# Physical Properties of Hydrocarbons

## Part 4—$C_2$ to $C_4$ Diolefins
## Part 5—Chlorinated Methanes
## Part 6—Chlorinated Ethylenes

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THE REASON for the phenomenal growth of hydrocarbon producing capacity can be attributed to the wide variety of valuable derivatives that can be economically produced from them. With this article, we begin a presentation of the physical properties of some of the derivatives of the $C_1$ to $C_4$ hydrocarbons.

The chlorinated methanes (methyl chloride, methylene chloride, chloroform, and carbon tetrachloride) are produced mainly by high temperature chlorination of methane. A large amount of carbon tetrachloride is also produced as a byproduct of perchloroethylene production. In 1964, over one billion pounds of these four compounds were produced. Carbon tetrachloride, which accounted for half this output, and chloroform are used mainly as starting points for the production of fluorocarbons. The biggest market for methyl chloride is in silicones. Methylene chloride is used largely in paint removers and degreasing formulations. With the large amount of chlorine required in the production of these compounds, it is not surprising that the five major producers —Allied Chemical, Dow Chemical, Diamond Alkali, Frontier, and Stauffer—are all basic in chlorine production.

Because the chlorinated methanes have been major products for many years, their physical properties have been studied fairly thoroughly. A number of books are good starting places for data.[1, 2, 3, 4, 5, 6]

**Vapor Pressure.** The vapor pressures of all four chlorinated methanes have been accurately determined over a wide range. The best single source is the data of Stull.[7] Supplementary data is also available in the aforementioned handbooks, the Matheson gas data book,[8] and an article by McGovern.[9]

**Heat of Vaporization.** The heat of vaporization is presented over a fairly wide temperature range in one handbook[3] for all four compounds. The data agree closely with data available from other sources, and appear to be very reliable. The data for methylene chloride above 160°C and chloroform above 120°C were obtained by using the Watson method:

$$\frac{H_V}{H_{V_1}} = \left(\frac{1 - Tr}{T - Tr_1}\right)^{0.38}$$

where

$H_V$ = heat of vaporization
and
$Tr$ = reduced temperature

Comparisons with experimental data indicate the error is less than 2 percent by this method for these compounds.

**Heat Capacity.** The vapor heat capacities have been taken from Kobe's excellent compilation.[10] For the liquid

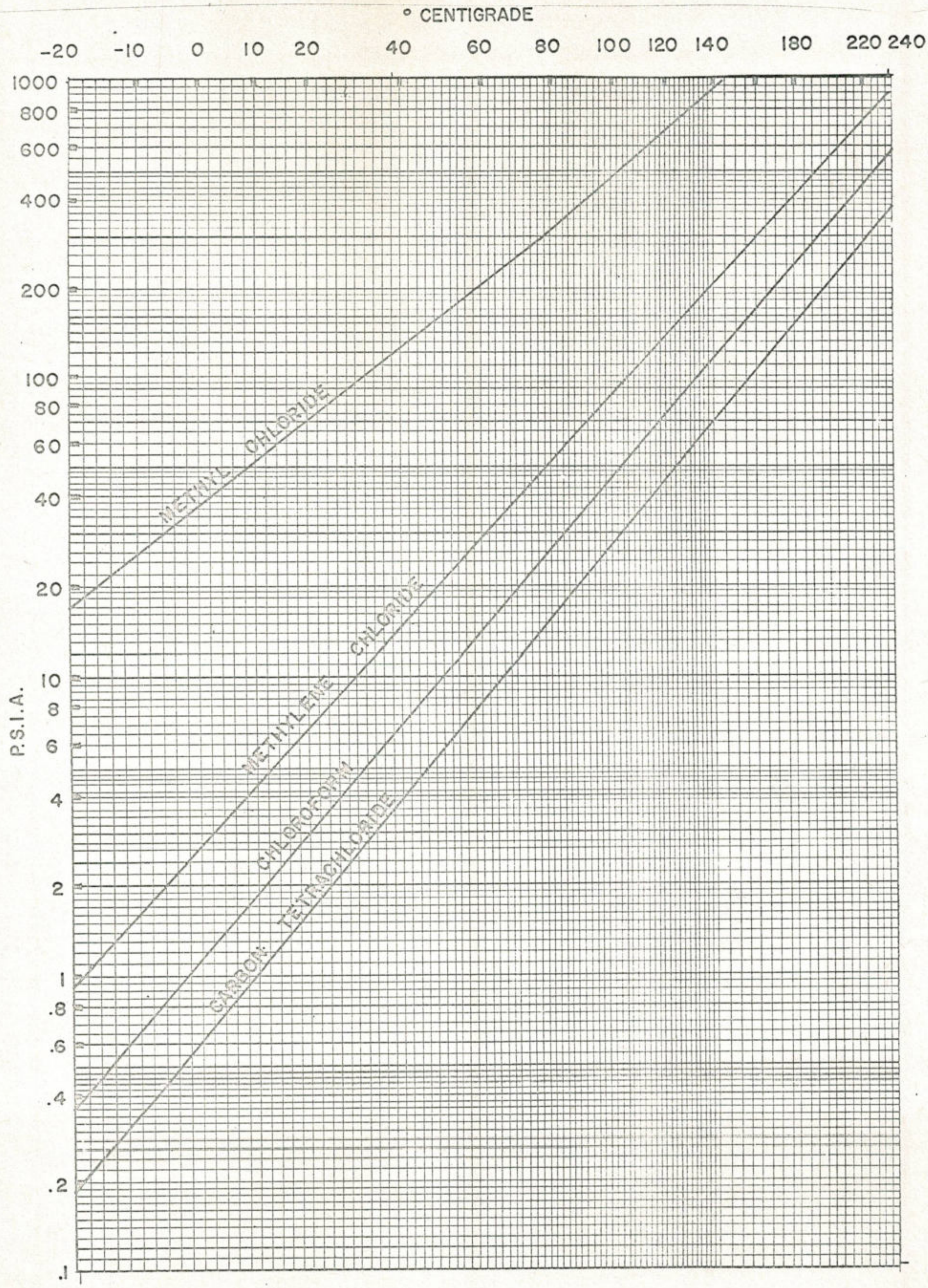


Fig. 5-1—Gives vapor pressure over a range of −20° C to +240° C.

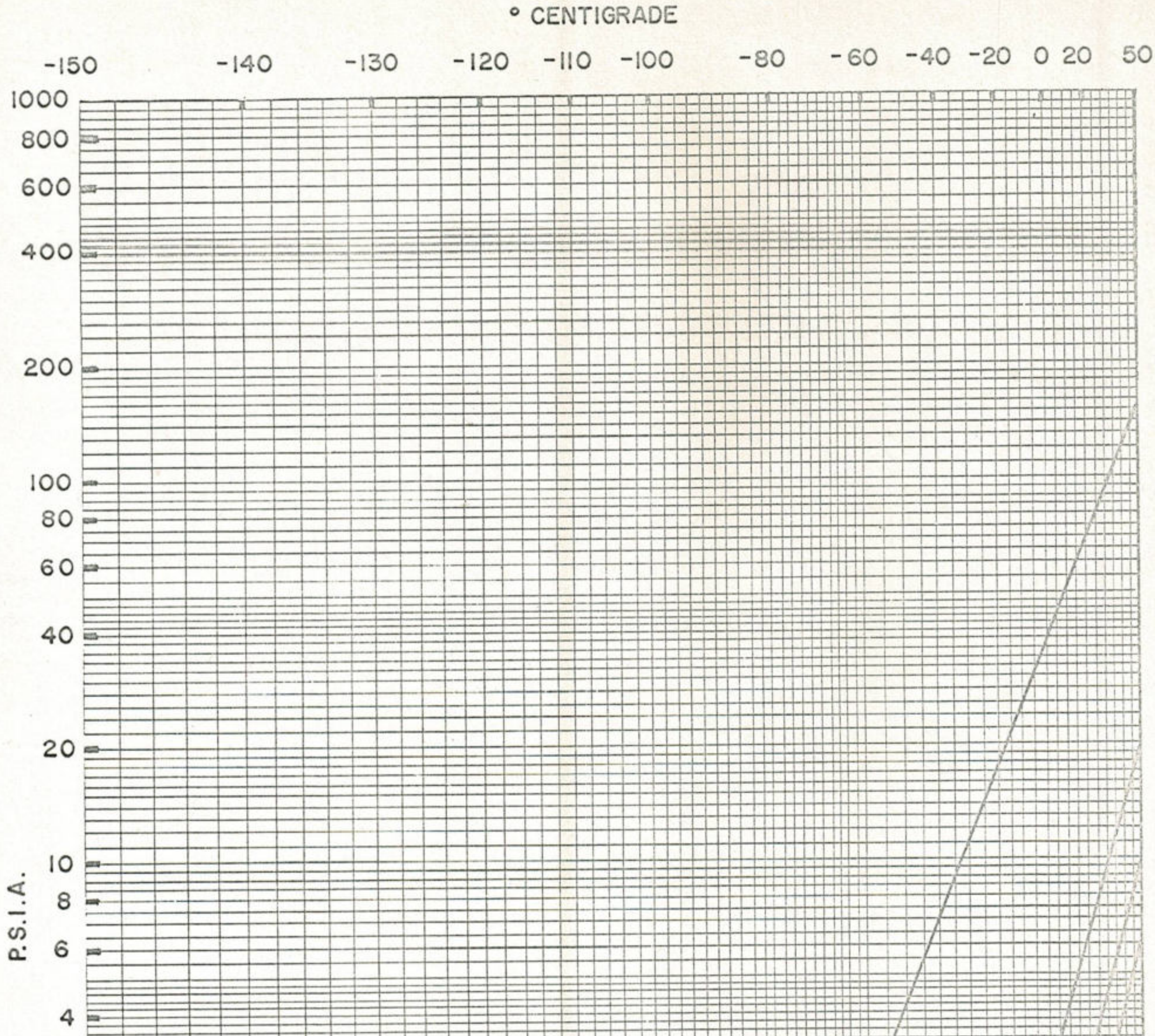


Fig. 5-2—Gives vapor pressure over a range of —100° C to +50° C.

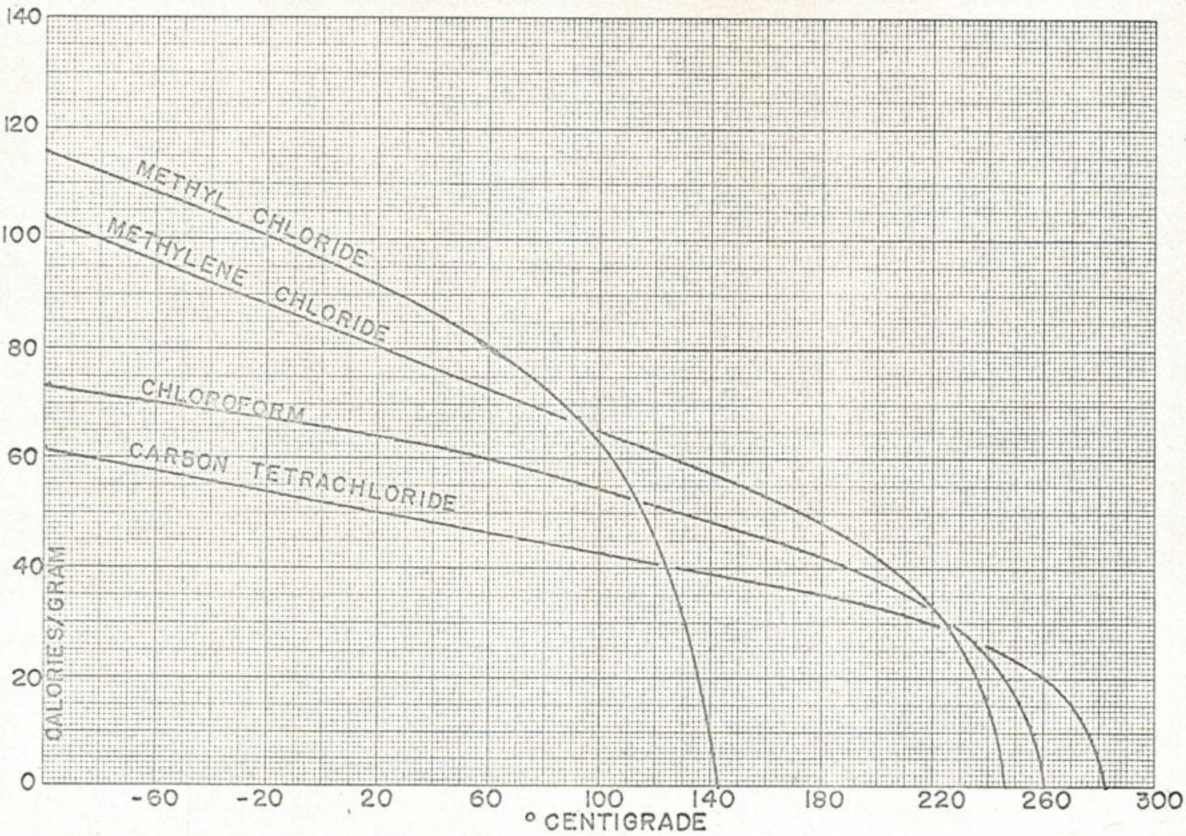


Fig. 5-3—Gives heat of vaporization over a range of −60° C to +280° C.

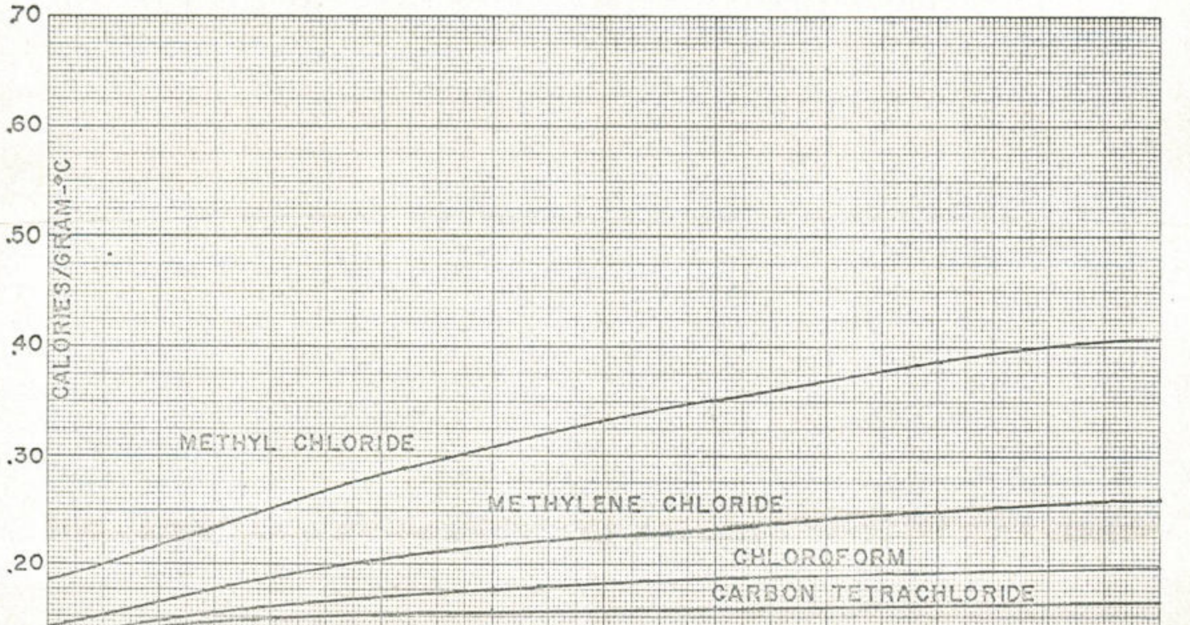


Fig. 5-4—Gives vapor heat capacity over a range of 0° C to +1,000° C.

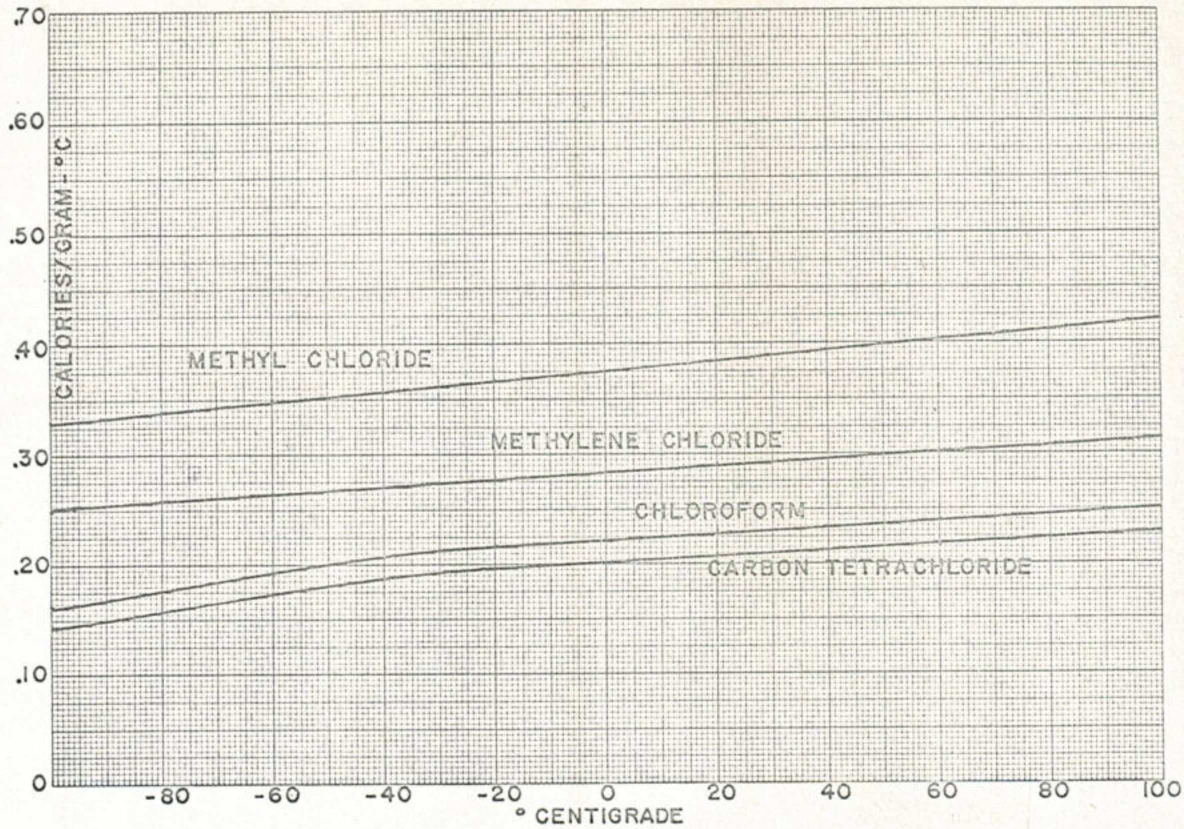


Fig. 5-5—Gives liquid heat capacity over a range of −80° C to +100° C.

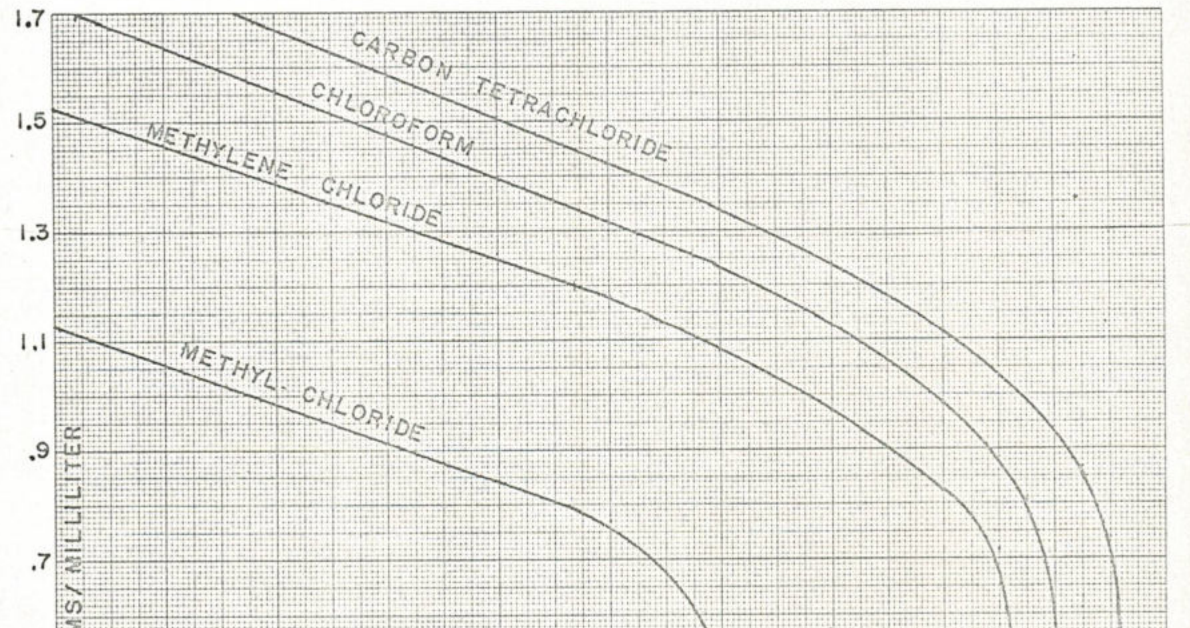


Fig. 5-6—Gives liquid density over a range of −60° C to +280° C.

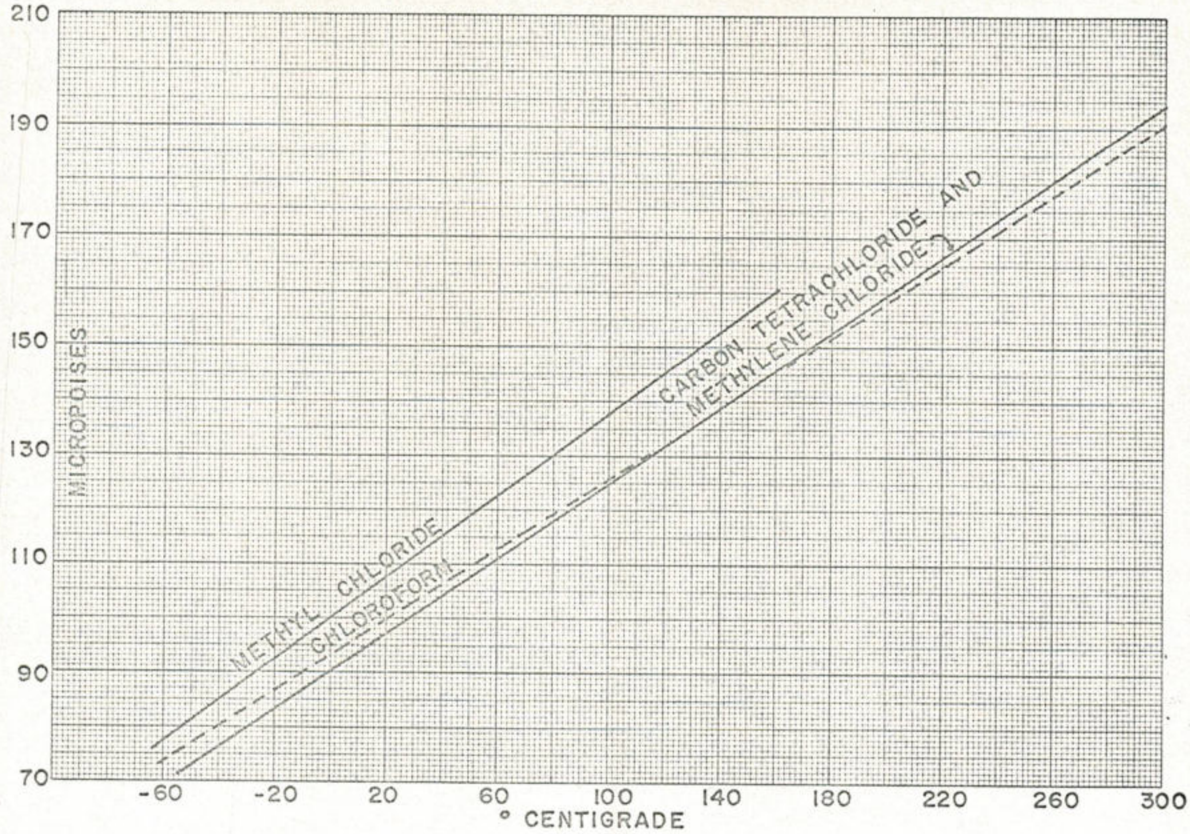


Fig. 5-7—Gives vapor viscosity over a range of −60° C to +300° C.

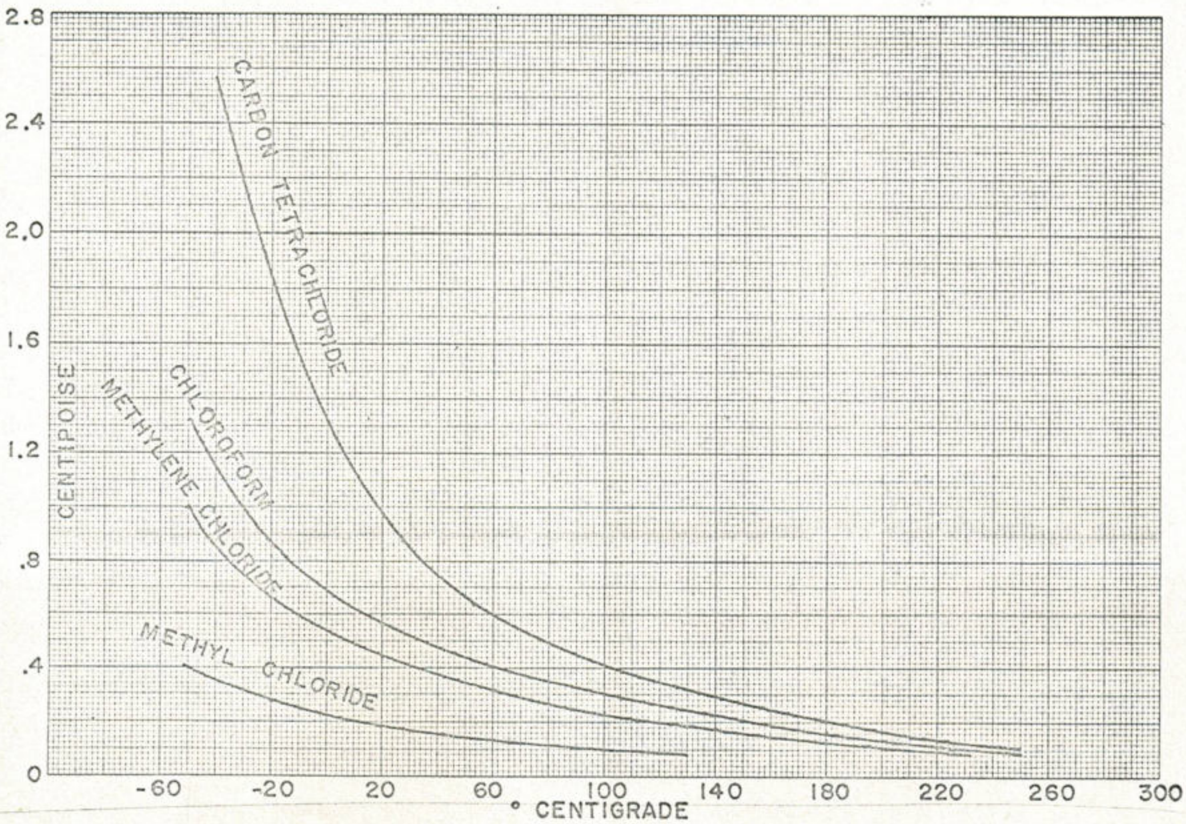


Fig. 5-8—Gives liquid viscosity over a range of −60° C to +250° C.

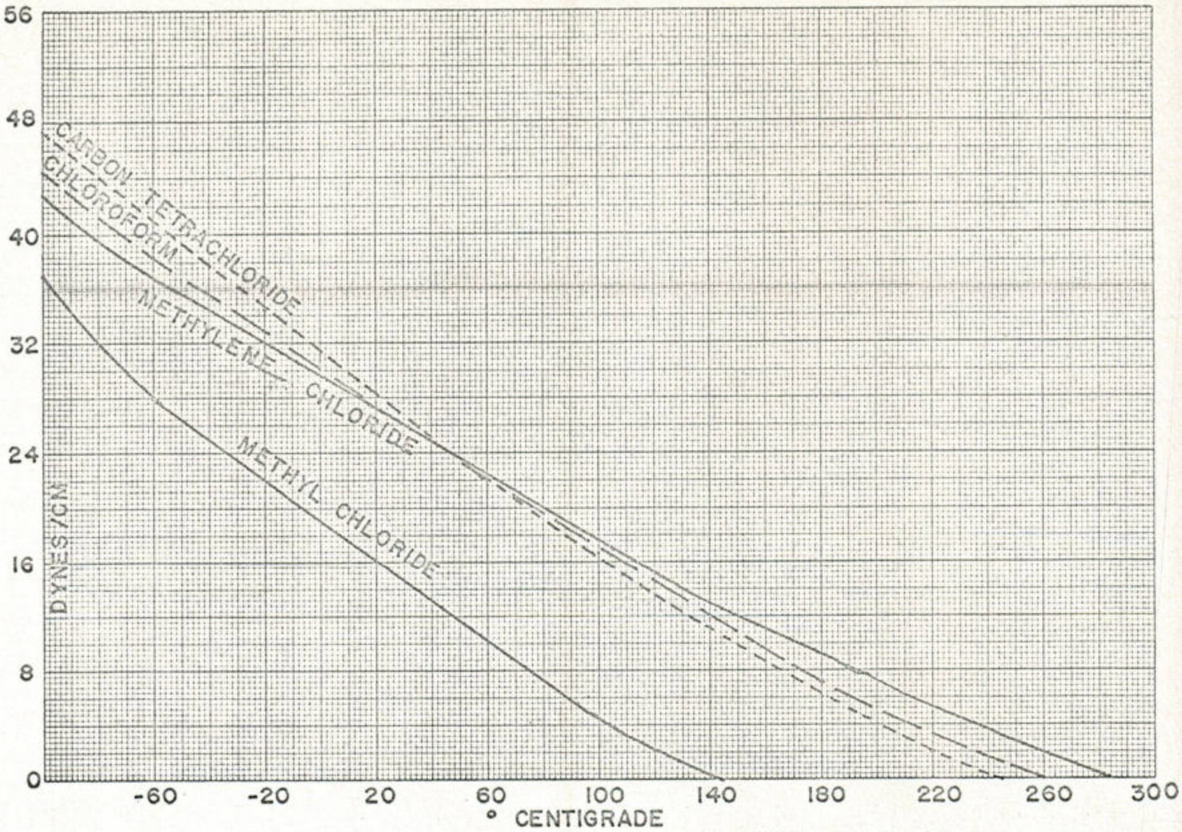


Fig. 5-9—Gives surface tension over a range of −60° C to +280° C.

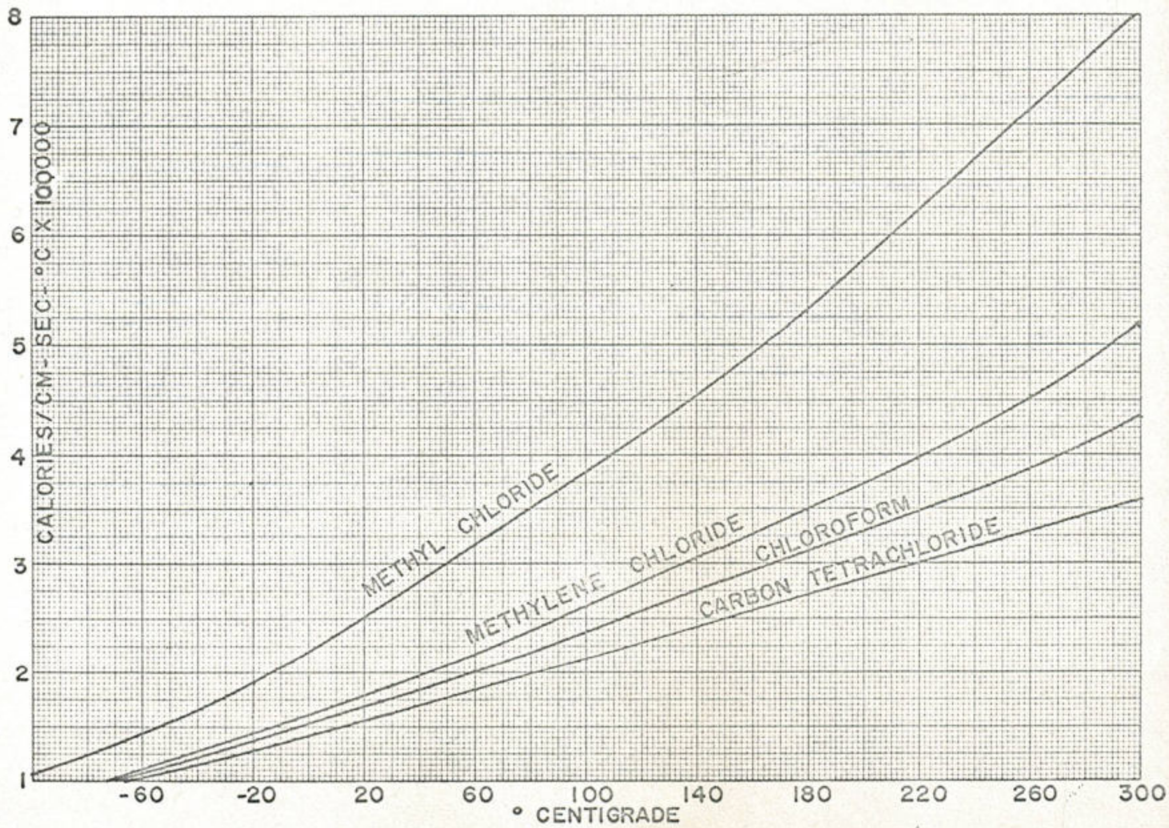


Fig. 5-10—Gives vapor thermal conductivity over a range of −60° to +300° C.

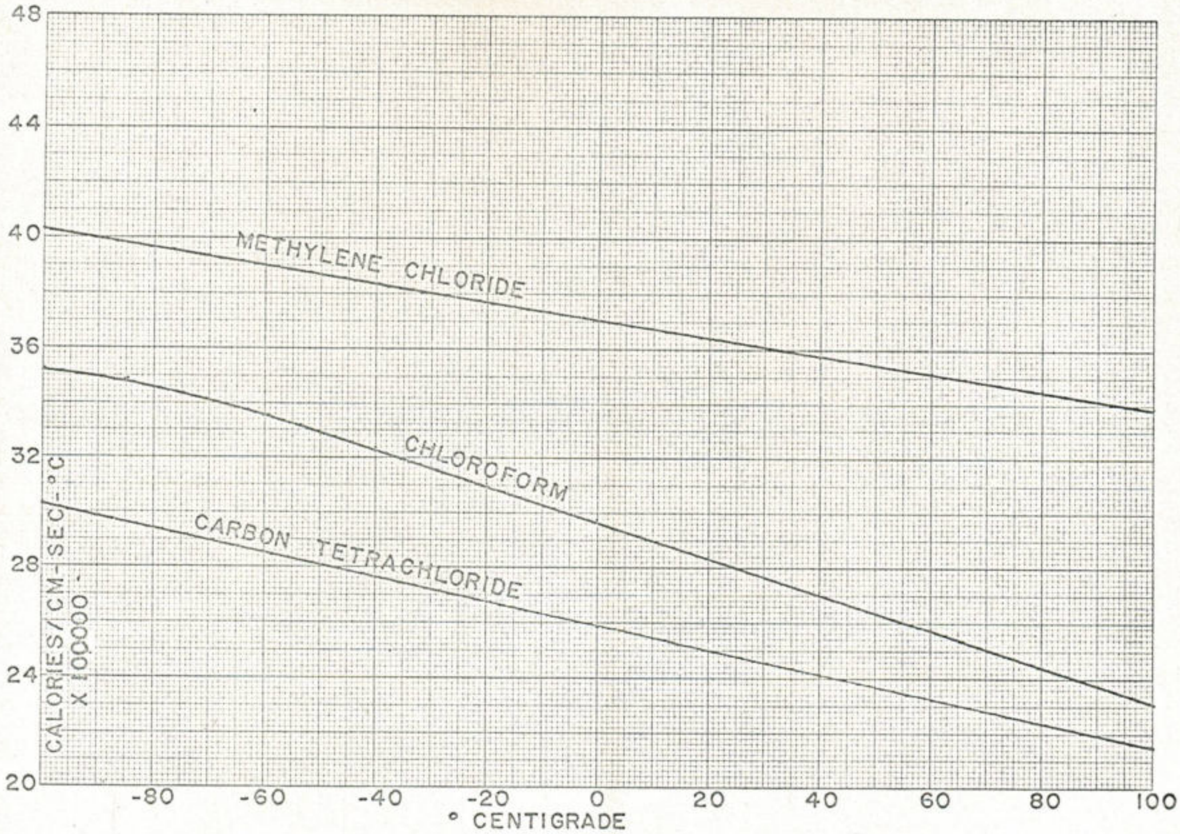


Fig. 5-11—Gives liquid thermal conductivity over a range of −80° C to +100° C.

heat capacity, Timmermans[5] gives extensive data for methylene chloride and carbon tetrachloride. Chloroform and methyl chloride are available from an alignment chart in Perry.[3] The data for chloroform and carbon tetrachloride have been supplemented by using the equation proposed by Chow and Bright:

$$C_p w^{2.8} = b$$

where

$C_p$ = liquid heat capacity

$w$ = density expansion factor (available from their graph)

$b$ = a constant determined for each compound

Compared with experimental data, the error ranged from 2-16 percent, averaging 9.5 percent.

**Liquid Density.** Timmermans[5] presents extensive data for carbon tetrachloride up to its critical temperature and for chloroform below 20°C. Reid and Sherwood[11], Dreisbach,[4] and McGovern,[9] provide some data on all four compounds. The data for chloroform and methylene chloride have been supplemented by the method of Lyderson, Greenhorn, and Hougen which relates the density to the critical properties. The accuracy is extremely good except close to the critical temperature, with errors normally being less than 1 percent when compared to experimental data.

**TABLE 5-1—Chlorinated Methanes**

| Compound | Boiling Point | Freezing Point | Molecular Weight | Critical Properties °C tc | psi Pc | g/ml dc |
|---|---|---|---|---|---|---|
| Methyl Chloride | −24.0 | −97.7 | 50.5 | 143.8 | 964 | 0.353 |
| Methylene Chloride | 40.7 | −96.7 | 84.9 | 245 | 893 | .472 (Calculated) |
| Chloroform | 61.3 | −63.5 | 119.4 | 260 | 805 | .516 |
| Carbon Tetrachloride | 76.7 | −22.6 | 153.8 | 283.1 | 660 | .5576 |

**Viscosity.** Vapor viscosity data for methyl chloride are presented over a wide temperature range by Lange[2] and Reid and Sherwood.[11] However, the viscosities reported by Lange above 150°C appear to be badly out of line and so these data are not included. Reid and Sherwood[11] present data for the other three compounds. Perry[3] covers chloroform over a wide temperature range (up to 600°C, although I have only plotted it up to 300°C). The data for carbon tetrachloride and methyl chloride have been supplemented by use of the Arnold equation which relates viscosity to molar volume, molecular weight, and critical temperature. The error averages about 1 percent. From the graph, it is evident that methylene chloride, chloroform, and carbon tetrachloride have nearly the same viscosity over a wide temperature range.

Liquid viscosities are available from several references.

Perry[3] presents nomographs for all four compounds. The data have been supplemented by plotting the log of the viscosity against the reciprocal of the temperature. This does not give the expected straight line for these compounds but enough data are available to allow accurate extrapolation of the curve at the extreme low and high temperatures.

**Surface Tension.** Data over a narrow temperature range are available from the handbooks.[2, 4, 5] In addition, Lange[2] presents equations for determining the surface tension of methyl chloride and carbon tetrachloride over a wide temperature range. A plot of the log of the surface tension versus the log of the critical temperature minus the temperature point yields a straight line that allows good extrapolation. However, because of the narrow range of available data, the extrapolation on chloroform and methylene chloride may give fairly large errors at the extreme temperature ends of the plot.

**Thermal Conductivity.** The vapor thermal conductivity for all four compounds has been extensively studied and good data are readily available.[2, 3, 11] In addition, the data can be accurately extrapolated by a straight line plot of the log of the thermal conductivity versus the log of the temperature.

Unfortunately, liquid thermal conductivity has not fared so well. Sakiadis[12, 13] has made a noble start toward cataloging the reliability of the data presently available in the literature. Much of the data in the current handbooks is based on experimental results obtained over 20 years ago when the accuracy was very poor and, consequently, the data scatter very badly. Mason[14] has supplied some of the best data on chlorinated hydrocarbons but his temperature range is rather narrow. The data presented here are based in large part on judgment as to which data are the most reliable, and supplemented by the estimation method of Weber, which relates thermal conductivity to liquid heat capacity, density, and molecular weight. In the 0 to 50°C range, the data appear fairly good. Beyond this range, the error may be as high as 15 percent. No data are presented for methyl chloride since the available data, both experimental and estimated, were too scattered to allow even a rough guess. There is certainly a lot of room for improvement in the data available on liquid thermal conductivity. A followup to the fine work done by Sakiadis and Coates would certainly be most welcome.

The effect of pressure on the thermal conductivity of liquids is small and can be ignored up to about 400 psig.


### About the author

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