Physical Properties of Hydrocarbons

PART 26–Miscellaneous Aldehydes

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There are almost endless varieties of aldehyde compounds that can be produced. Many of them are products used in specialty applications or as intermediates in the production of other compounds. This article presents the physical properties of four typical compounds that have achieved commercial importance.

Phosgene was the most effective poisonous gas used in World War I. In recent years, it has become a major commercial product as a raw material in the production of isocyanates. Almost 300 million pounds were consumed in isocyanates in 1966. Another 50 million pounds were used in the production of polycarbonates and pesticides.

Chloral is used in the production of DDT and in medicines. Like phosgene, it is an extremely hazardous chemical. It is generally produced by the chlorination of ethyl alcohol, followed by reaction with sulfuric acid.

Acetyl chloride is so corrosive that it is often manufactured and used "in situ," especially as a catalyst for preparation of acetic acid. It is also used as an acetylating agent for producing specialty chemicals.

The use of acrolein as a raw material for the production of glycerine has boosted acrolein into major chemical status in the 1960's. High toxicity and a tendency to polymerize have limited the commercial uses of acrolein, but its availability from propylene via oxidation or condensation of acetaldehyde and formaldehyde makes it available at a price that should enable it to grow steadily as a raw material choice.

The high reactivity and extreme toxicity of these compounds have limited the amount of experimental work on physical properties. Consequently, estimation methods have been used extensively to provide data over a wide temperature range.

Critical Properties and Vapor Pressure. The critical properties of phosgene have been determined experimentally.[1, 2, 3] The method of Vowles[4] has been used to estimate the other critical temperatures with a probable error of less than 5°C, and the critical densities within 0.01 grams/milliliter. The critical pressures were estimated by the method of Lyderson.[4]

Stull presents vapor pressure data on phosgene up to the critical point.[1] Data up to the boiling point only are available for the other three compounds.[1,5,6] The method described in previous articles has been used to calculate the vapor pressure of these compounds up to the critical point.[7] The method gave an average error of 1.4 percent when compared to experimental data for phosgene.

Heat of Vaporization. O'Hara and Fahien[8] have calculated the heat of vaporization of phosgene up to its critical point, using vapor pressure data. The heat of vaporization has been measured at the boiling point for phosgene[9] and acetyl chloride.[10] The method of Riedel[4] has been used to estimate the heat of vaporization of chloral and acrolein at their boiling points. The boiling point data have been extrapolated over a wide temperature range by Kharbanda's nomograph.[11]

Heat Capacity. The vapor heat capacity of phosgene is available in the literature.[12, 13] The method of Rihani

TABLE 26-1—Physical Properties of Miscellaneous Aldehydes

	Boiling Point °C	Melting Point °C	Molecular Weight	Critical Properties T_c °C	P_c PSIA	d_c g/ml
Phosgene	8.3	−128	98.92	181.7	821	0.520
Chloral	97.6	− 57	147.40	303*	646*	0.505*
Acetyl Chloride	50.8	−113	78.50	246*	845*	0.394*
Acrolein	52.5	− 88	56.06	254*	737*	0.296*

* Estimated.

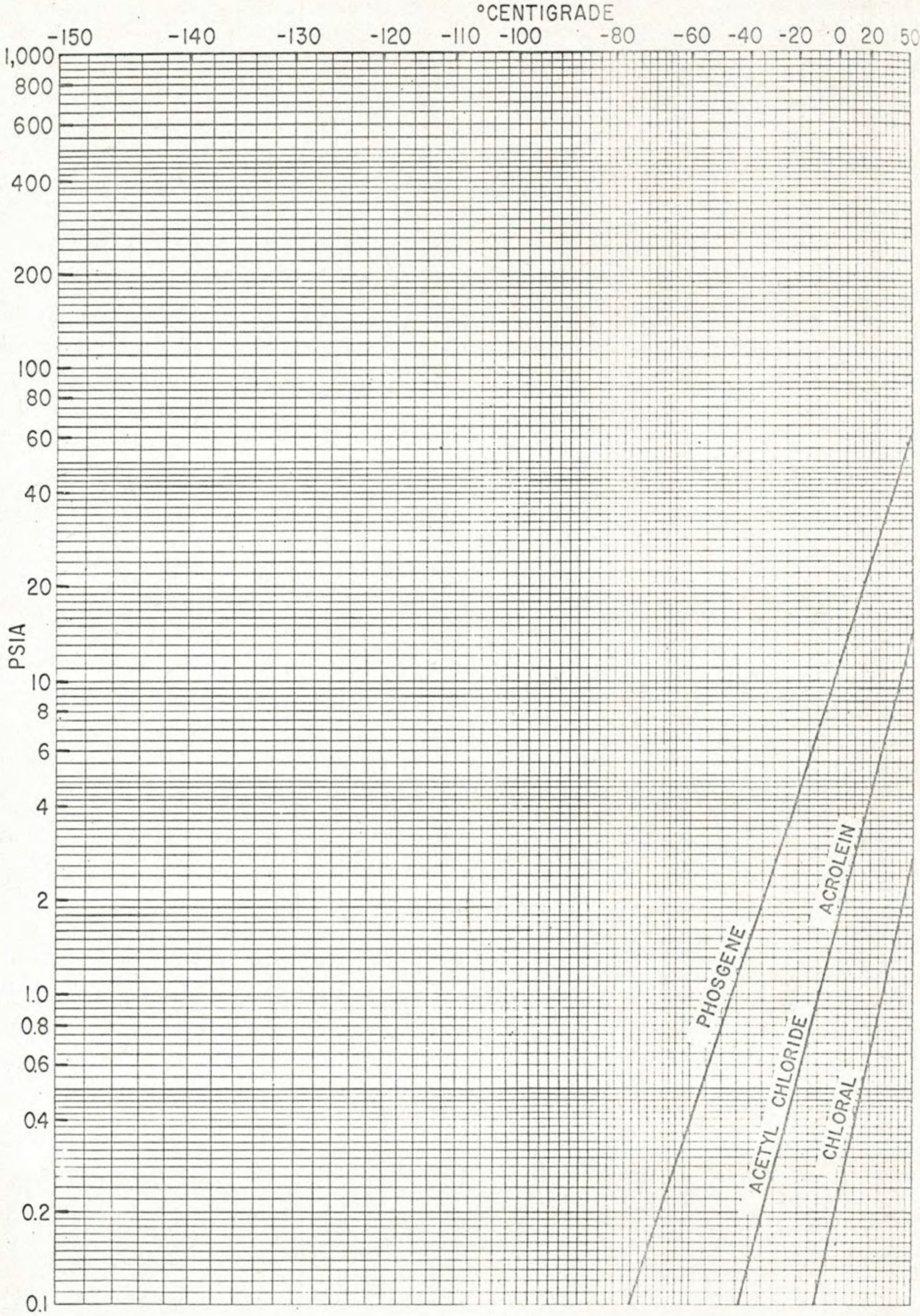

Fig. 26-1—Gives vapor pressure of miscellaneous aldehydes from −80° C to +50° C.

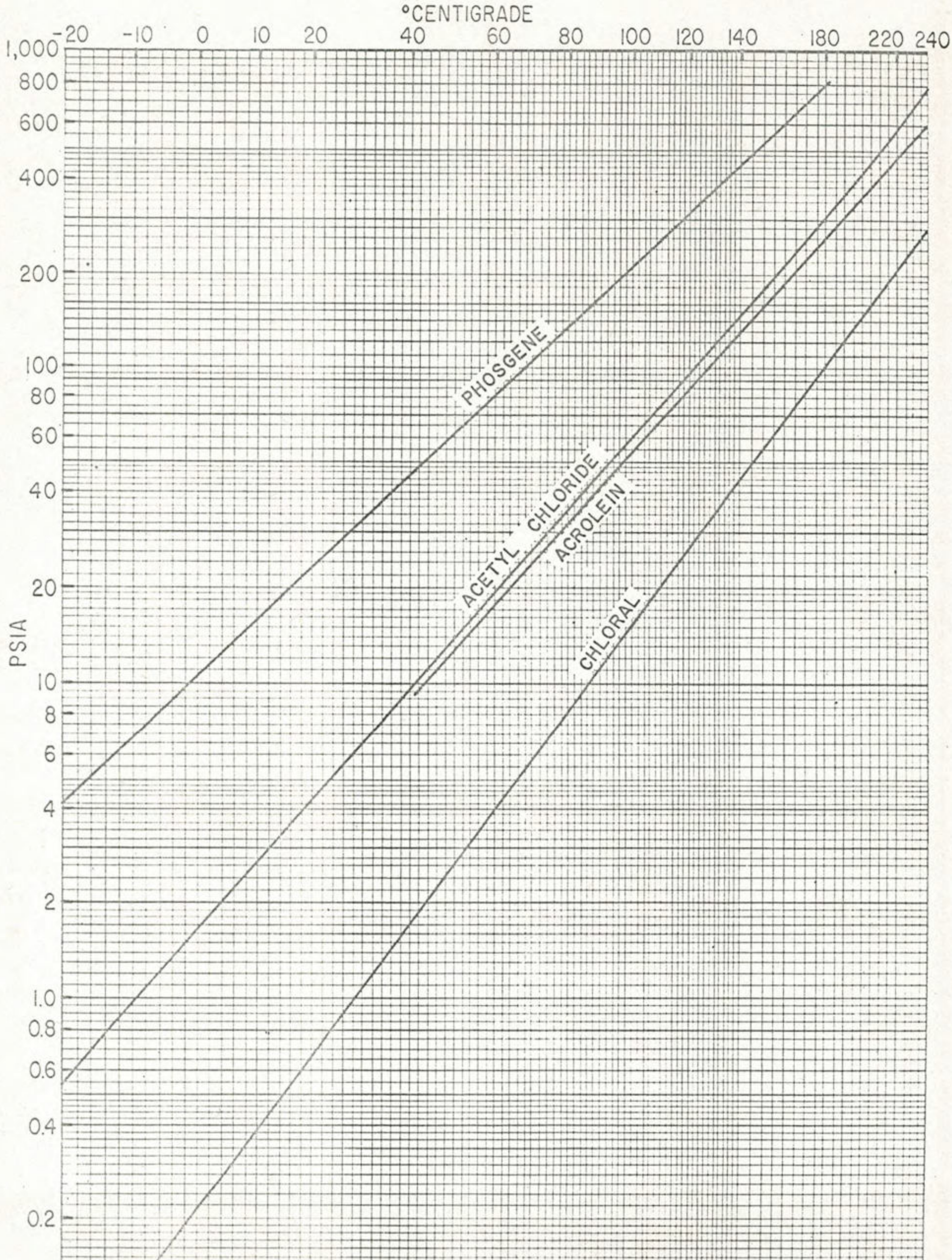

Fig. 26-2—Gives vapor pressure of miscellaneous aldehydes from −20° C to +240° C.

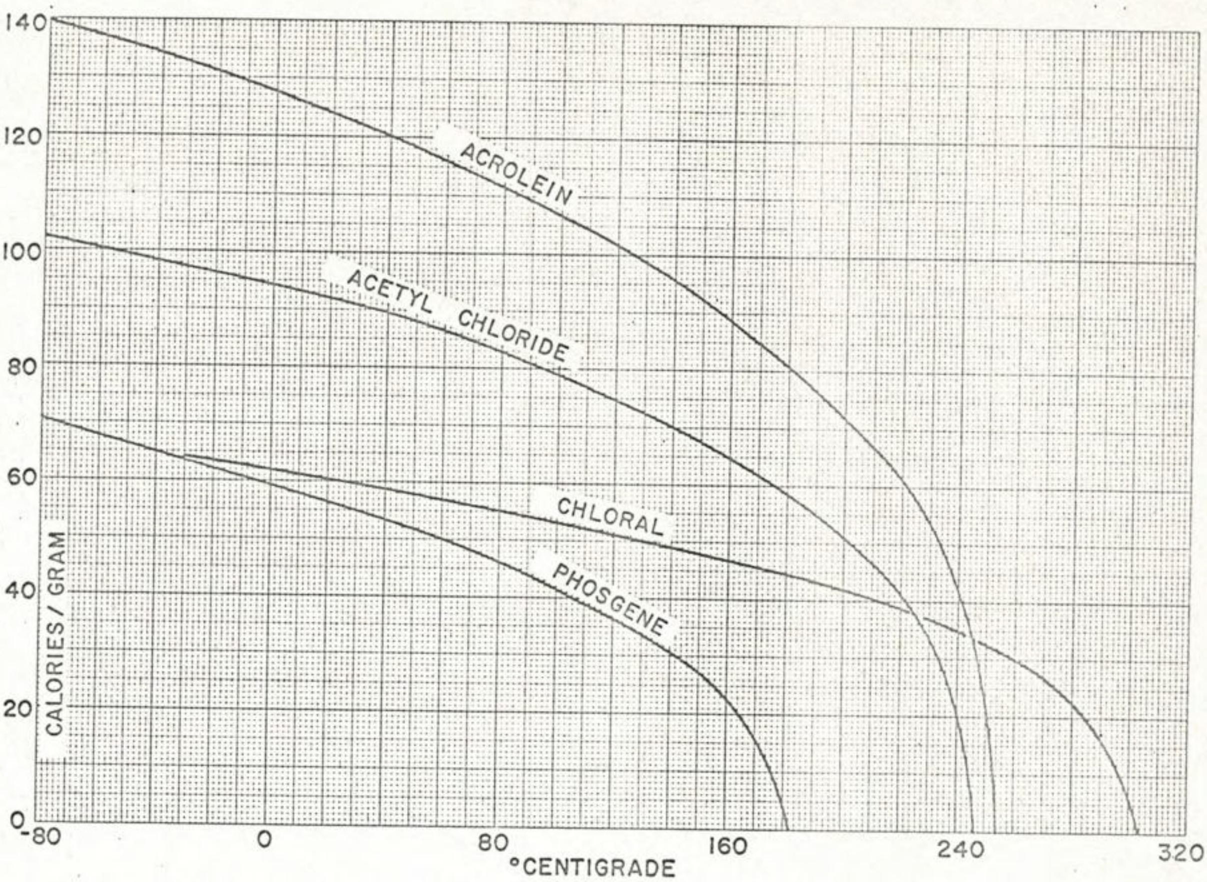

Fig. 26-3—Gives heat vaporization of miscellaneous aldehydes from −80° C to +290° C.

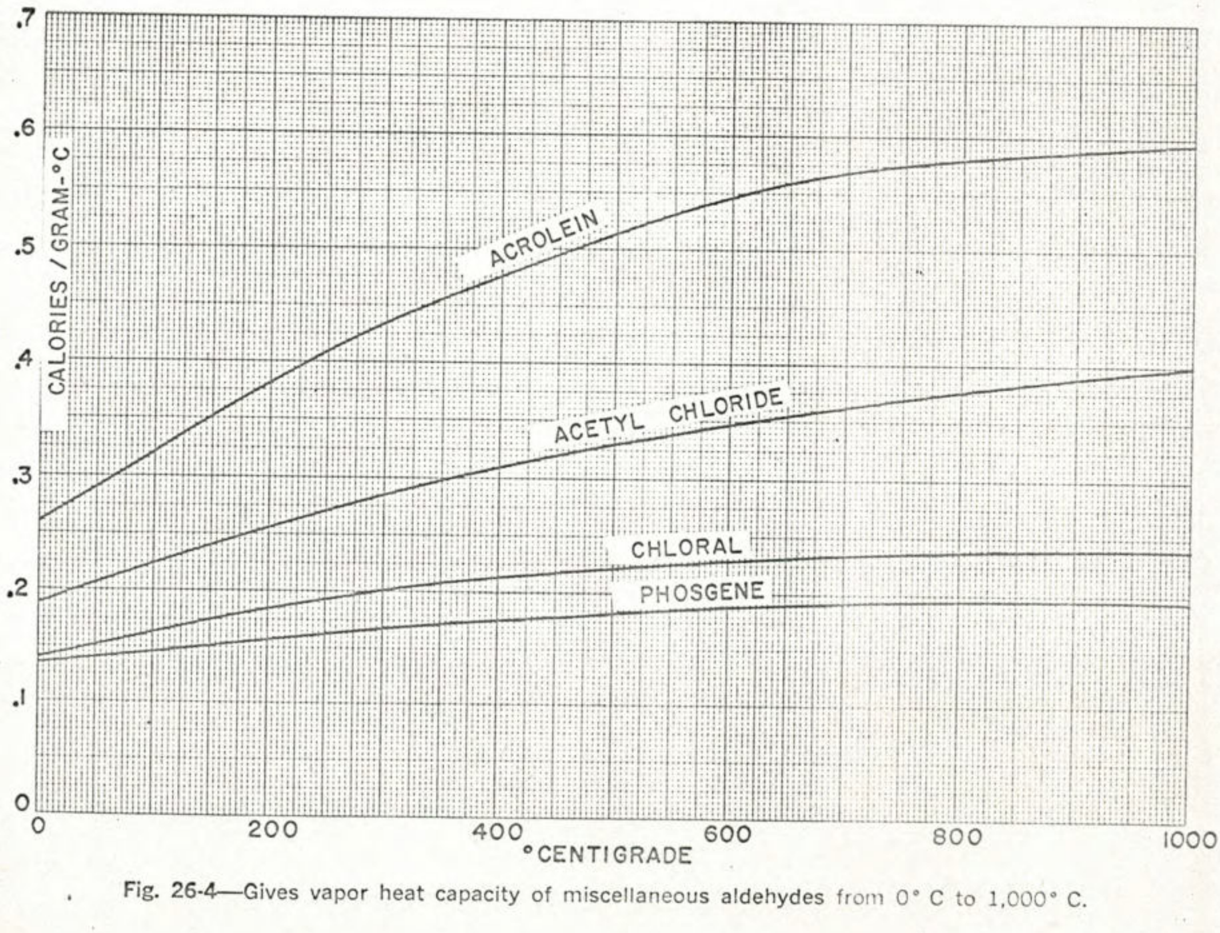

Fig. 26-4—Gives vapor heat capacity of miscellaneous aldehydes from 0° C to 1,000° C.

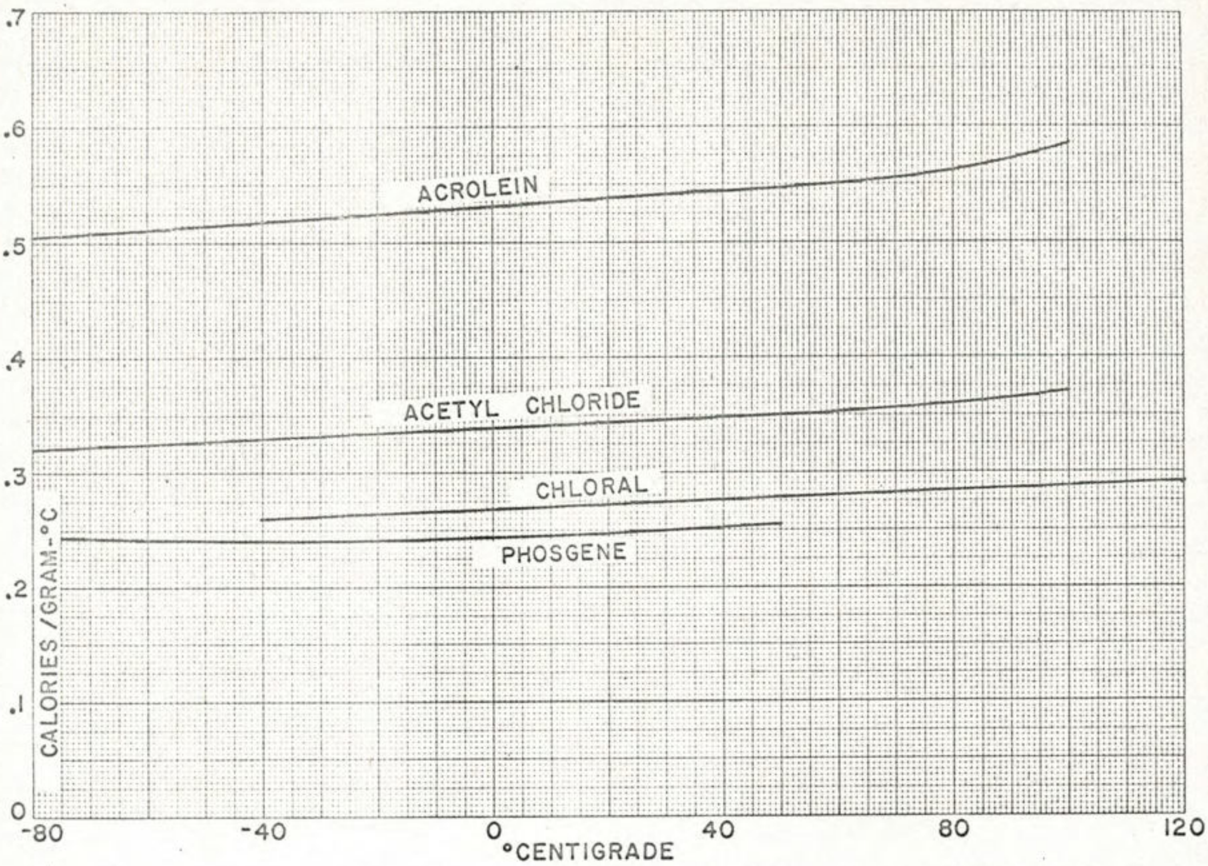

Fig. 26-5—Gives liquid heat capacity for miscellaneous aldehydes from −80° C to +100° C.

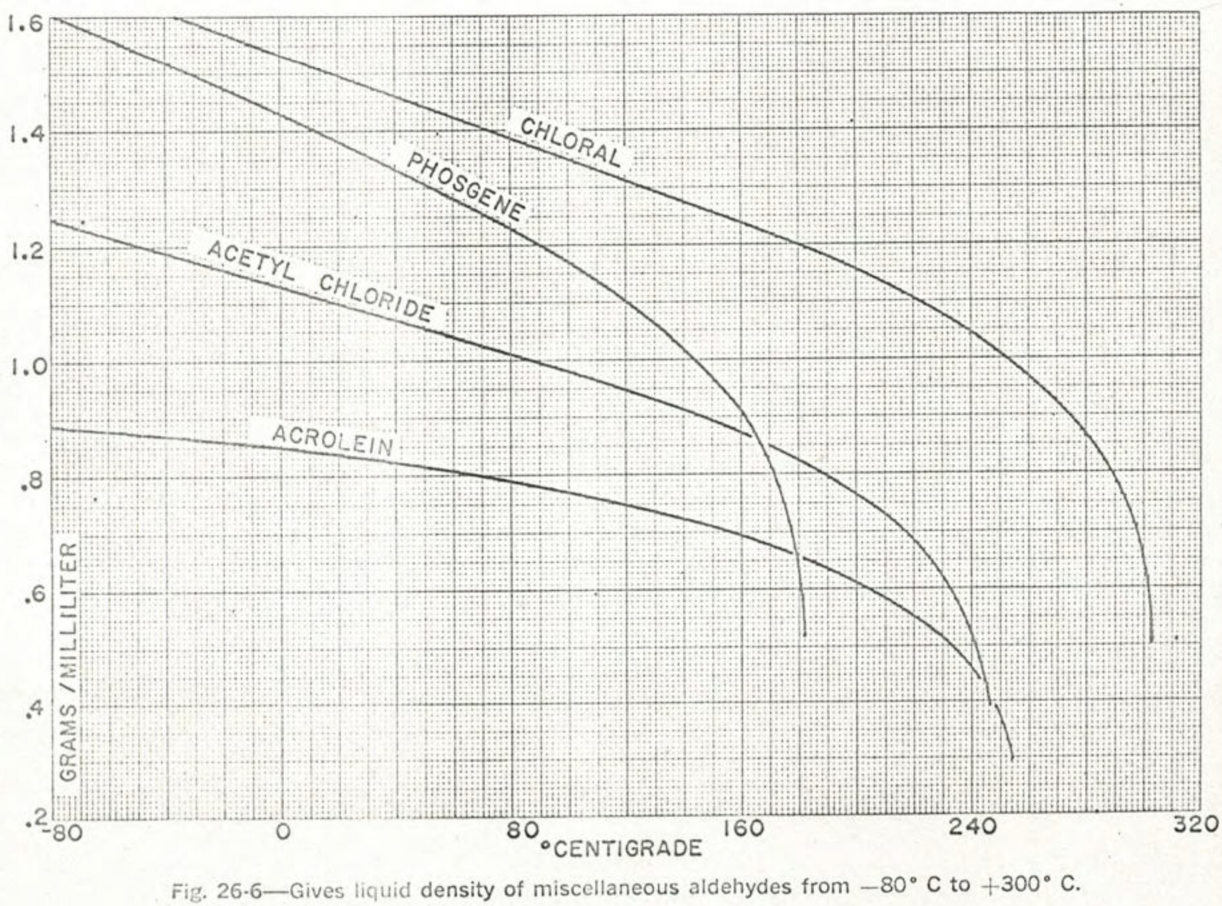

Fig. 26-6—Gives liquid density of miscellaneous aldehydes from −80° C to +300° C.

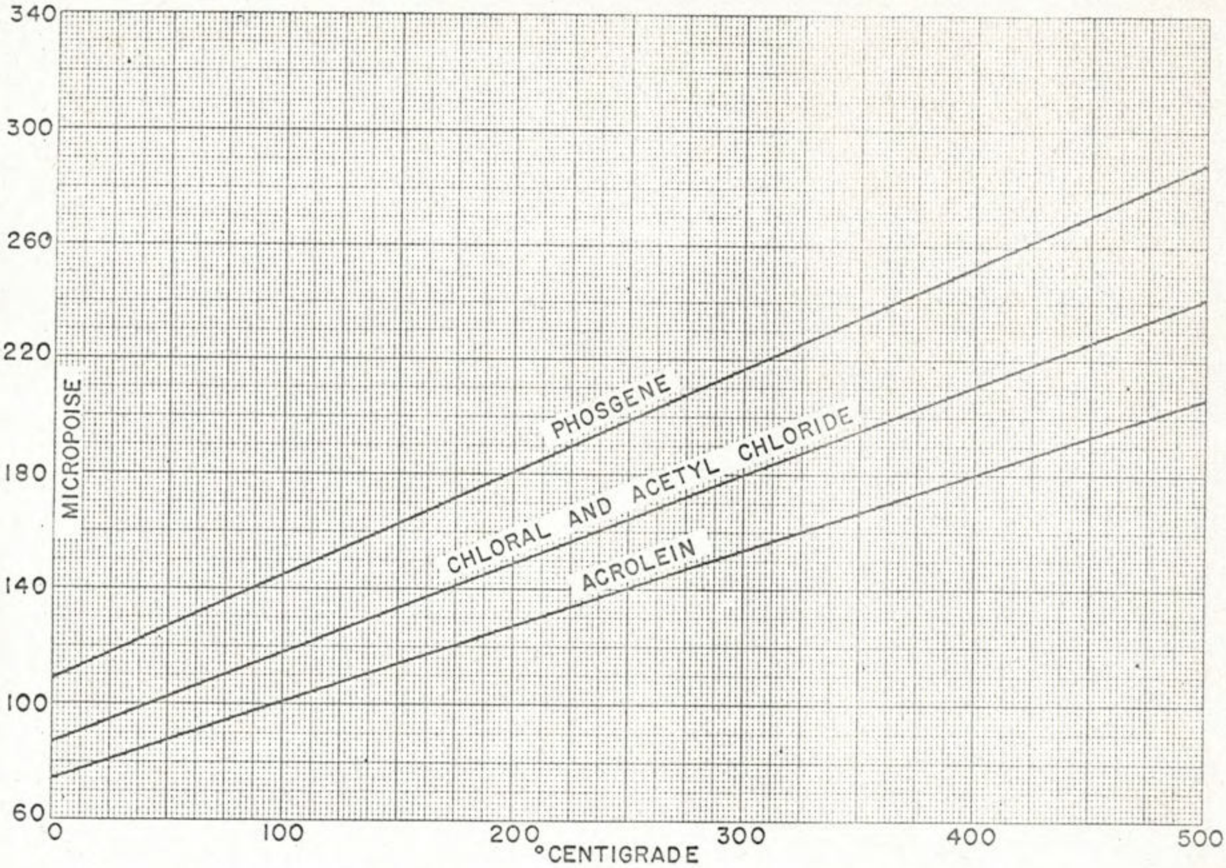

Fig. 26-7—Gives vapor viscosity of miscellaneous aldehydes from 0° C to +500° C.

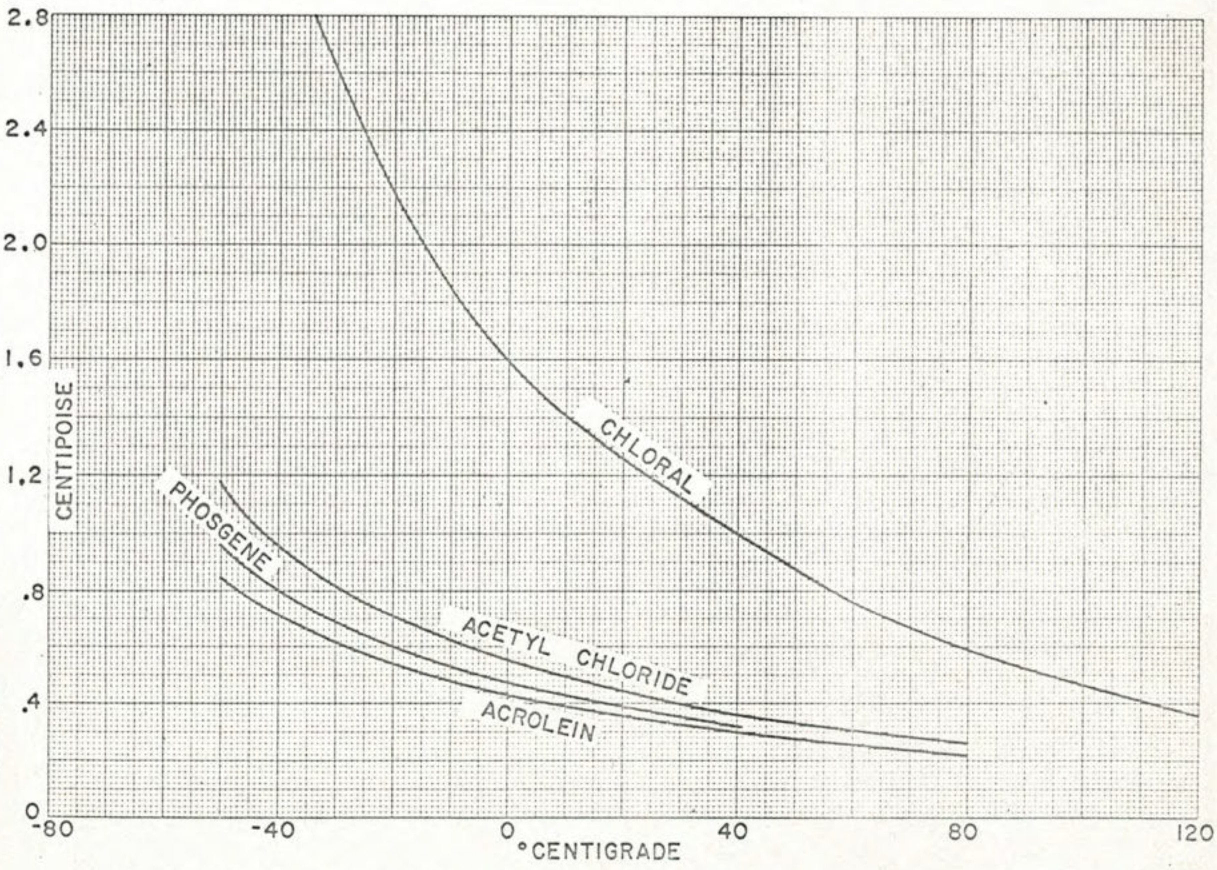

Fig. 26-8—Gives liquid viscosity of miscellaneous aldehydes from −80° C to +120° C.

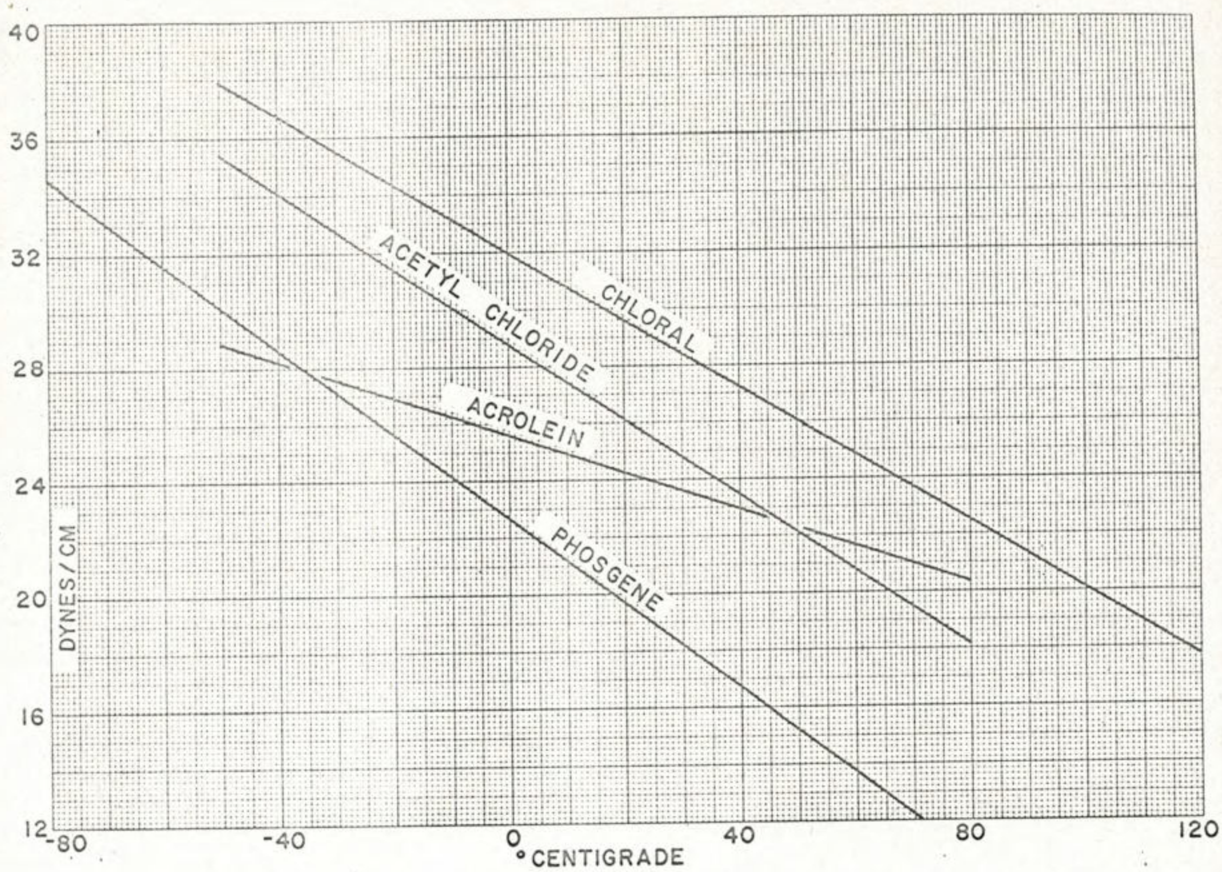

Fig. 26-9—Gives surface tension of miscellaneous aldehydes from −80° C to +120° C.

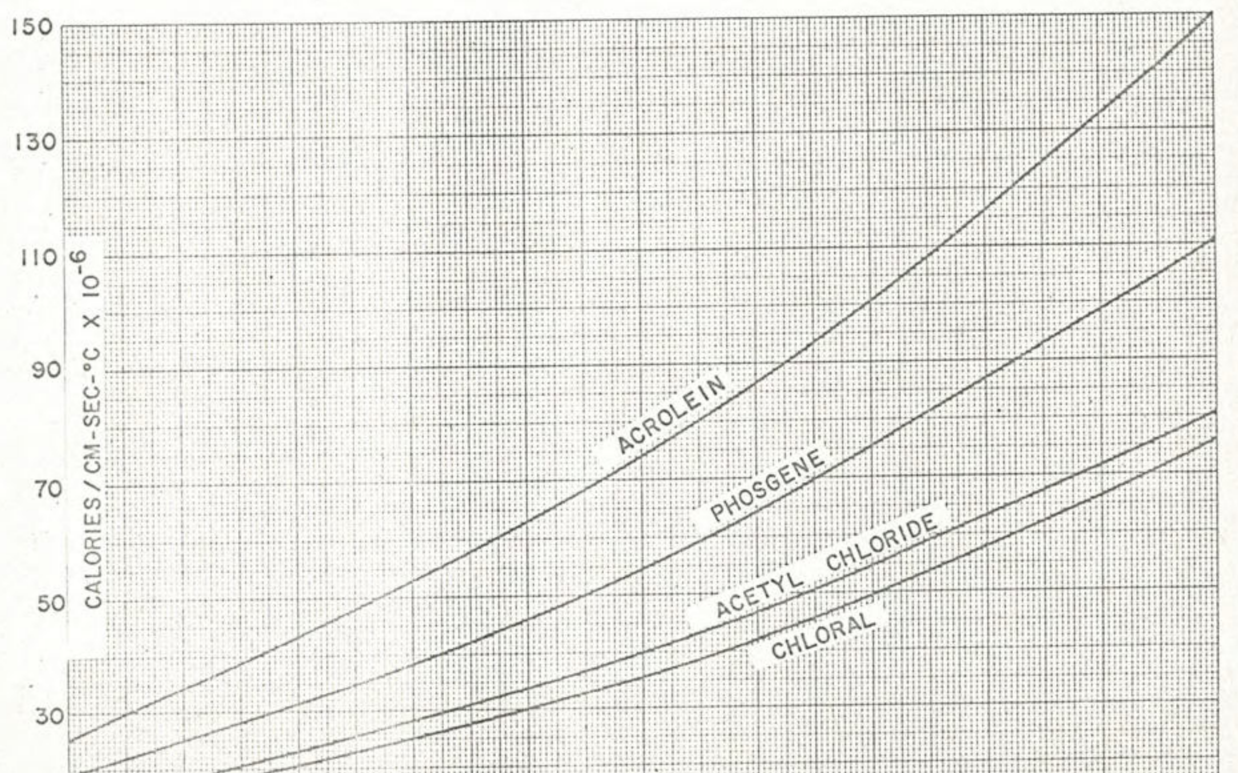

Fig. 26-10—Gives vapor thermal conductivity of miscellaneous aldehydes from 0° C to +500° C.

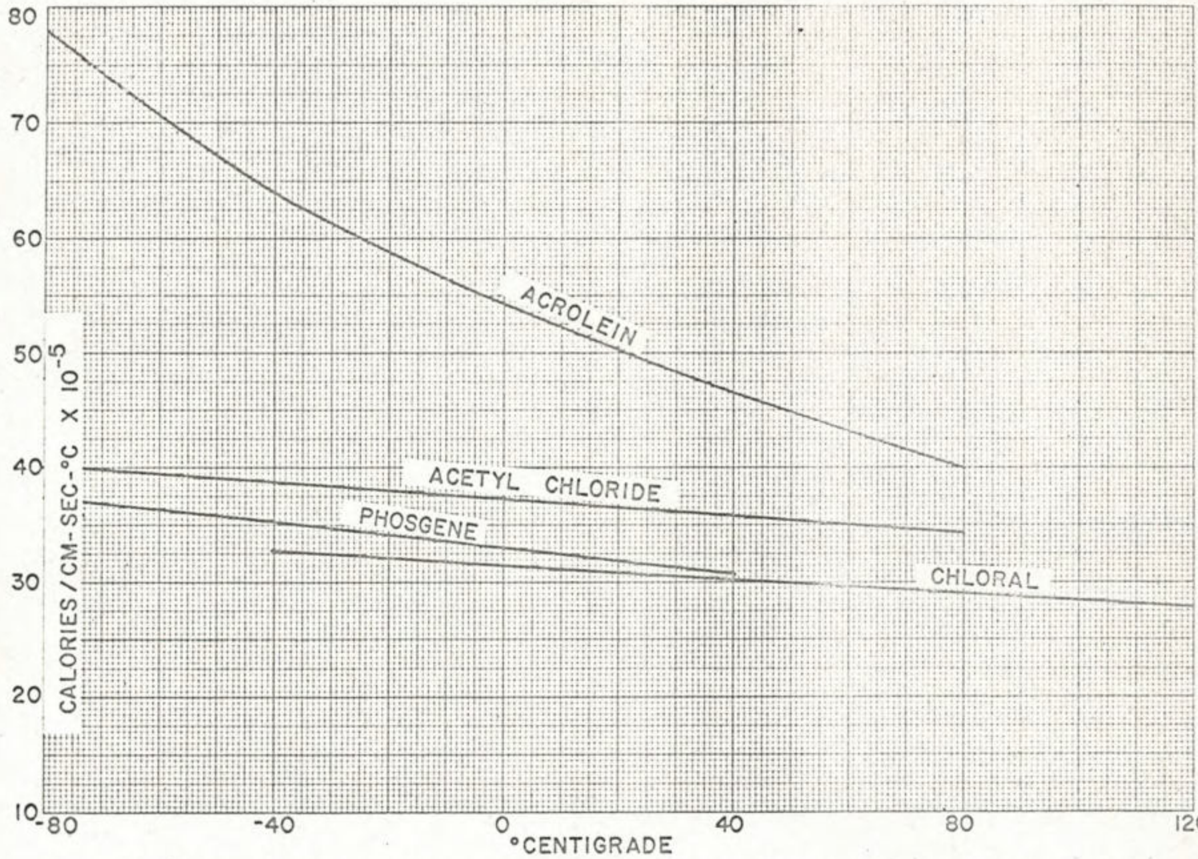

Fig. 26-11—Gives liquid thermal conductivity of miscellaneous aldehydes from −80° C to +120° C.

and Doraiswamy[14] has been used to calculate the heat capacity of the other three compounds, with a probable error of 3-5 percent.

The liquid heat capacity of phosgene has been measured up to its boiling point.[9,13] The only other data is acetyl chloride at 0°C.[6] Consequently, the heat capacity of chloral and acrolein at 20°C has been estimated from their molecular structure and extrapolated over the temperature range by the method discussed in previous articles. The probable error is 5-10 percent.

Density. The density of phosgene has been measured up to its critical point.[2] The room temperature densities of the other three compounds are reported in the literature.[6] The method of Lydersen, Greenkorn, and Hougen has been used to estimate the densities up to the critical temperature.[4] The error is normally 1-3 percent.

Viscosity. The vapor viscosities have been estimated by the method of Bromley and Wilkes.[15]

Only the liquid viscosity of chloral has been experimentally determined.[2] The viscosities of the other three compounds have been estimated by the method proposed by Thomas.[4] The error is probably 10-15 percent for these polar compounds.

Surface Tension. The surface tension of phosgene, chloral, and acetyl chloride have been measured from 0 - 50° C. Kharbanda's nomograph has been used to extend the data over a wider temperature range.[16] The method of Sugden was used to estimate the surface tension of acrolein.[17] The probable error is less than 5 percent.

Thermal Conductivity. The vapor and liquid thermal conductivities have been estimated by methods discussed in previous articles.[18, 19]

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Indexing Terms: Acetyl Chloride-9, Acrolein-9, Chloral-9, Computations-4, Heat-7, Liquid Phase-5, Phosgene-9, Physical Properties-7, Pressure-6, Properties/Characteristics-7, Temperature-6, Vapor hase-5.

Part 27, "Ketones," will appear in an early issue.