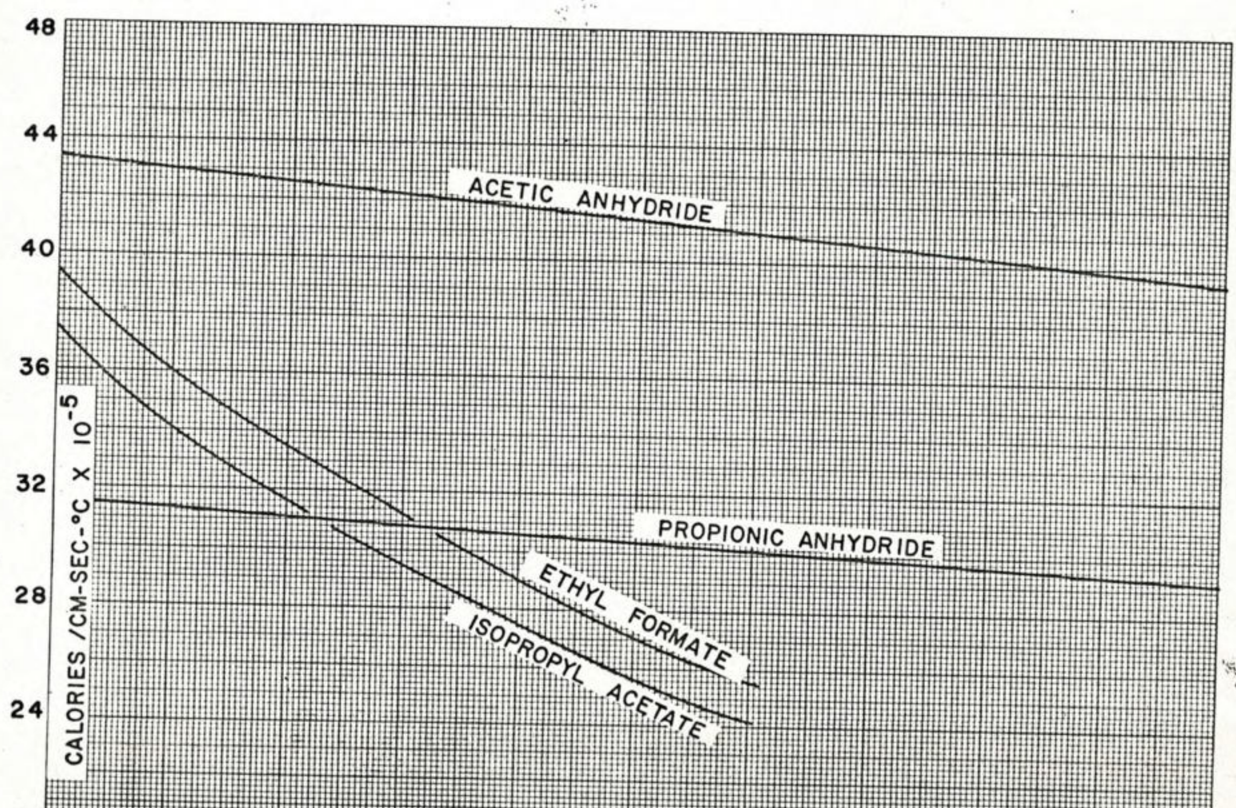

Fig. 31-11—Gives liquid thermal conductivity of esters from 0° C to +200° C.

pressures above the boiling point were estimated by a previously described method.[4]

Heat of Vaporization. The heats of vaporization have been measured at the boiling point for all but isopropyl acetate.[3,5] The heat of vaporization of isopropyl acetate was calculated from vapor pressure data at the boiling point by Giacalone's method.[3] The error should be only a few percent. Kharbanda's nomograph was used to extend the data to the critical temperature.[6]

Heat Capacity. The vapor heat capacities were calculated by the method proposed by Rihani and Doraiswamy, with a probable error of 1-2 percent.[7]

The liquid heat capacities have been determined at 20° C for acetic anhydride and propionic anhydride.[5] The heat capacities at 20° C were estimated for ethyl formate and isopropyl acetate by the method of Johnson and Huang.[3] The data were extended by the equation: heat capacity times density equals a constant. The probable error is about 5 percent.

Density. Timmermans reports the density of ethyl formate from 0° C to the critical point.[2] The 0-50° C densities are available from the literature for the other compounds.[2,5] The densities of all four compounds were calculated by Lydersen's method.[3] Compared to experimental data, eight points gave an average error of 0.4 percent.

Viscosity. The vapor viscosities were calculated by the method of Wilkes and Bromley, with a probable error of 2-5 percent.[8]

The liquid viscosities of acetic anhydride and propionic anhydride have been reported in the literature from 0-160° C.[9] The limited data on ethyl formate and isopropyl acetate[9] have been extended by using the method of Thomas to calculate the viscosities at other temperatures.[3] This method gives excellent results for esters, with the error normally less than 5 percent.

Acetic anhydride is often encountered as a solution in acetic acid. Fig. 31-8 shows the effect of acetic anhydride concentration on the liquid viscosity at 15° C and 77° C.[9]

Surface Tension. Data are available from 0° C to the critical point for ethyl formate;[9] for acetic anhydride from 0° C to 140° C;[5, 9, 10] and at room temperature for propionic anhydride.[11] Sugden's method has been used to calculate the surface tensions at other temperatures.[12]

Thermal Conductivity. The vapor and liquid thermal conductivities have been estimated by methods described in previous articles.[13,14]

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Part 32—Cyclic Ethers

Part 33—Methylamines

Part 34—Ethylamines

will appear in coming issues.

Earlier parts of this series included:

- **Part 25—C_1-C_4 Acids**
- **Part 26—Miscellaneous Aldehydes**
- **Part 27—Ketones**
- **Part 28—Ethers**
- **Part 29—Acetates**
- **Part 30—Acrylates.**