Physical Properties of Hydrocarbons

Part 5—Chlorinated Methanes
Part 6—Chlorinated Ethylenes

Robert W. Gallant

The Dow Chemical Co., Plaquemine, La.

THE FAST RISE of vinyl chloride from a minor chemical to a one-billion pound per year giant in 20 years is one of the great success stories of the chemical industry. Although much of the credit belongs to the excellent properties of the polymer, no small credit is also due to the continuing drop in price of the monomer made possible by the steady improvement in manufacturing technology. Today acetylene has been largely replaced as the starting raw material by ethylene. Continuing advances in oxychlorination know-how holds the promise of even lower monomer costs in the future.

Although somewhat dwarfed by vinyl chloride, vinylidene chloride has carved out an important market for itself in Saran polymers. Perchloroethylene production is over 400 million pounds/year, with virtually all of it going into dry cleaning solvents. Trichloroethylene's output of 350 million pounds/year goes largely into metal degreasing.

It is surprising that so little experimental data are available in the literature for a compound as important as vinyl chloride. Trichloroethylene and perchlorethylene have been studied quite extensively, but vinylidene chloride has been virtually neglected except at 20° C. It has been necessary to use estimation methods rather extensively for all four compounds. Unfortunately, the highly reliable estimation methods developed for hydrocarbons generally yield poor results with these polar, highly chlorinated compounds. Even estimation methods that give good results with the chlorinated methanes often give erratic, unreliable results here. This area represents fertile ground for some improved estimation methods. Certainly some extensive physical property work on a one-billion pound per year chemical like vinyl chloride would be very worthwhile.

Vapor Pressure. Stull[1] presents data for all four compounds up to the boiling point. Vinyl chloride vapor pressure at high temperatures is presented in four other references.[2, 3, 4, 5] Vapor pressure data above one atmosphere are also available for vinylidene chloride,[3] trichloroethylene,[6, 7, 8] and perchloroethylene.[6]

Heat of Vaporization. Only limited data are available for both vinyl chloride[10] and vinylidene chloride.[11, 12] Trichloroethylene[7, 12] and perchloroethylene[7] are covered over a fairly wide temperature range. The data have been extended to a wider temperature range by use of the Watson equation. When compared with nine experimental temperature points, the results obtained from this method showed a maximum error of 2.9 percent and an average error of 1.0 percent.

Heat Capacity. Once again, the best source of vapor heat capacity data is Kobe.[13] For liquid heat capacity, only perchloroethylene[7, 12] and trichloroethylene[7] have been covered over a wide temperature range. The data for vinyl chloride and vinylidene chloride are available only at 25° C and even at this temperature, various sources do not agree. None of the present estimation methods seem
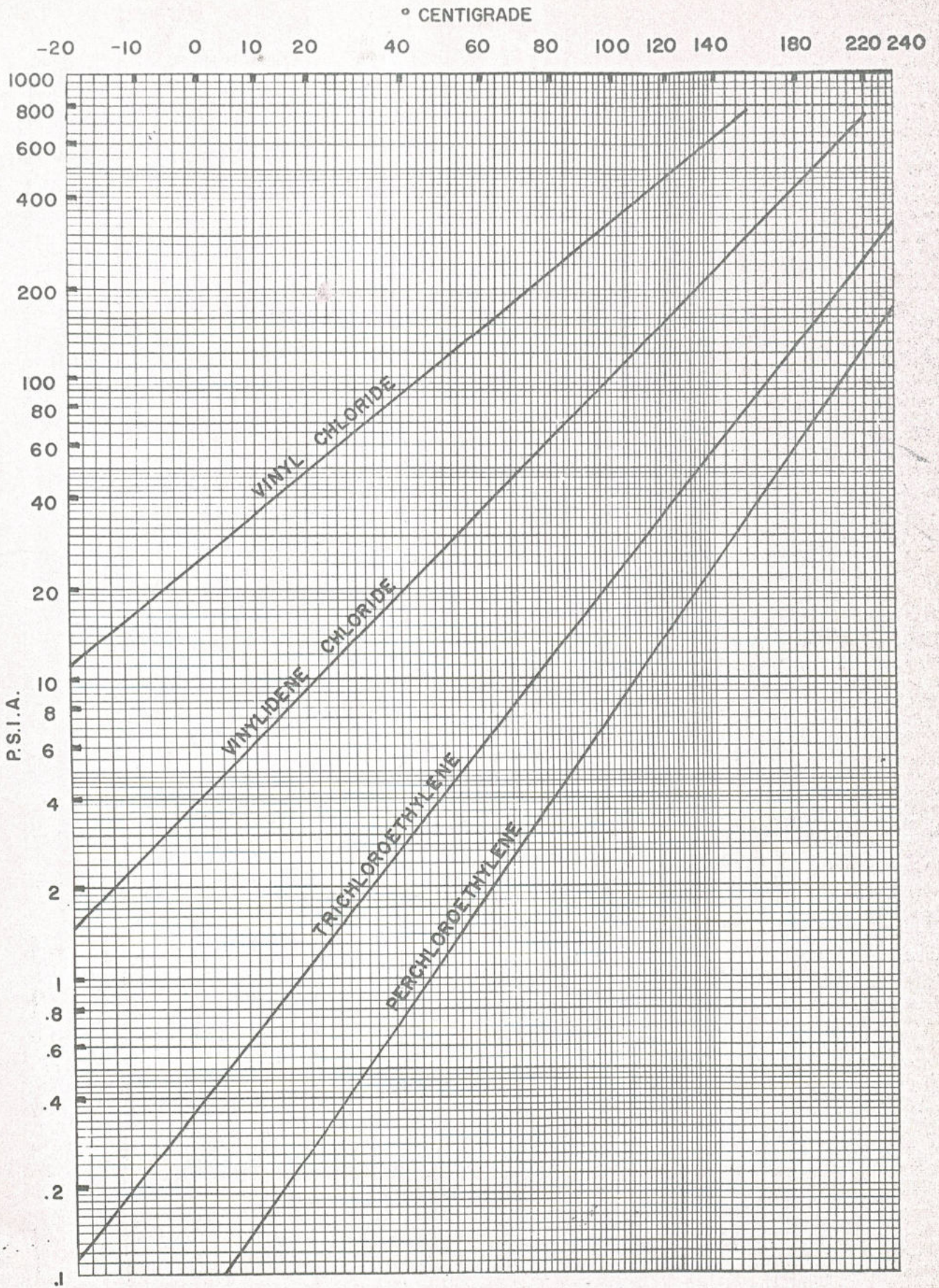
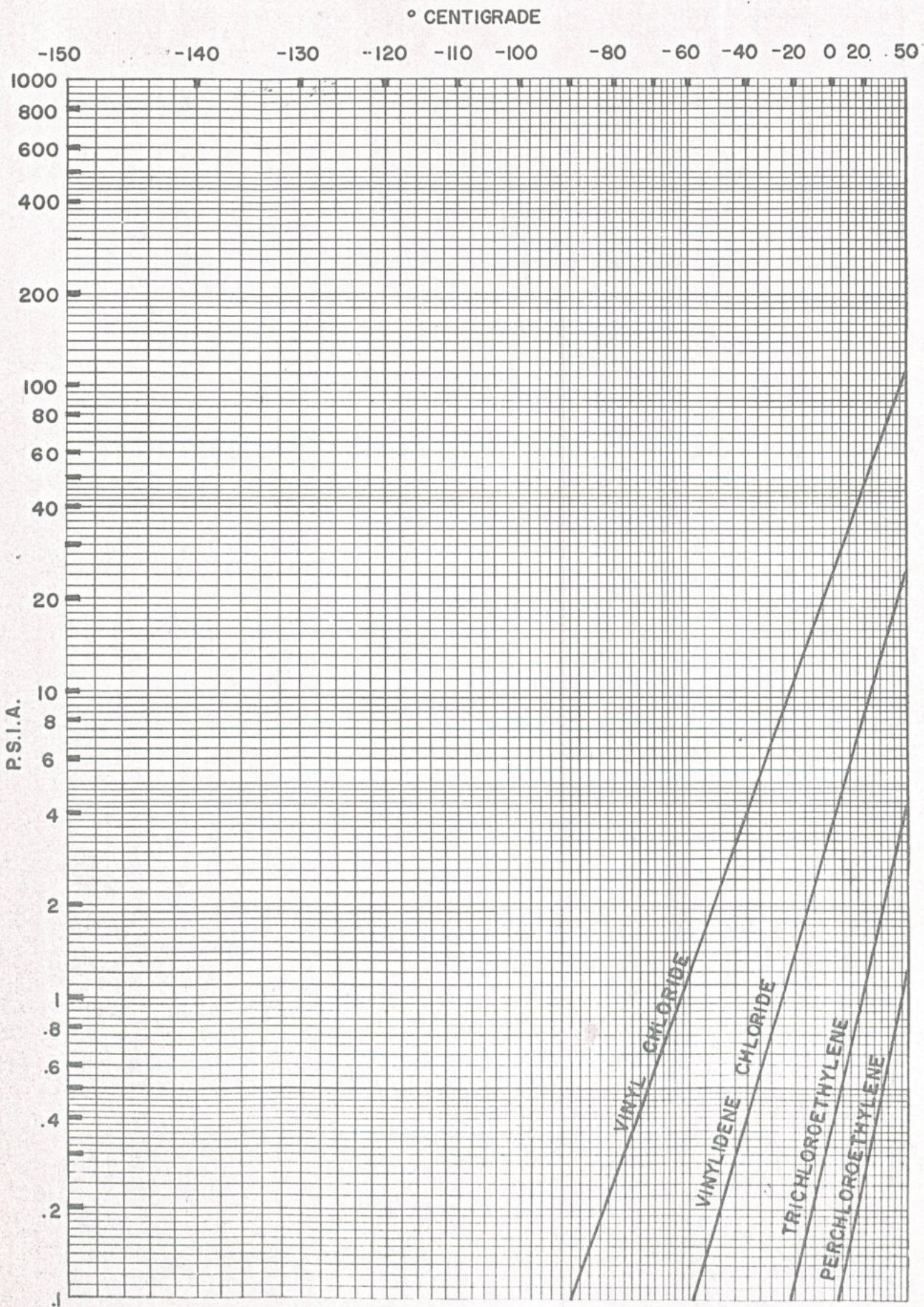Fig. 6-1—Gives vapor pressure over a range of −20° C to +240° C.

° CENTIGRADE

-150   -140   -130   -120   -110   -100   -80   -60   -40   -20   0 20   50

P.S.I.A.

1000
800
600
400

200

100
80
60

40

20

10
8
6

4

2

1
.8

.6

.4

.2

.1

VINYL CHLORIDE

VINYLIDENE CHLORIDE

TRICHLOROETHYLENE

PERCHLOROETHYLENE

Fig. 6-2—Gives vapor pressure over a range of −90° C to +50° C.
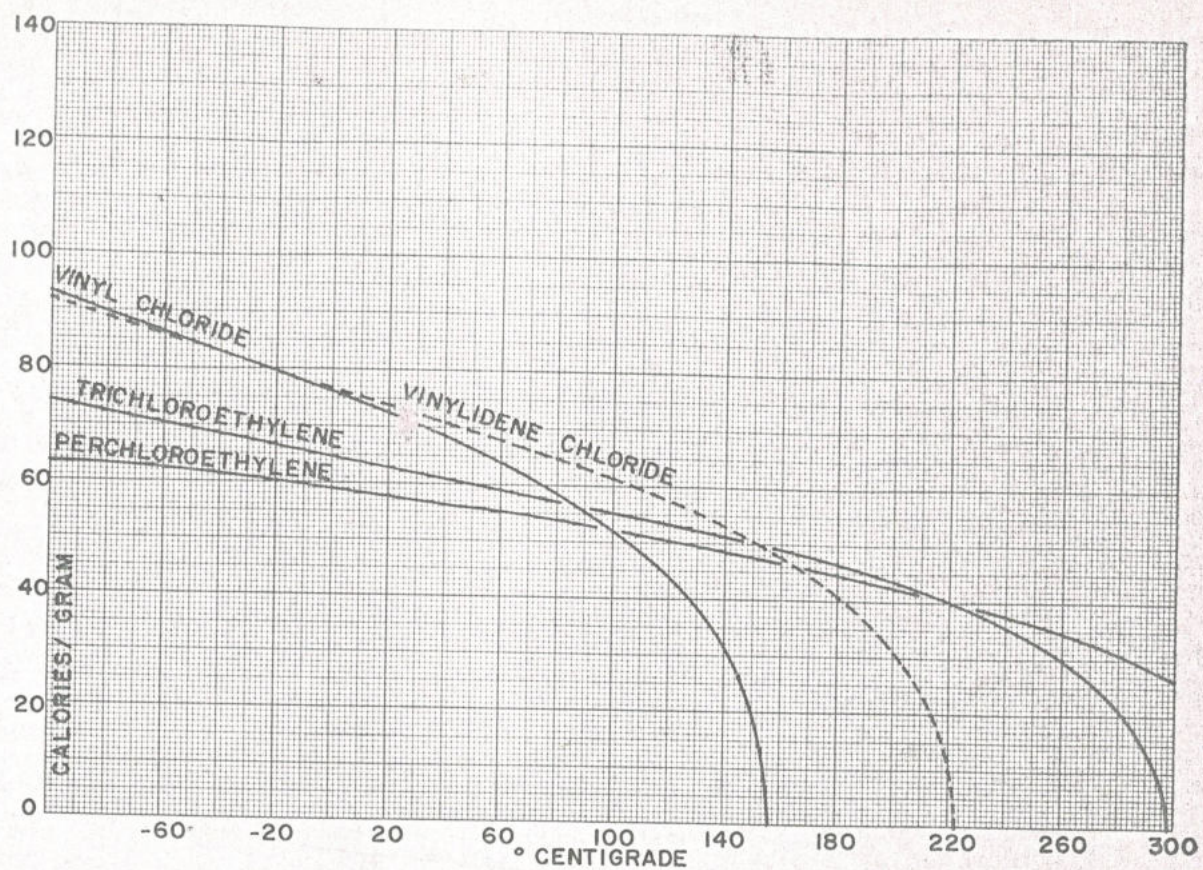
Fig. 6-3—Gives heat of vaporization over a range of −60° C to +300° C.
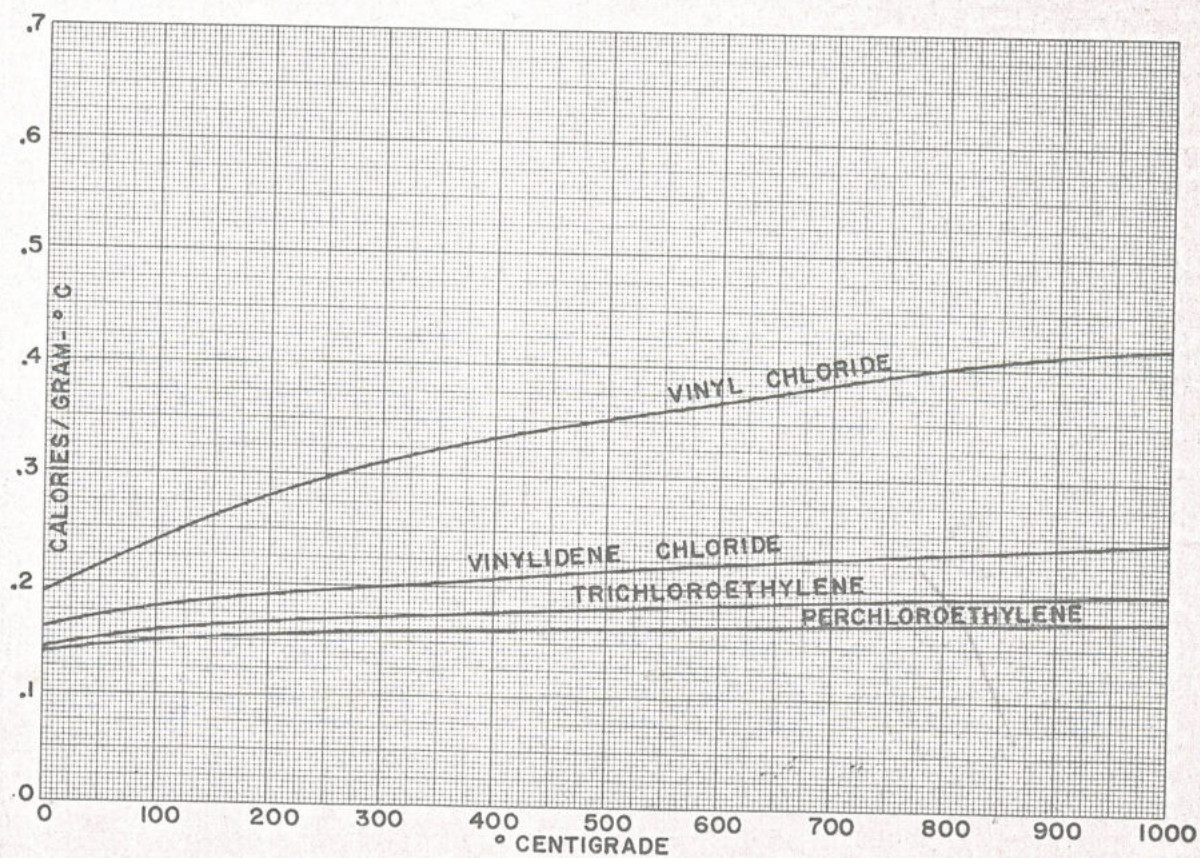

Fig. 6-4—Gives vapor heat capacity over a range of 0° C to +1,000° C.
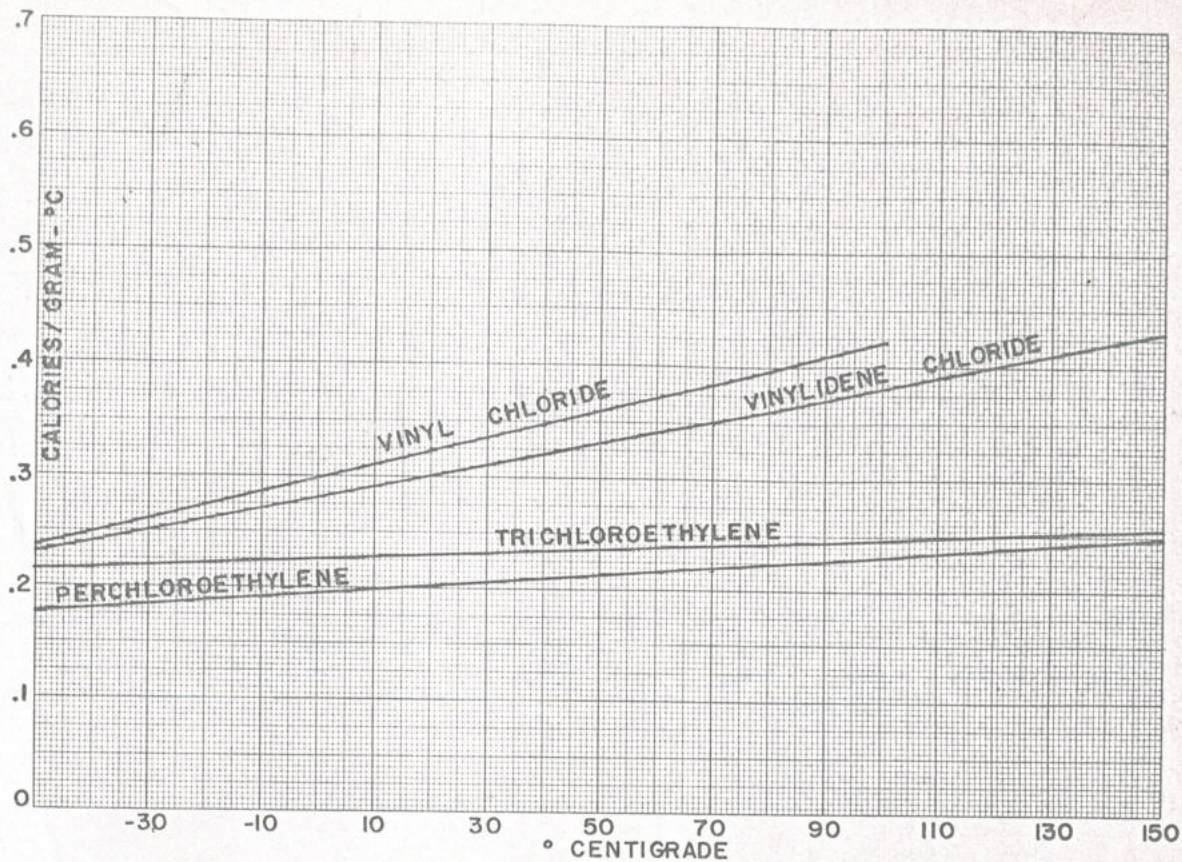
Fig. 6-5—Gives liquid heat capacity over a range of −30° C to +150° C.
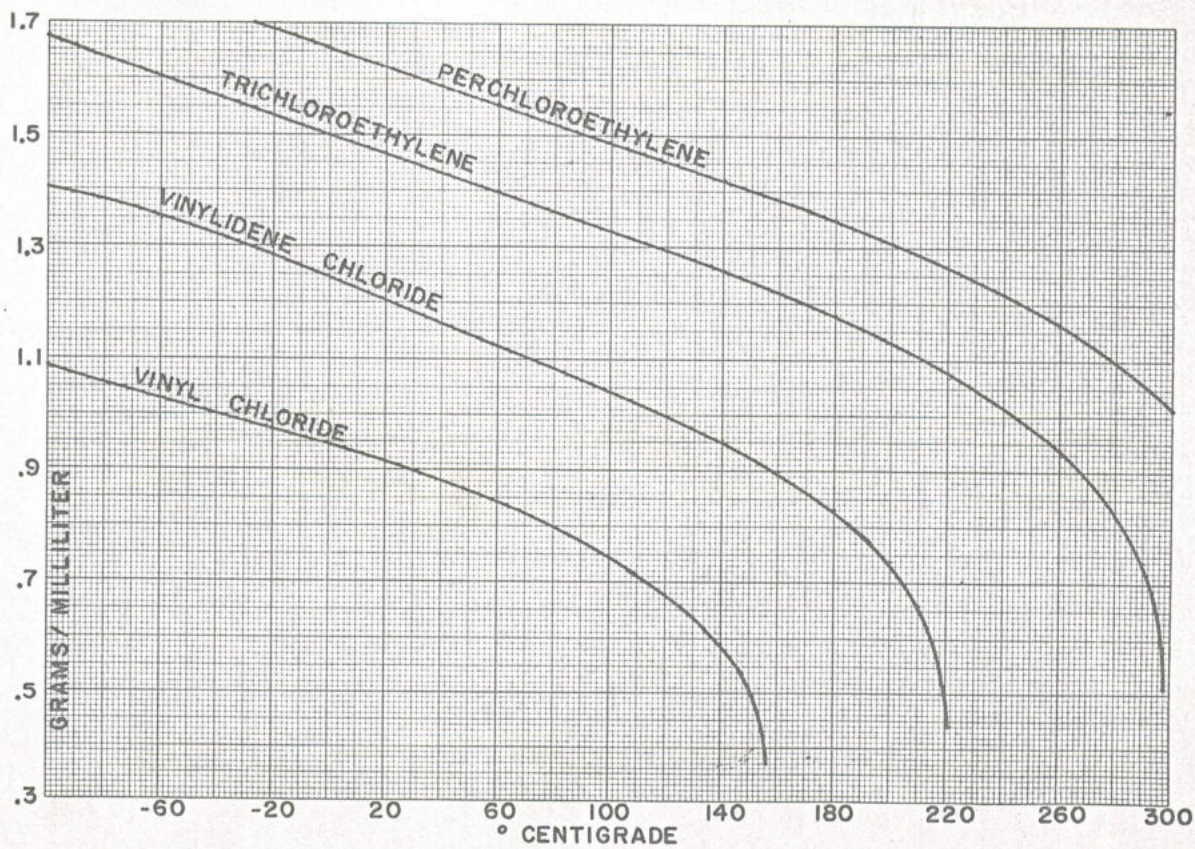
Fig. 6-6—Gives liquid density over a range of −60° C to +300° C.
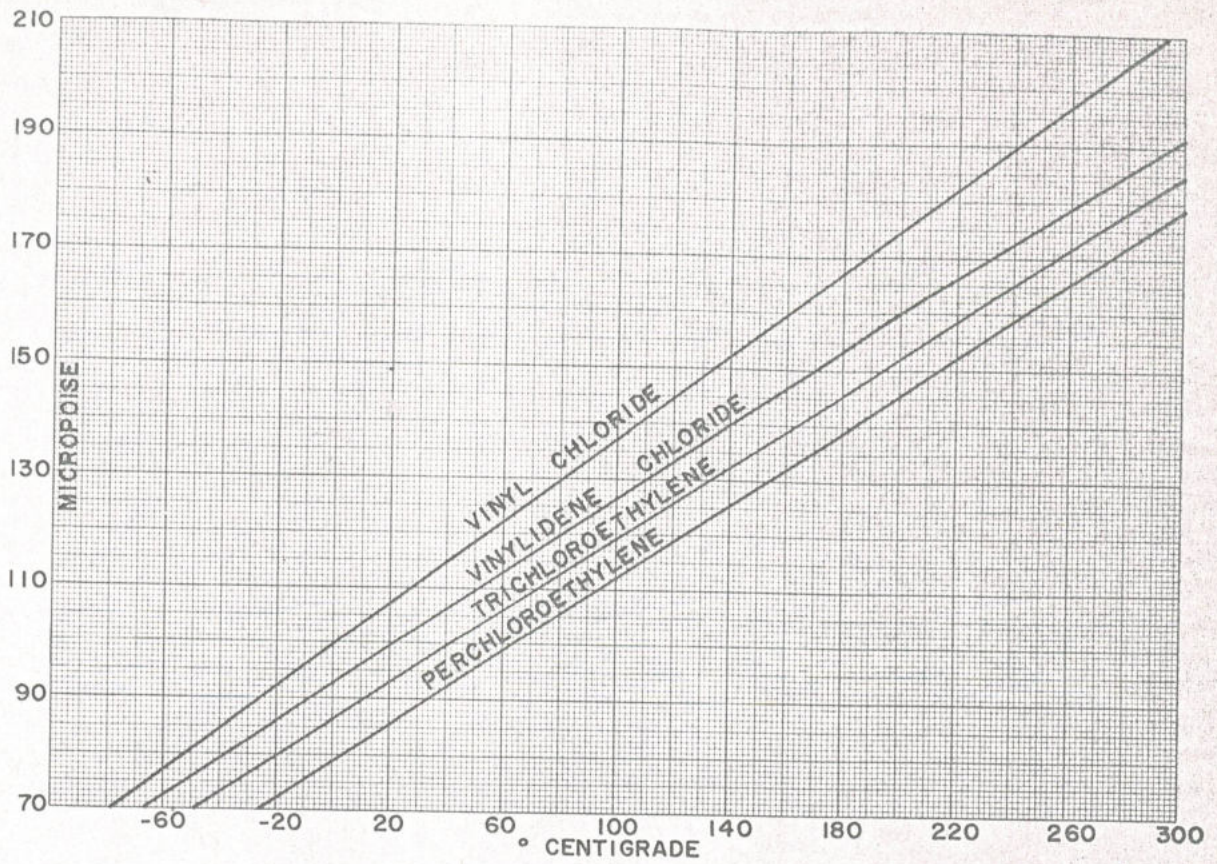
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Fig. 6-7—Gives vapor viscosity over a range of −60° C to +300° C.

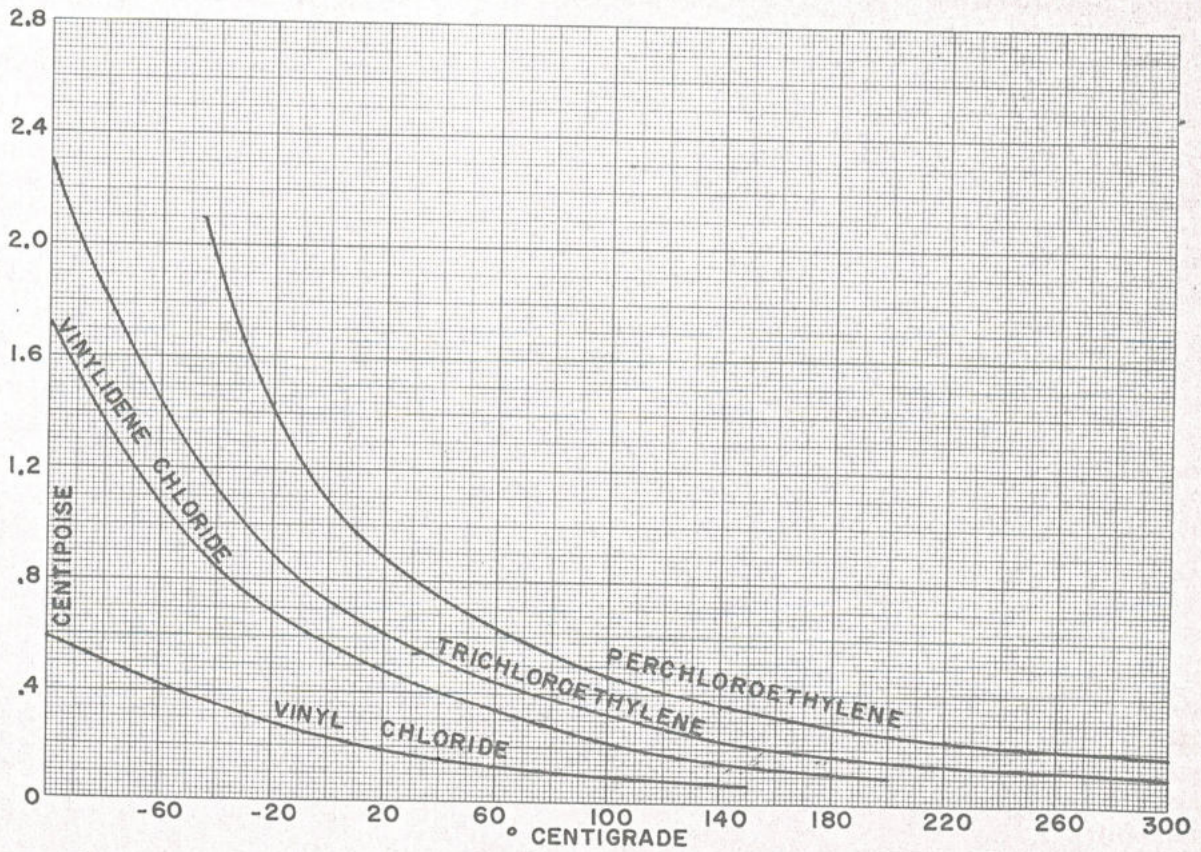
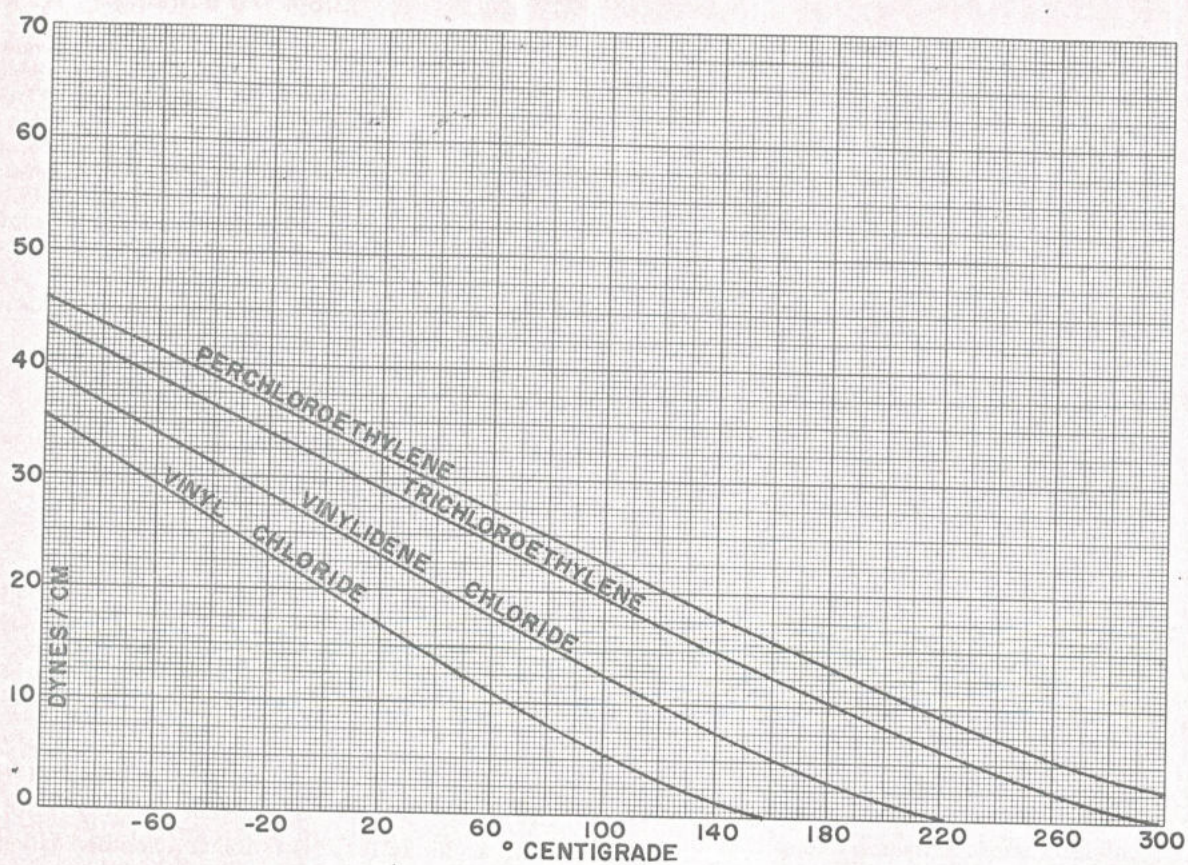Fig. 6-8—Gives liquid viscosity over a range of −60° C to +300° C.

Fig. 6-9—Gives surface tension over a range of −60° C to + 300° C.
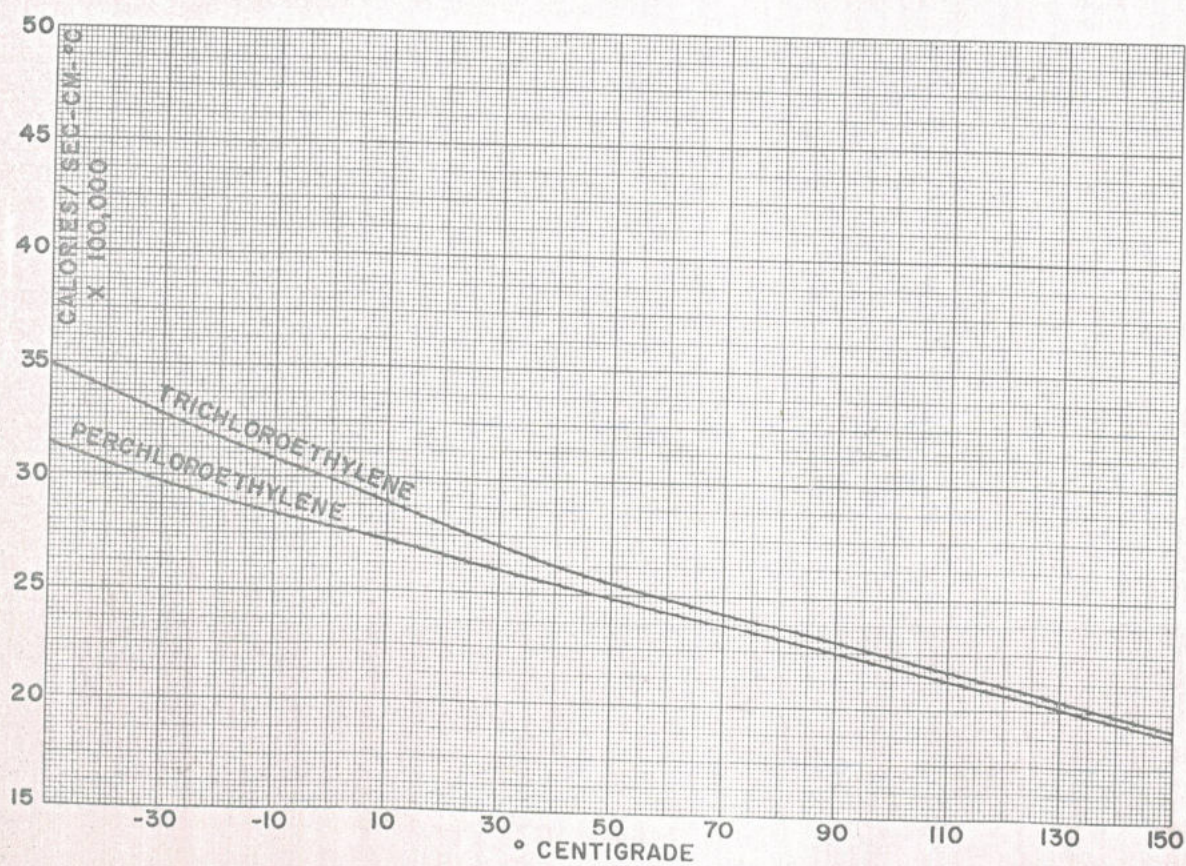
Fig. 6-10—Gives liquid thermal conductivity over a range of −30° C to +150° C.

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to give accurate results for highly chlorinated polar compounds. The atomic-group additive method of Johnson and Huang was used to determine the liquid heat capacity at 20° C for vinyl chloride and vinylidene chloride. This was extrapolated over the temperature range by the equation

$$Cp \ w^{2.8} = b$$

where

Cp = heat capacity
w = expansion factor (available from chart)
b = a constant for each compound

This method will probably yield errors up to 25 percent for polar compounds of this type.

Density. There are surprisingly little data in the literature on density outside the 10-30° C range for any of the chlorinated ethylenes. Vinyl chloride is covered in a product bulletin.[4] McGovern[7] is the only good source for trichloroethylene and perchloroethylene. The data have been extrapolated over the wide temperature range by the method of Lyderson, Greenknorn and Hougen. The error for 11 calculated points ranged from 1-3 percent when compared with experimental values.

Viscosity. The only available data for vapor viscosity in the literature are that of Zaloudik[14] for vinyl chloride and McGovern[7] for trichloroethylene and perchloroethylene. The data have been supplemented by using the method of Bromley and Wilke to estimate the vapor viscosity over a wide temperature range. The maximum error for 11 temperature points was 10 percent and averaged 4.1 percent.

The liquid viscosity for all four compounds is available from a number of sources. Vinyl chloride[4,10] is available up to 30° C. Vinylidene chloride data scatter rather badly.[11,12,15] Trichloroethylene[7,10,12] and perchloroethylene[3,7,10,11] data appear to be quite reliable. The low and high temperature values were obtained by plotting the liquid viscosity against the reciprocal of the temperature. As with the chlorinated methanes, this does not yield the expected straight line but still represents a good approximation.

Surface Tension. As with many of the liquid phase properties of these compounds, surface tension has been experimentally determined only over the narrow 0-40° C range.[3,4,10] For vinylidene chloride, however, there were no literature data and so its surface tension at 20° C was calculated by the equation

$$\sigma = \left(\frac{[P]\rho}{m}\right)^4$$

About the author

R. W. GALLANT *is a group leader in the research and development department of The Dow Chemical Co., Plaquemine, La. His duties include process design, production plant trouble-shooting, pilot plant operations, product development, and process development. Mr. Gallant received a B.S. in chemical engineering from the University of Florida.*

where

σ = surface tension at 20° C
$[P]$ = Parachor, estimated from the molecular structure
ρ = liquid density at 20° C
M = molecular weight

The anticipated error by this method is 3-5 percent. The data for all four compounds were extrapolated over a wide temperature range by Kharbanda's nomograph of

$$\sigma_2 = \sigma_1 \left(\frac{T_c - T_2}{T_c - T_1}\right)^{1.2}$$

where

σ = surface tension at temperature T
T_c = critical temperature

The accuracy for this estimation method is very good, averaging 1-2 percent error.

Thermal Conductivity. There are no experimental data for either the vapor or liquid thermal conductivity of vinyl chloride or vinylidene chloride. Mason[16] has experimentally determined the liquid thermal conductivity and his data appear to be more reliable than the earlier reported data.[7,9] McGovern presents the vapor thermal conductivity of trichloroethylene and perchloroethylene but the estimation method used is not very reliable. None of the present estimation methods gave a reasonable temperature-thermal conductivity trend for the vapor phase. Hence, only the liquid thermal conductivity is presented here, and then only for the experimentally determined trichloroethylene and perchloroethylene since estimation methods gave highly unreliable results for the liquid phase also.

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[15] "Vinylidene Chloride Product Bulletin," The Dow Chemical Co., Midland, Mich.
[16] Mason, H. L., *Transactions of the ASME,* pp. 817-821 (July 1954).

TABLE 6-1—Chlorinated Ethylenes

Compound	Boiling Point °C	Freezing Point °C	Molecular Weight	Critical Properties		
				°C tc	psia Pc	g/ml dc
Vinyl Chloride	−13.4	−153.7	62.5	156.5	809	0.370
Vinylidene Chloride	31.7	−122.5	96.95	221	758	.440
Trichloroethylene	86.7	− 86.7	131.4	298	710	.513
Perchloroethylene	121.1	− 22.8	165.8	340	650	.573