

# Physical Properties of Hydrocarbons

## Part 7—Chlorinated Aliphatics

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ONE OF THE UNIQUE results of the large, integrated chemical plants is the presence of the chemical intermediate. This is a compound that is almost unknown to the company purchasing agent or salesman, but to the chemical engineer in the plant, it is a major plant product whose economics play a big role in the company's profitability.

No group fits this role better than the chlorinated aliphatics—ethyl chloride, ethylene dichloride, propyl chloride, and propylene dichloride. As a group, their production rate is near 4 billion lbs/yr. But in terms of merchant sales, they probably fall short of 1 billion pounds.

Ethylene dichloride (1, 2-dichloroethane) stands as king of the intermediates field. Largely used in the production of vinyl chloride for the plastics field, it has grown into a 2 billion lbs/yr giant and should reach about 3 billion lbs/yr by 1970. With ethylene steadily replacing acetylene as a favorite starting material for vinyl chloride, ethylene dichloride will be a regular visitor to the design engineer's desk.

Ethyl chloride is produced almost exclusively for use in the production of tetraethyl lead. Thus, it is not surprising that Ethyl Corporation accounts for almost half of the yearly output of 700 million pounds.

Propylene dichloride (1, 2-dichloropropane) has not fared as well as its ethylene counterpart in the advance of technology. The move away from the chlorohydrin route and toward direct oxidation of propylene for propylene oxide presages a drop in its availability as a by-product. Additionally, methane and ethylene have become the preferred starting materials for carbon tetrachloride and perchloroethylene. Already replaced by allyl chloride and direct oxidation of propylene in production of synthetic glycerine, propylene dichloride will continue to lose ground as an intermediate.

Propyl chloride (1-chloropropane) has never achieved much prominence as either a product or an intermediate. The low reactivity of its chlorine atom makes it a poor choice for most reaction steps.

The physical properties of ethyl chloride have been rather extensively studied. Very little experimental work has been done on the other three compounds except in the 0—50°C range.

**Vapor Pressure.** Stull<sup>1</sup> presents vapor pressure data for all four compounds up to the boiling point, and for ethyl chloride and ethylene dichloride to the critical point. Timmermans<sup>2</sup> covers propyl chloride to the critical temperature. McGovern<sup>3</sup> provides data on propylene dichloride up to 200 psia.

**Heat of Vaporization.** Extensive heat of vaporization data are available only for ethyl chloride.<sup>4,5</sup> Data for chloropropane are available from a generalized nomograph by Othmer.<sup>6</sup> For ethylene dichloride and propylene dichloride, the available data<sup>7,8</sup> were extrapolated over the temperature range by the Watson equation.

**Heat Capacity.** The vapor heat capacities of ethyl chloride and ethylene dichloride are available from the compilation by Kobe.<sup>9</sup> Green<sup>10</sup> presents data for chloropropane. The estimation method proposed by Anderson, Beyer, and Watson in which

$$C_p = A + BT + CT^2$$

where

*A*, *B*, and *C* are constants determined by the molecular structure of the compound and *T* = Temperature, °K. was used to calculate the vapor heat capacity of propylene dichloride and extend the data for chloropropane. The accuracy of this method is quite good. When compared to experimental data on other compounds, the error ranged from 1—5 percent.

Liquid heat capacities are available over the —50°C to +50°C range for ethyl chloride<sup>5,11</sup> and ethylene dichloride.<sup>5,12,13</sup> The method of Coates and Sakiadis<sup>14</sup> has been used to extend these data, and to calculate the liquid heat capacity of propyl chloride and propylene dichloride. This is a complex estimation method but is the most accurate method for highly polar compounds. The average error is about 5 percent.

**Density.** Only ethyl chloride has been experimentally determined over a wide temperature range.<sup>15</sup> The other meager data<sup>2,7</sup> have been supplemented by the method of Lyderson, Greenkorn, and Hougen, which relates the density to the critical properties and a reduced density correlation. The error ranges from 2—5 percent.

**Viscosity.** The vapor viscosity of ethyl chloride is available from the literature.<sup>5,16</sup> The viscosities of the other three compounds have been estimated by use of the Arnold equation.

$$\mu_0 = \frac{0.00270 M^{0.5} T_c^{0.5}}{V_b^{0.5}} \frac{T_r^{1.5}}{T_r + 1.47 \frac{T_b}{T_c}}$$

where

- $\mu_0$  = Viscosity
- M* = Molecular weight
- V<sub>b</sub>* = Vapor volume at boiling point
- T<sub>c</sub>* = Critical temperature
- T<sub>b</sub>* = Boiling point
- T<sub>r</sub>* = Reduced temperature

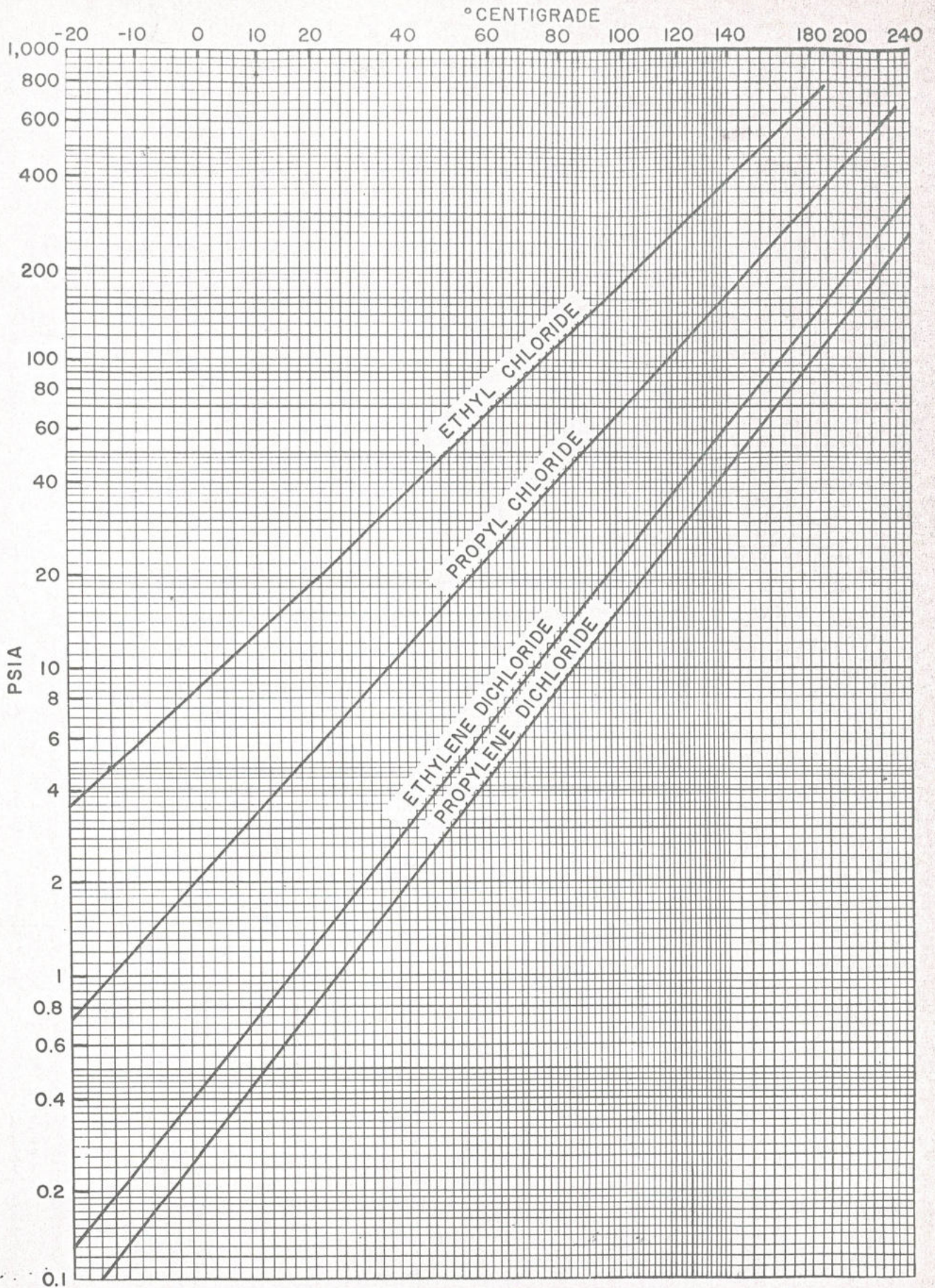


Fig. 7-1—Gives vapor pressure over a range of  $-20^{\circ}\text{C}$  to  $+240^{\circ}\text{C}$ .

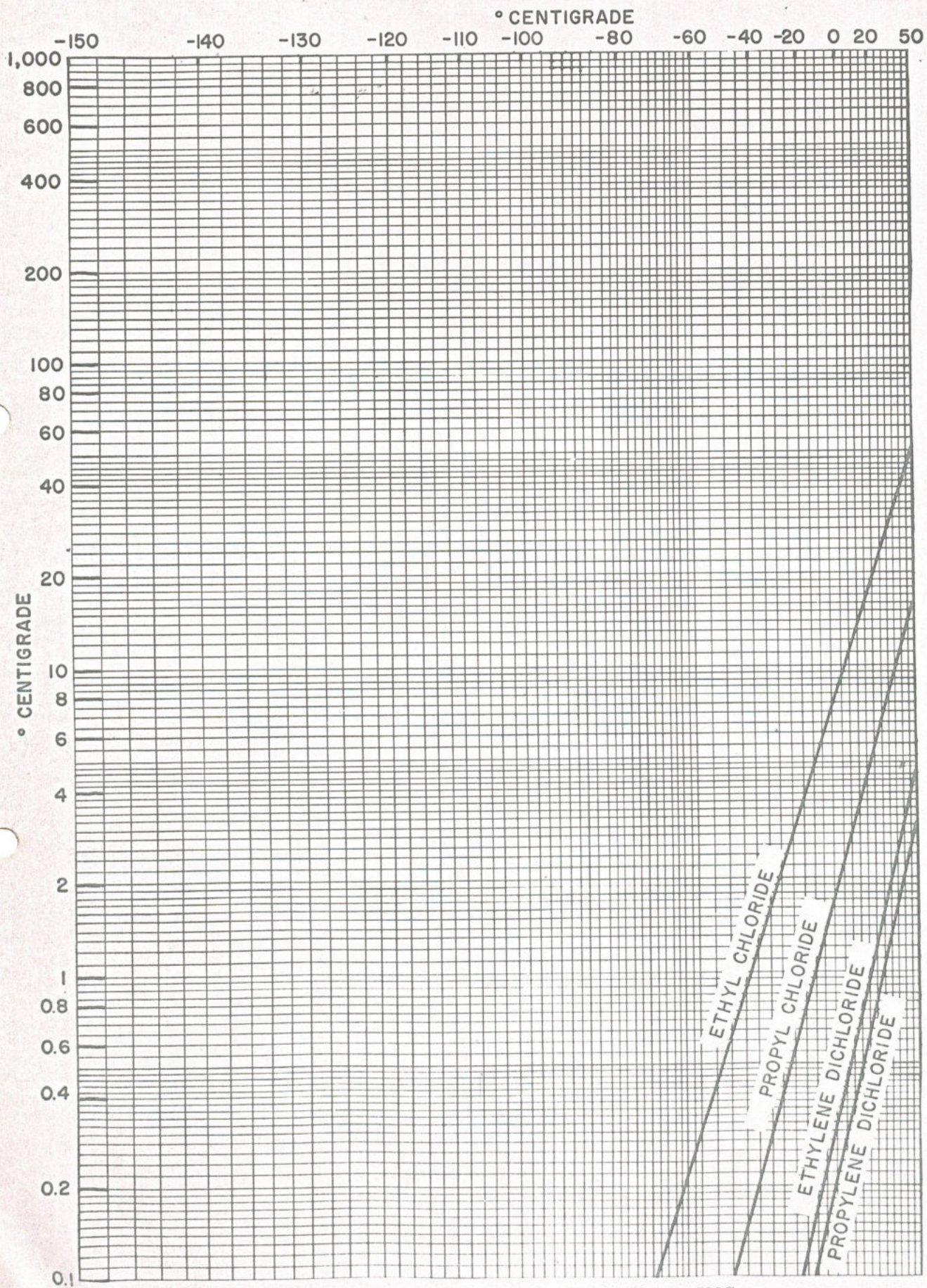


Fig. 7-2—Gives vapor pressure over a range of  $-150^{\circ}\text{C}$  to  $+50^{\circ}\text{C}$ .

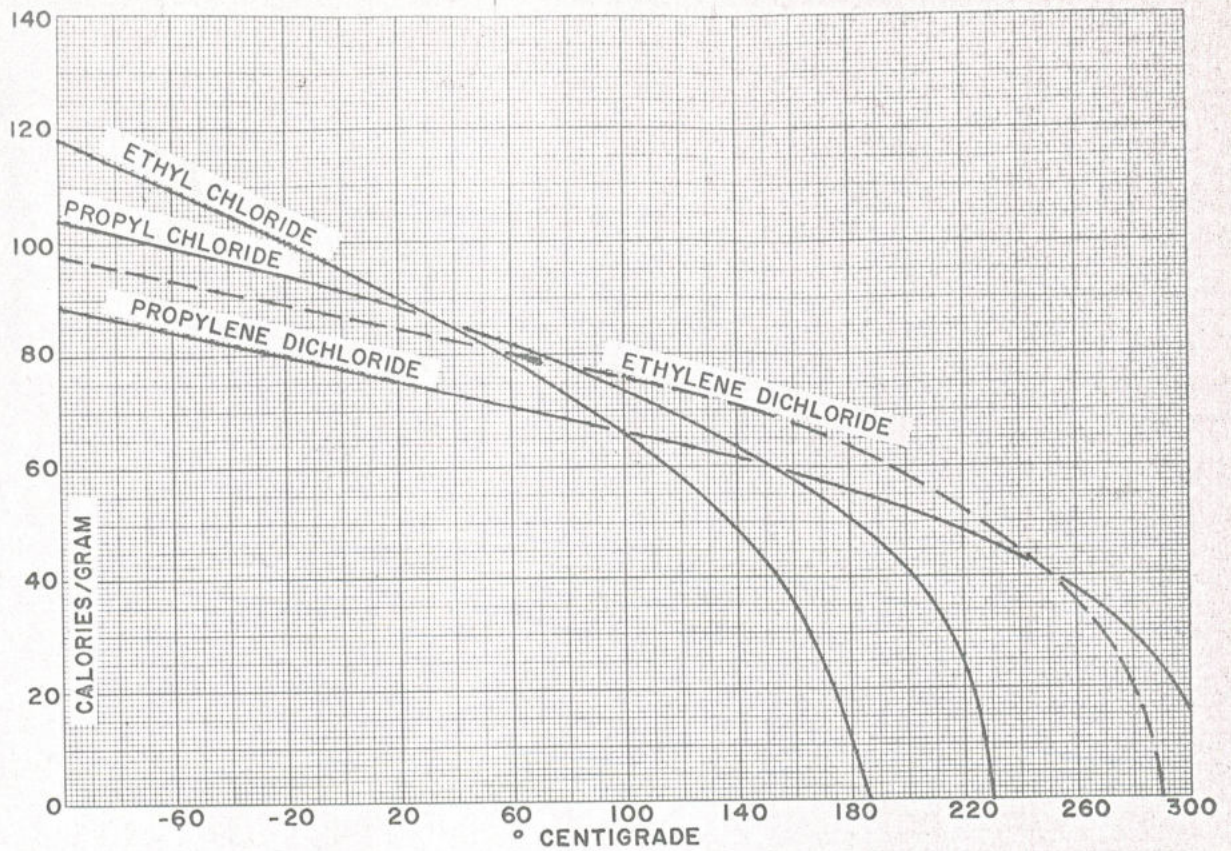


Fig. 7.3—Gives heat of vaporization over a range of  $-60^{\circ}\text{C}$  to  $+300^{\circ}\text{C}$ .

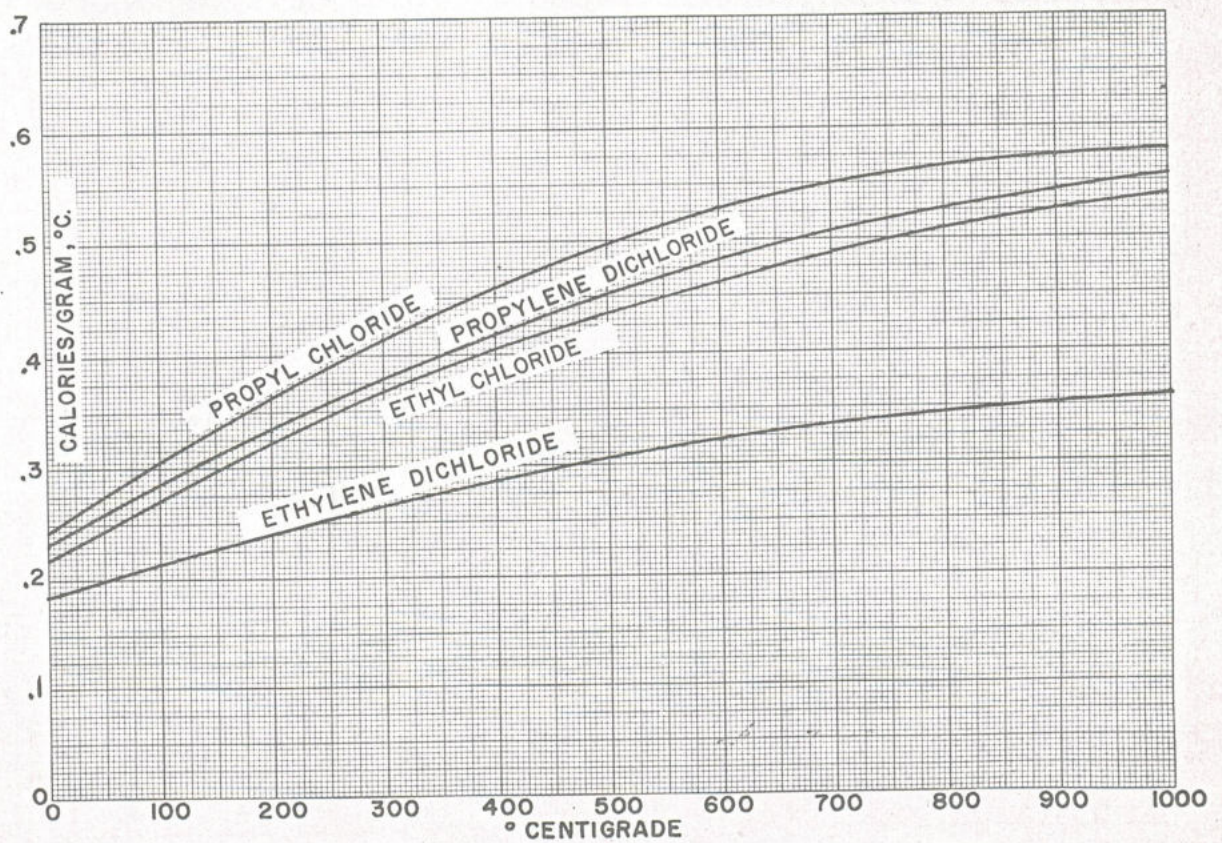


Fig. 7.4—Gives vapor heat capacity over range of  $0^{\circ}\text{C}$  to  $+1,000^{\circ}\text{C}$ .

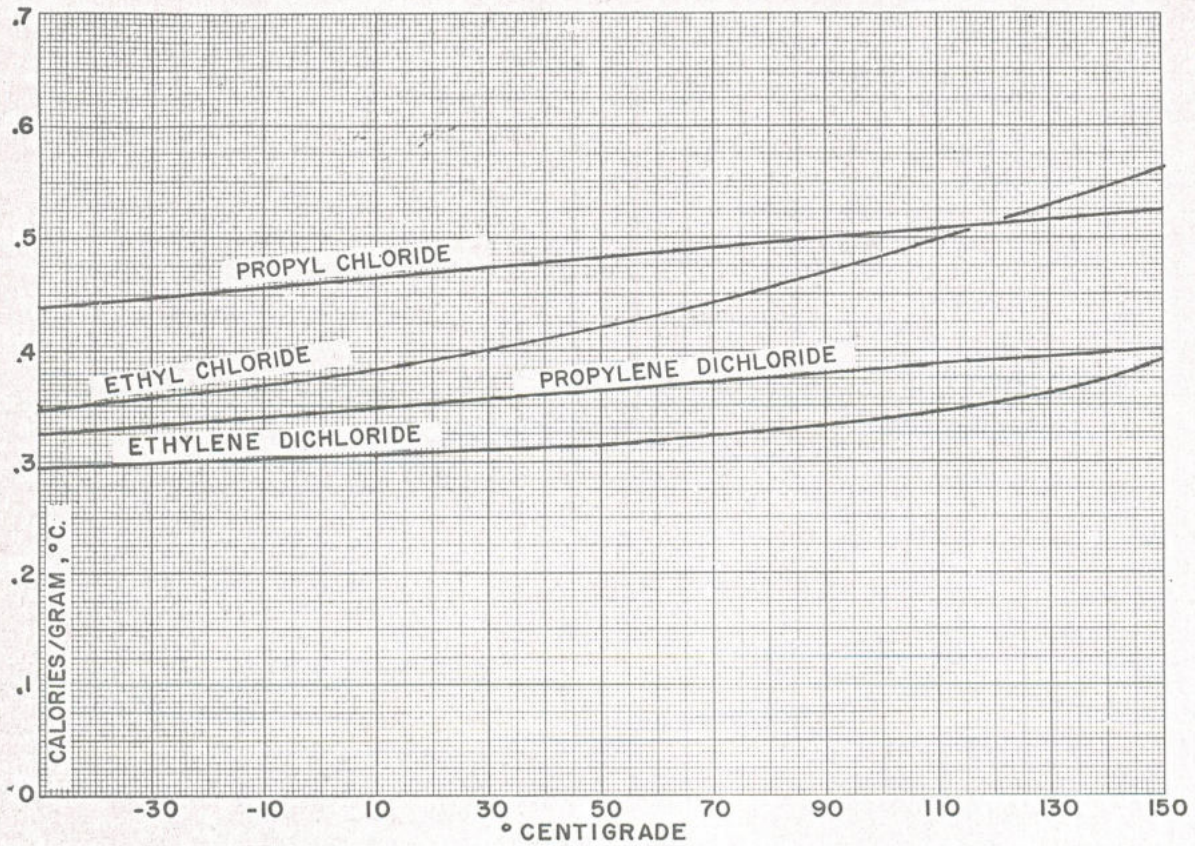


Fig. 7-5—Gives liquid heat capacity over a range of  $-30^{\circ}\text{C}$  to  $+150^{\circ}\text{C}$ .

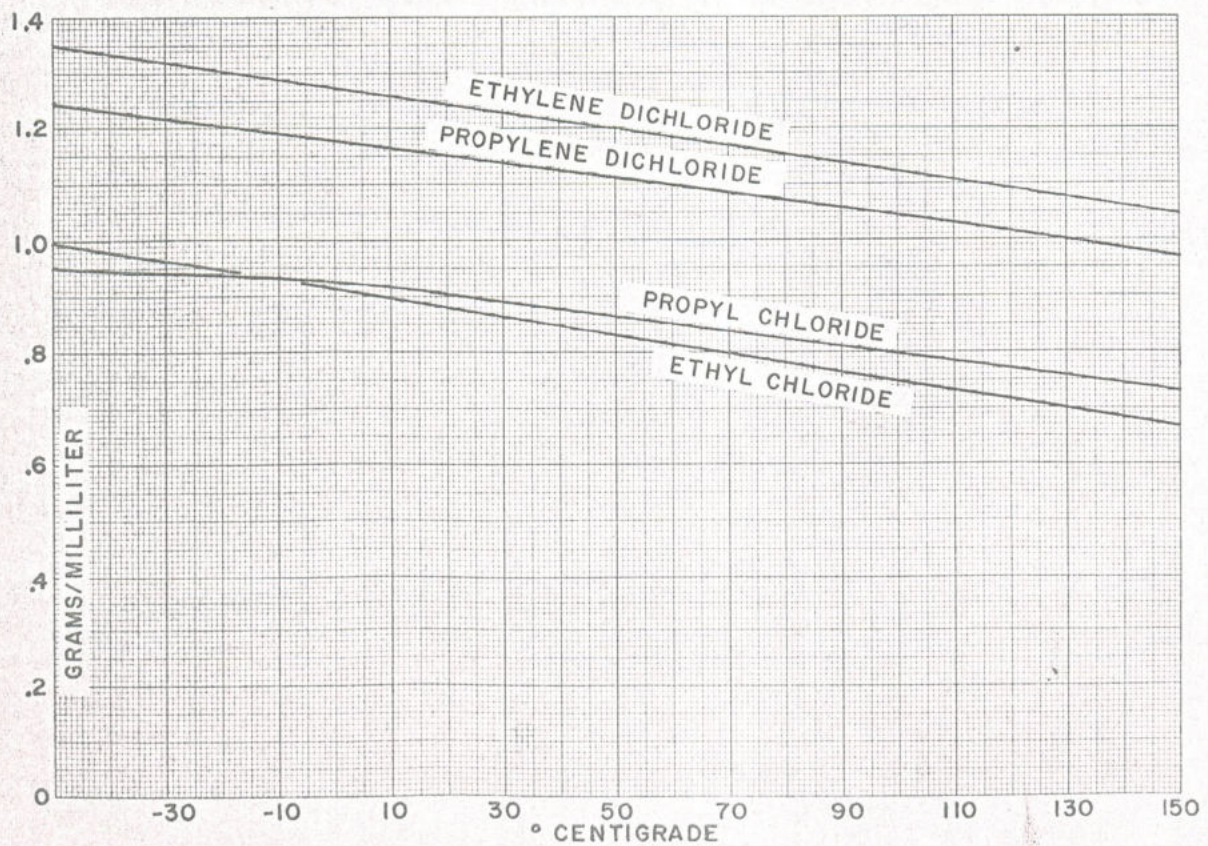


Fig. 7-6—Gives liquid density over a range of  $-30^{\circ}\text{C}$  to  $+150^{\circ}\text{C}$ .

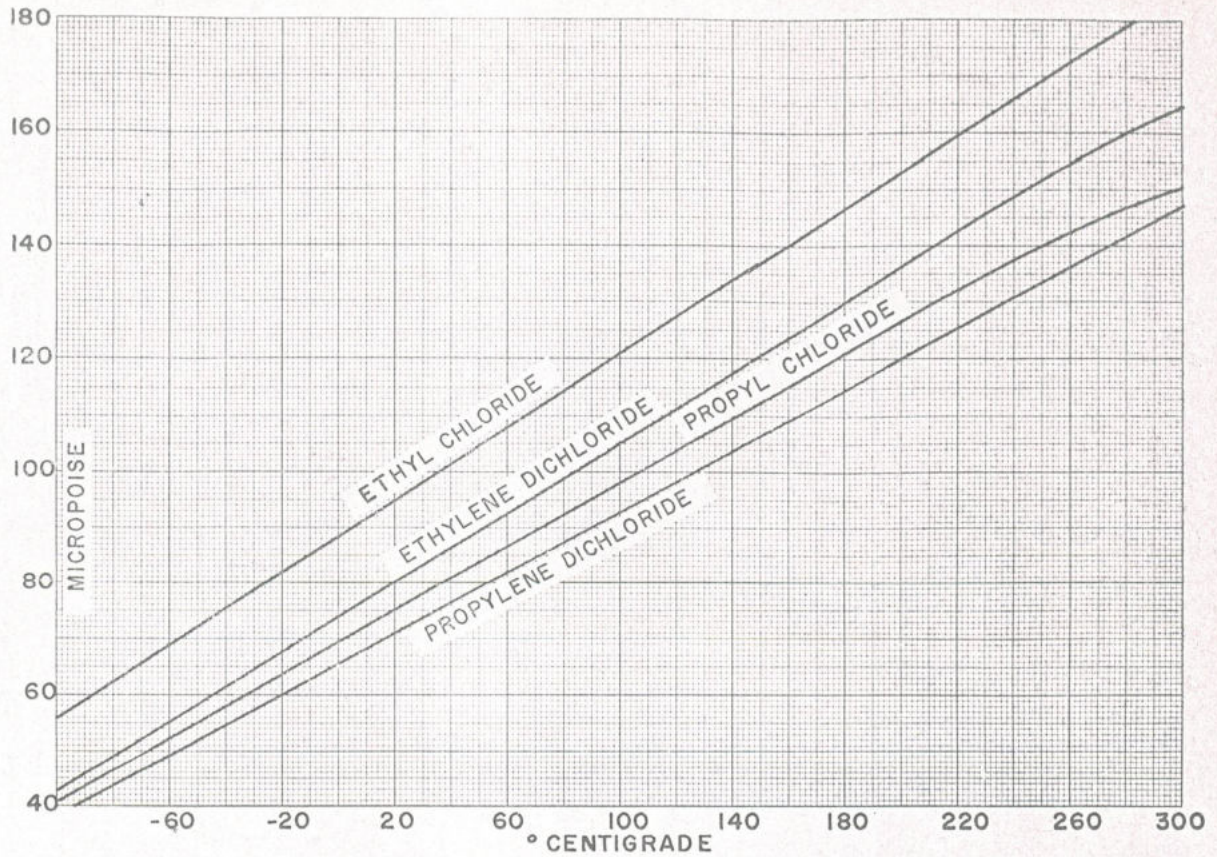


Fig. 7-7—Gives vapor viscosity over a range of  $-60^{\circ}\text{C}$  to  $+300^{\circ}\text{C}$ .

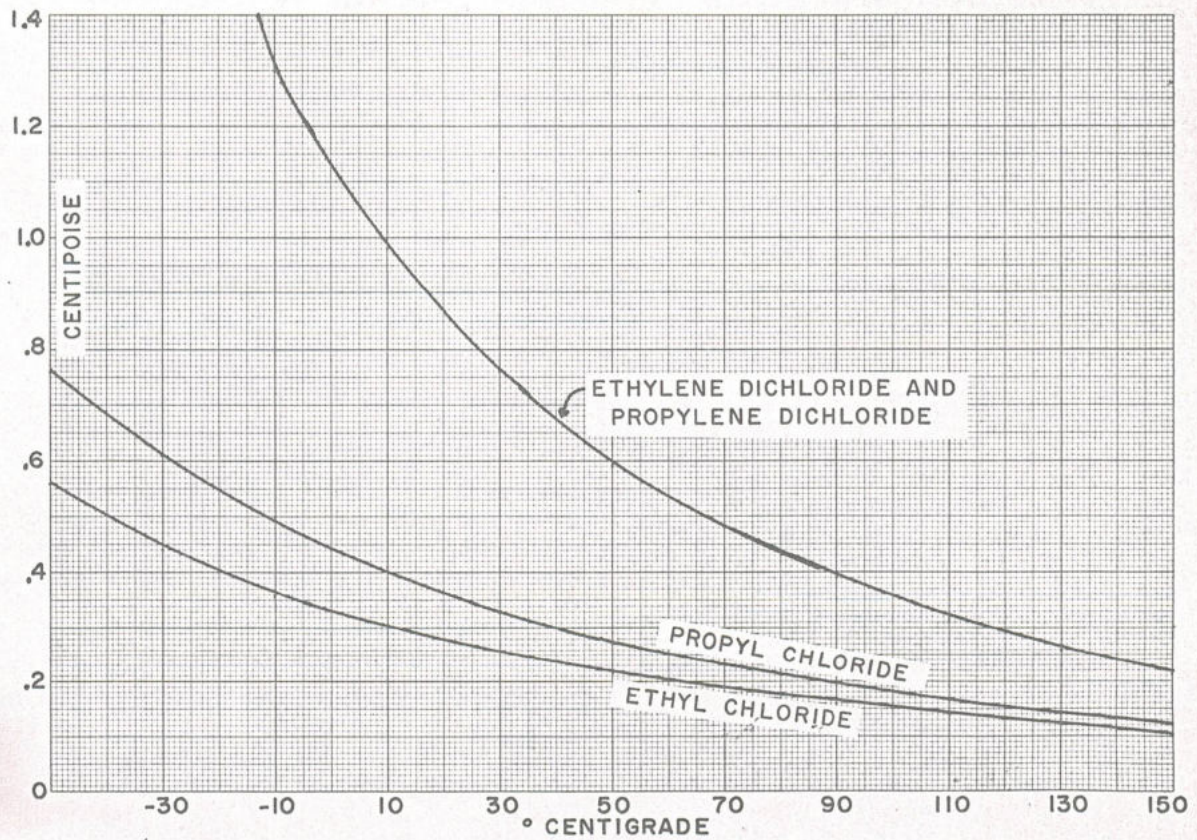


Fig. 7-8—Gives liquid viscosity over a range of  $-30^{\circ}\text{C}$  to  $+150^{\circ}\text{C}$ .

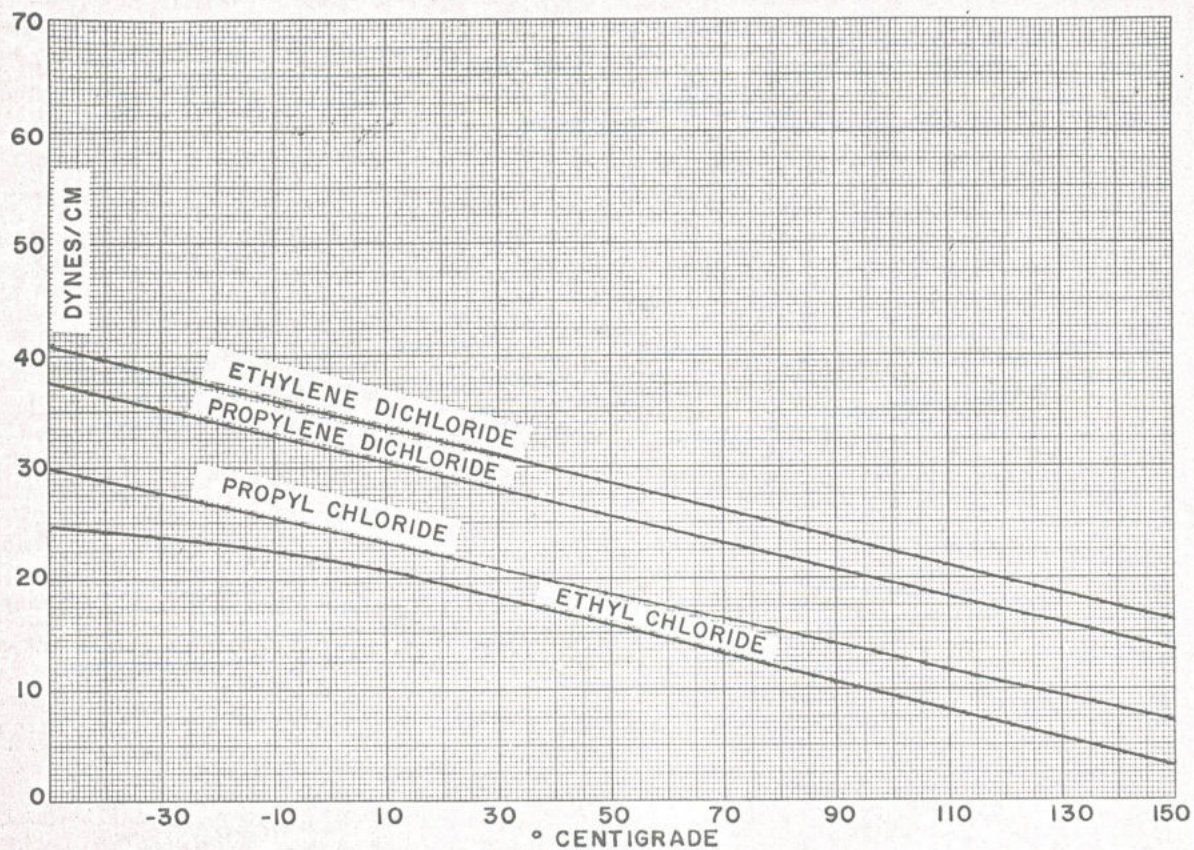


Fig. 7-9—Gives surface tension over a range of  $-30^{\circ}\text{C}$  to  $+500^{\circ}\text{C}$ .

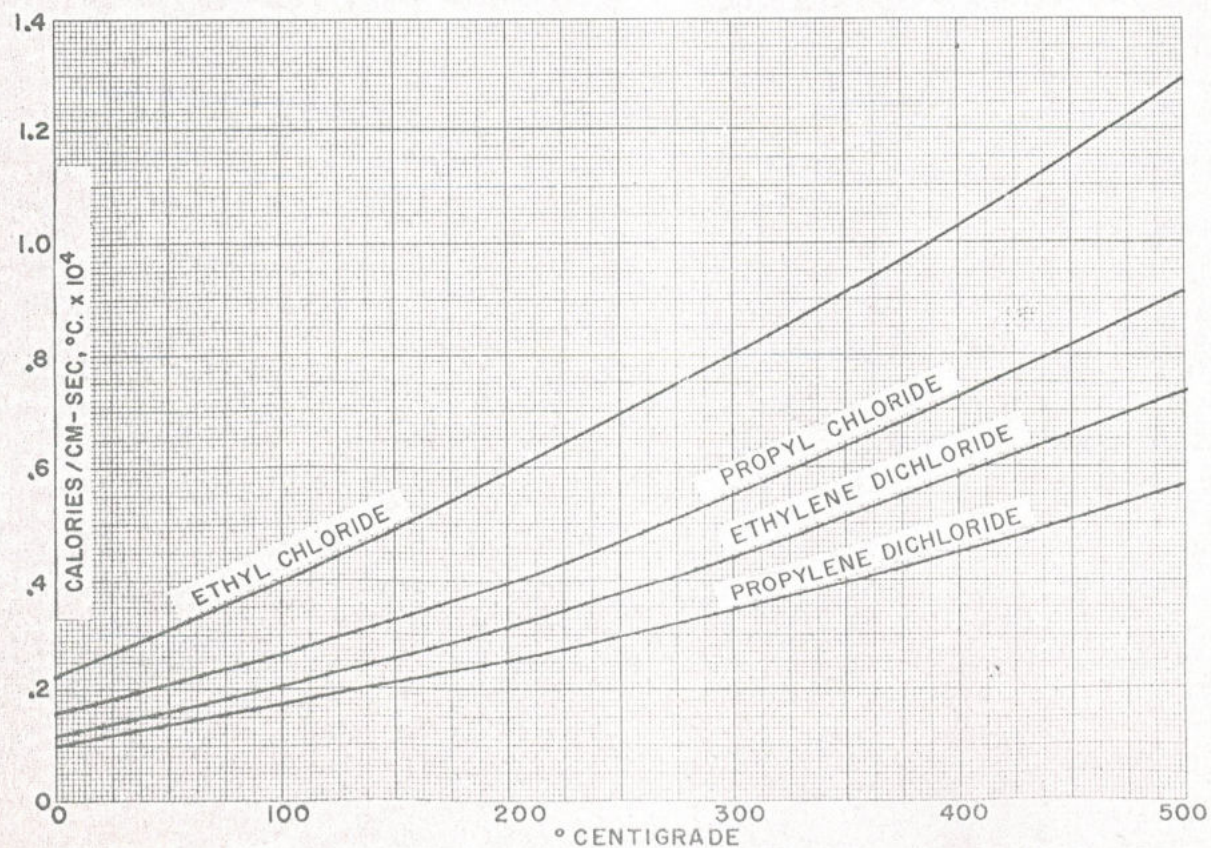


Fig. 7-10—Gives vapor thermal conductivity over a range of  $0^{\circ}\text{C}$  to  $+500^{\circ}\text{C}$ .

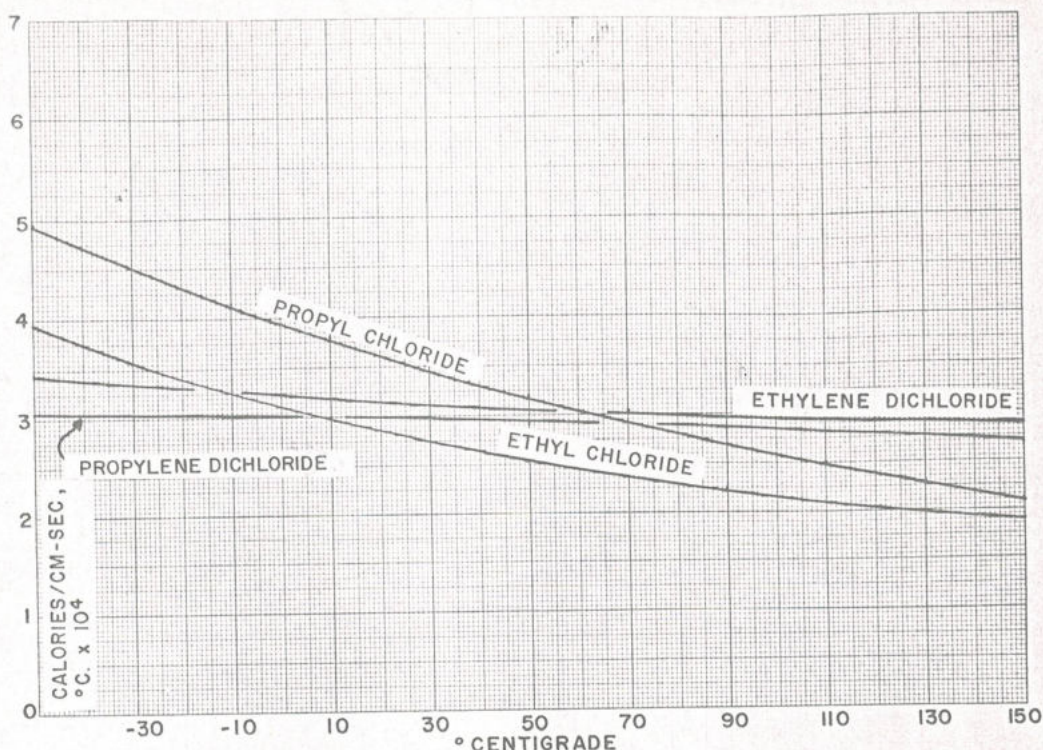


Fig. 7-11—Gives liquid thermal conductivity over range of  $-30^{\circ}\text{C}$  to  $+150^{\circ}\text{C}$ .

When compared with experimental data, the error was 1 — 4 percent.

The liquid viscosities for all four compounds are available in the literature over varying temperature ranges.<sup>2, 5, 7, 17</sup> The data have been extrapolated over a wider temperature range by plotting the log of the viscosity against the reciprocal of the temperature.

**Surface Tension.** Data are available for ethylene dichloride from two sources<sup>18, 19</sup> but the agreement is rather poor at low temperatures. The 10 — 40°C range reported by Dreisbach<sup>7</sup> and Timmermans<sup>2</sup> for the other compounds has been extended by the Nomograph of Kharbanda, which relates the change in surface tension of  $(T_c - T)^{1.2}$ . The error is normally about 2 percent, but the author found errors of 5 — 10 percent for these polar compounds.

**Thermal Conductivity.** The vapor thermal conductivity has been studied for ethyl chloride.<sup>5</sup> The thermal conductivity for the other three compounds has been estimated by the method of Owens and Thodos.<sup>20</sup> When compared to the experimental results for ethyl chloride, the error averaged 2 percent. This is exceptionally good for a polar compound of this type. Only the critical properties are needed to use this method. This represents a major improvement over previous methods.

TABLE 7-1—Chlorinated Aliphatics

Compound	Boiling Point	Freezing Point	Molecular Weight	Critical Properties		
				°C tc	psia Pc	g/ml dc
Chloroethane	12.3	-137	64.52	187	761	0.33
1, 2-Dichloro-ethane	83.5	-35.5	98.97	290	780	.45
1-Chloropropane	46.5	-122.6	78.54	230	663	.37
1, 2-Dichloro-propane	96.4	-100.5	112.99	304	641	.41

It is always a pleasure to find a new estimation method that improves the state of the art. Robbins and Kingrea<sup>21</sup> have developed an equation for the liquid thermal conductivity that works very well even on polar compounds. The equation represents a theoretical approach coupled with some empirical additions to improve the accuracy. The equation requires knowledge of the liquid density and heat capacity over the temperature range. If these are available, the error will normally be less than 5 percent. Since no reliable experimental data are available on the four compounds, the data were all determined by this estimation method.

LITERATURE CITED

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<sup>8</sup> Mellan, I., *Source Book of Industrial Solvents, Vol. II*, Reinhold Publishing Corporation, New York (1957).  
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<sup>13</sup> Pitzer, K. S., *Ibid* 62, pp. 331-35 (1940).  
<sup>14</sup> Reid, R. C. and Sherwood, T. K., *The Properties of Gases and Liquids*, McGraw-Hill Book Company, New York (1958).  
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<sup>18</sup> Gallaugher, A. F., *Ibid* 59, pp. 2514-21 (1937).  
<sup>19</sup> Hojendahl, K., *Kgl. Danske Videnskab Selskab, Mat-Fys. Medd.* 24 (2) (1946).  
<sup>20</sup> Owens, E. J. and Thodos, G., *AIChE J.* 6 (4), pp. 676-81 (1960).  
<sup>21</sup> Robbins, L. A., and Kingrea, C. L., *Division of Refining* 42, (III), pp. 52-60 (1962).

Part 8 will appear in an early issue