

# Physical Properties of Hydrocarbons

## Part 22—Fluorinated Hydrocarbons

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THE PREVIOUS two parts in this series have presented the physical properties of chlorofluorohydrocarbons. This concluding part covers four commercially important fluorinated hydrocarbons. Two of these—trifluoromethane and hexafluoroethane—find general use as refrigerants and aerosols. Vinyl fluoride and vinylidene fluoride are monomers for plastics. The relatively high price of the monomers precludes any general competition with such large-volume plastics as polyvinylchloride, polyethylene or polystyrene. The fluorocarbon plastics have carved out specialty markets where their unique properties offset the high cost.

Because of the extremely low boiling points and limited number of market applications, the physical properties of these compounds have not been studied extensively.

**Vapor Pressure and Critical Properties.** The critical properties of all four compounds are available from the literature.<sup>1,2,3</sup> Vapor pressure data have been determined for trifluoromethane<sup>1,2,4</sup> and hexafluoroethane.<sup>1</sup> The vapor pressures of vinyl fluoride and vinylidene fluoride were calculated from the equation,

$$\log Pr = A(1 - 1/Tr)$$

where

$Pr$  = reduced pressure

$Tr$  = reduced temperature

$A$  = a constant, calculated from an experimental value (i.e., the boiling point)

This method gave an average error of 1.3 percent when compared to experimental data on similar compounds.

**Heat of Vaporization.** Mears and co-workers have measured the heat of vaporization of vinylidene fluoride over the temperature range of  $-40^{\circ}\text{C}$  to the critical point.<sup>3</sup> The heat of vaporization at the boiling point has been determined by Valentine<sup>4</sup> for trifluoromethane and by Pace and Aston<sup>5</sup> for hexafluoroethane. No data are available on vinyl fluoride. Consequently, the heat of vaporization at the boiling point has been estimated by the method of Giacalone,<sup>6</sup> which relates the heat of vaporization to the reduced pressure and reduced temperature. For similar compounds, this method yielded an average error of 2 percent. The data for all four compounds were extended over a wider range by the Kharbanda monograph<sup>7</sup> of the

Watson equation, with a probable error of about 2 percent.

**Heat Capacity.** The vapor heat capacities have been determined for trifluoromethane<sup>4</sup> from  $-173^{\circ}$  to  $+227^{\circ}\text{C}$  and for hexafluoroethane<sup>8</sup> from  $-50^{\circ}$  to  $+90^{\circ}\text{C}$ . The method of Rihani and Doraiswamy<sup>9</sup> has been used to calculate the heat capacities of all four compounds from  $-100^{\circ}$  to  $+900^{\circ}\text{C}$ . Above  $100^{\circ}\text{C}$ , this method is very accurate.

Valentine<sup>4</sup> has measured the liquid heat capacity of trifluoromethane from  $-155^{\circ}$  to  $-82^{\circ}\text{C}$ . Pace and Aston<sup>5</sup> determined it for hexafluoroethane from  $-98^{\circ}$  to  $-78^{\circ}\text{C}$ . No data are available for vinyl fluoride or vinylidene fluoride. Methods for estimating liquid heat capacity without any experimental data give very poor results for halogenated compounds. The author estimated a liquid heat capacity for these two compounds at  $-40^{\circ}\text{C}$  by comparing their molecular structures with similar compounds for which experimental data are available. The value of 0.28 calories/gram  $-^{\circ}\text{C}$  was chosen for vinyl fluoride and 0.26 for vinylidene fluoride. The error is probably less than 10 percent. The data for all four compounds have been extended over the  $-120^{\circ}$  to  $0^{\circ}\text{C}$  range by the method described in the previous article. This method yielded an average error of 1.8 percent when compared to five experimental values for trifluoromethane and hexafluoroethane.

**Density.** Density data are available for trifluoromethane<sup>2</sup> from  $-67^{\circ}\text{C}$  to the critical point and for vinylidene fluoride<sup>3</sup> from  $-45^{\circ}\text{C}$  to the critical point. Data on the other two compounds are available only at one temperature point.<sup>1</sup> The method of Lyderson, Greenkorn and Hougen<sup>6</sup> has been used to extend the data. This method gave an average error of 1.0 percent and a maximum error of 3.1 percent when compared to 8 experimental values.

TABLE 22-1—Physical Properties of Fluorinated Hydrocarbons

Compound	Commercial Trade Name	Boiling Point $^{\circ}\text{C}$	Freezing Point $^{\circ}\text{C}$	Molecular Weight	Critical Properties		
					$^{\circ}\text{C}$ $T_c$	psia $P_c$	g/ml $d_c$
Trifluoromethane.....	Fluorocarbon-23	-82.0	-155.2	70.0	25.9	701.4	.525
Hexafluoromethane....	Fluorocarbon-116	-78.2	-100.6	138.0	19.7	432	.601
Vinyl Fluoride.....	.....	-72.0	-160	46.0	54.7	760	.320
Vinylidene Fluoride....	.....	-85.7	.....	64.0	30.1	643	.417



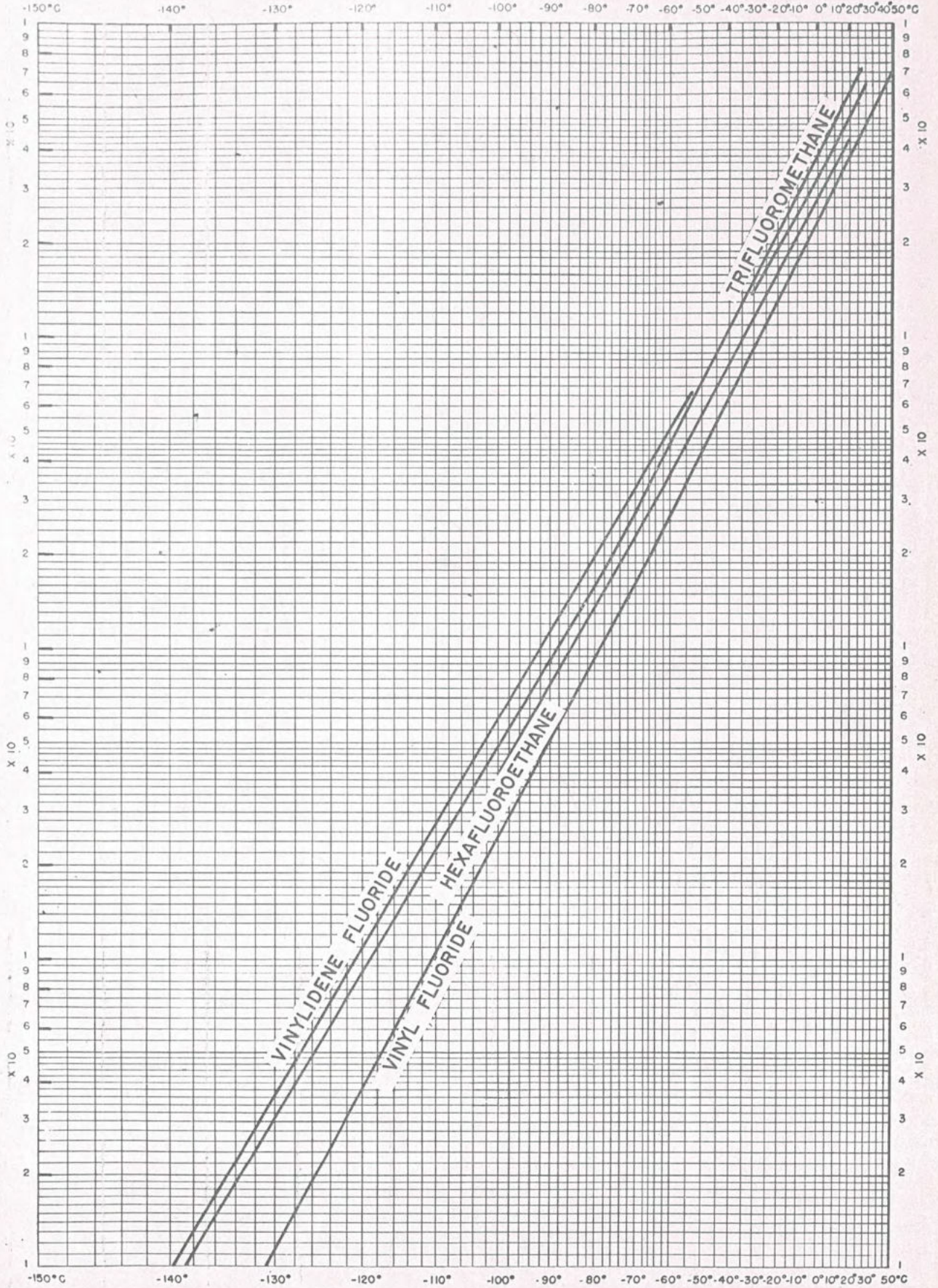


Fig. 22-1—Gives vapor pressure of fluorinated hydrocarbons from -140° C to +50° C.



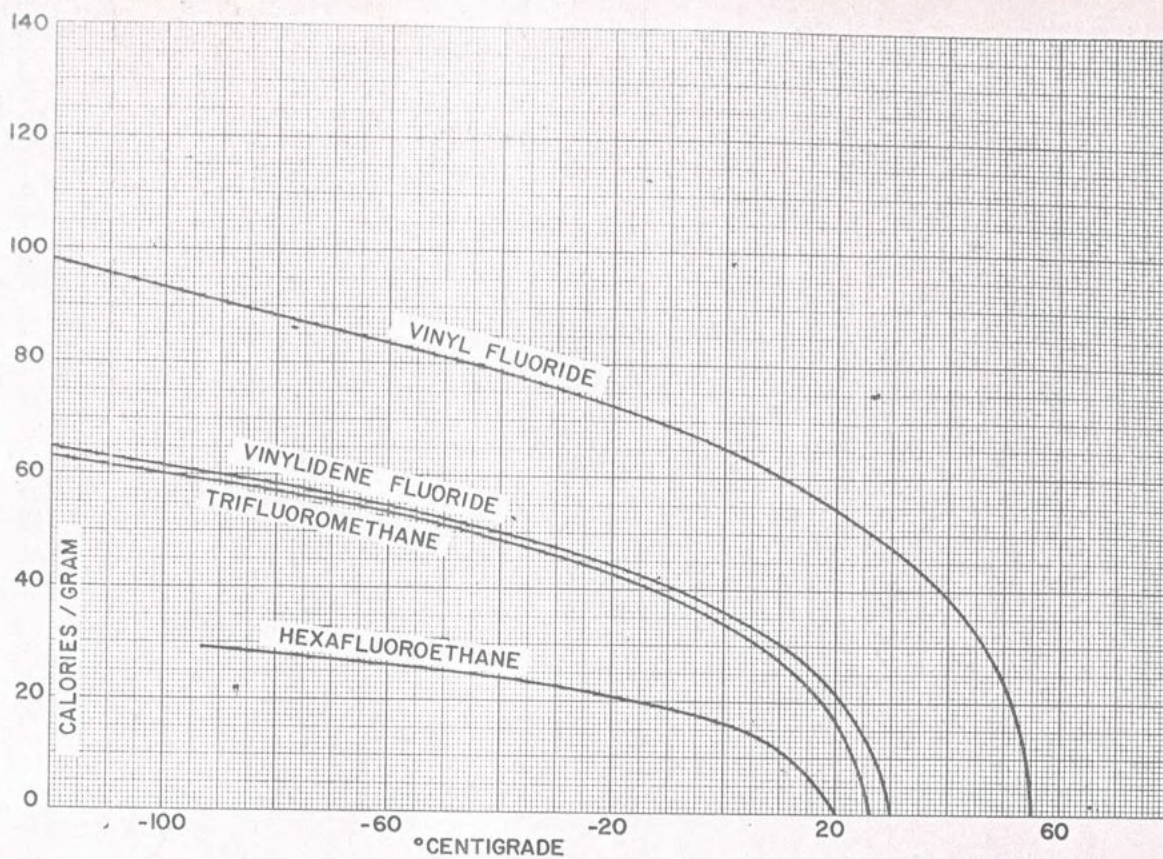


Fig. 22-2—Gives heat of vaporization of fluorinated hydrocarbons from  $-120^{\circ}\text{C}$  to  $+60^{\circ}\text{C}$ .

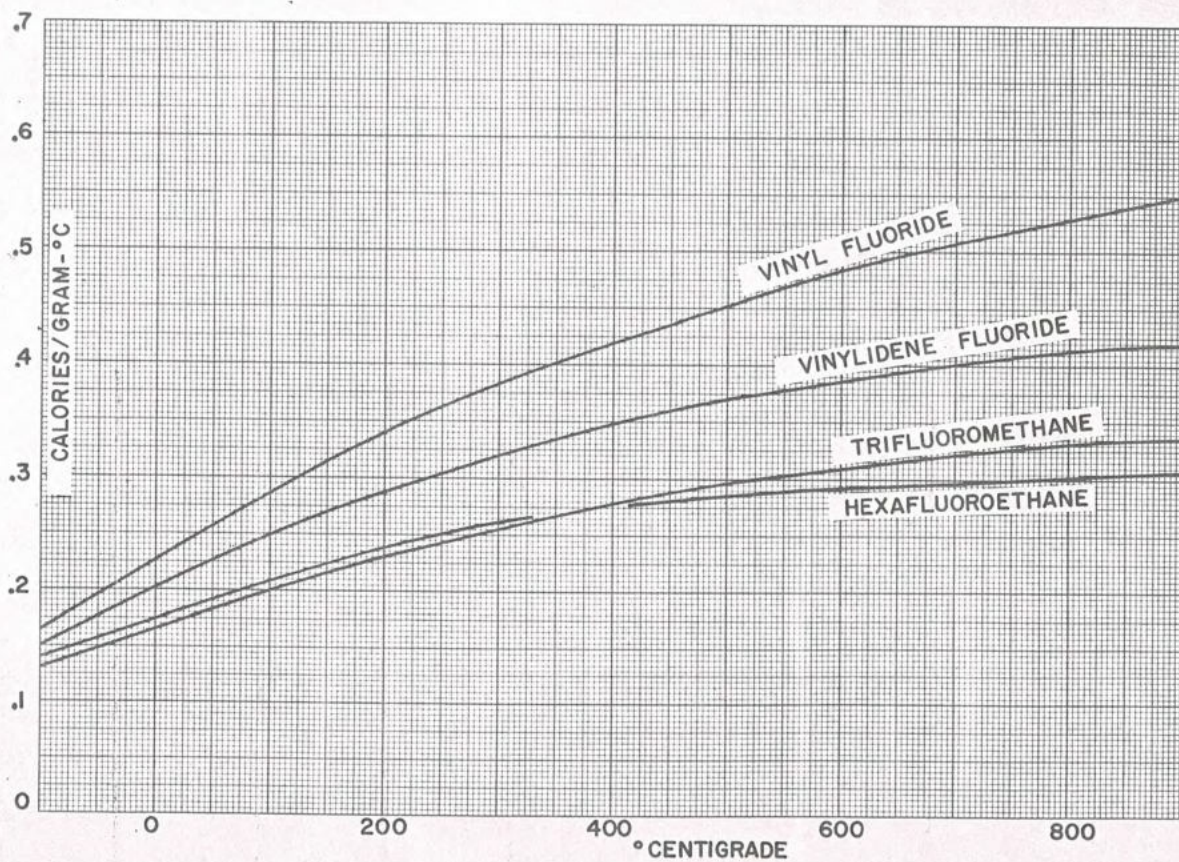


Fig. 22-3—Gives vapor heat capacity of fluorinated hydrocarbons from  $100^{\circ}\text{C}$  to  $+900^{\circ}\text{C}$ .



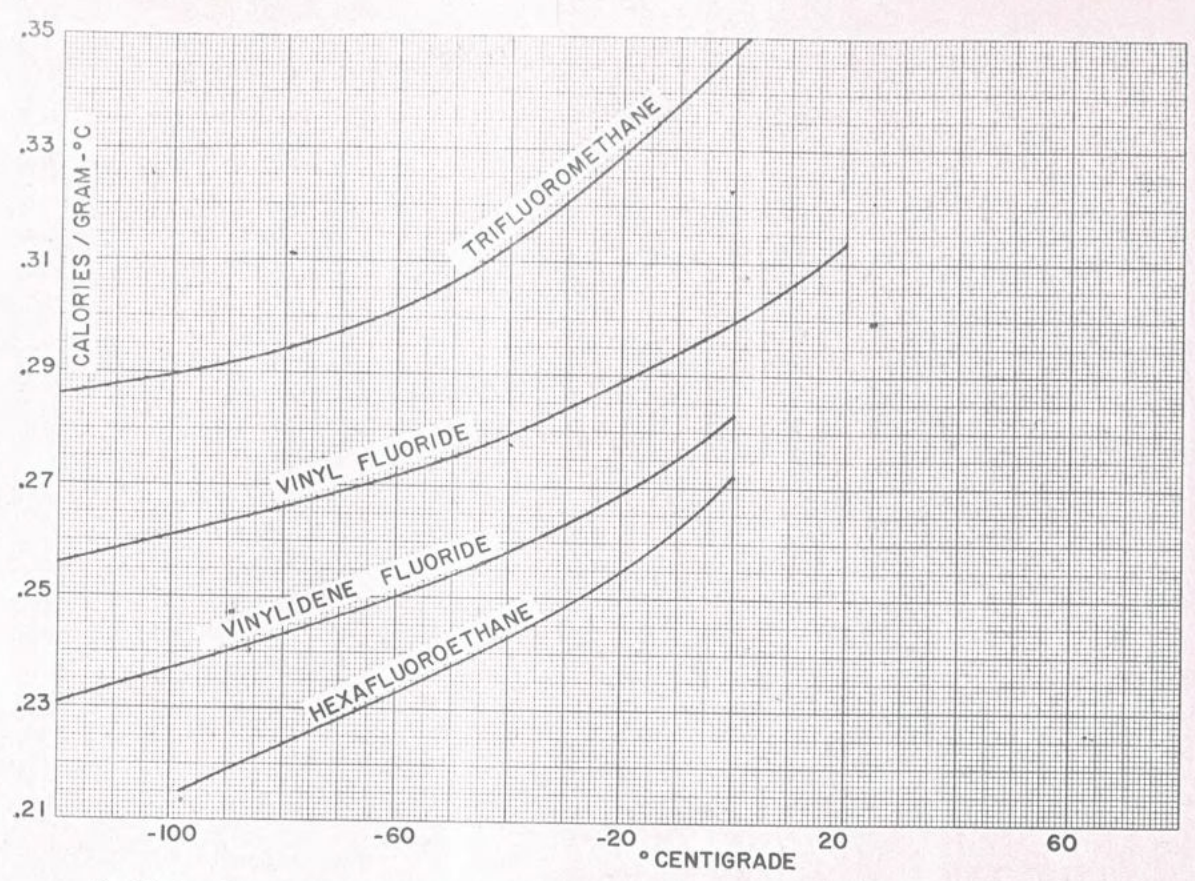


Fig. 22-4—Gives liquid heat capacity of fluorinated hydrocarbons from - 120° C to + 20° C.

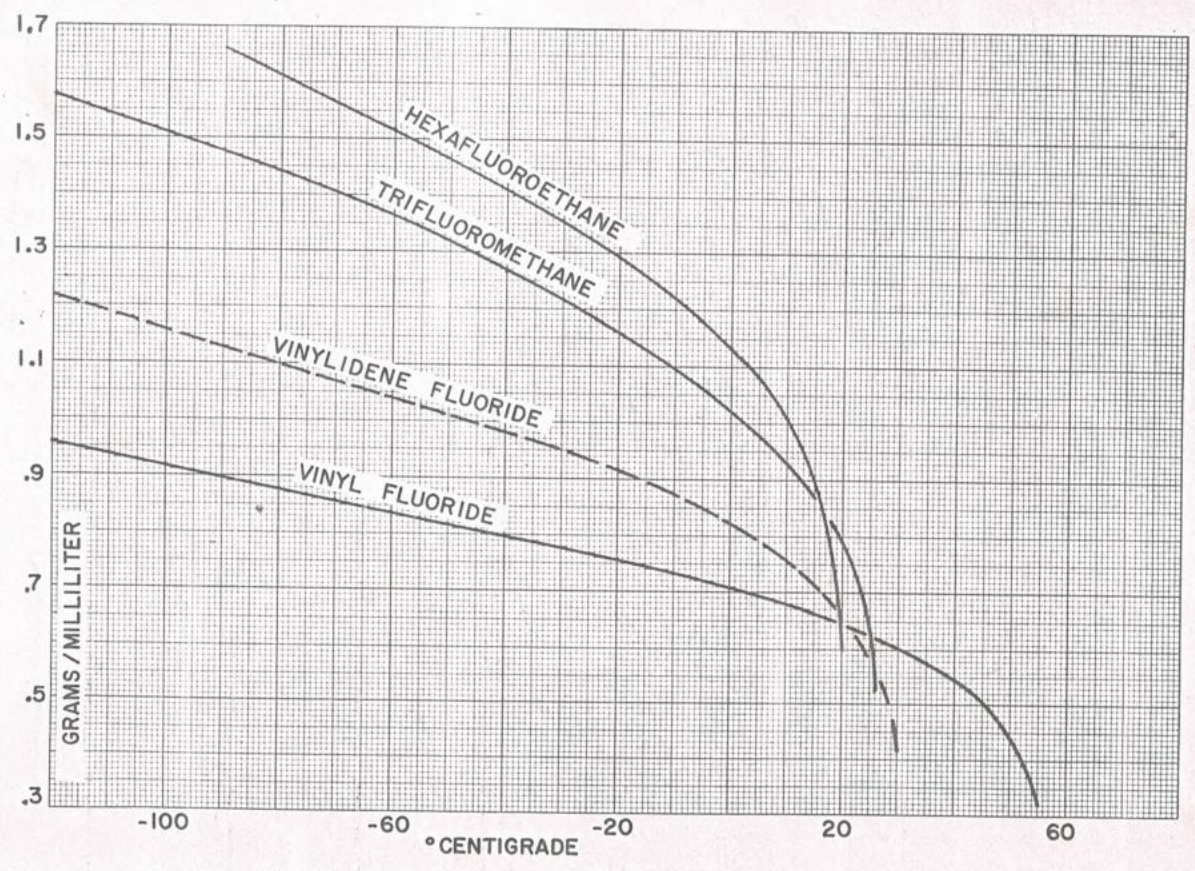


Fig. 22-5—Gives liquid density of fluorinated hydrocarbons from - 120° C to + 55° C.



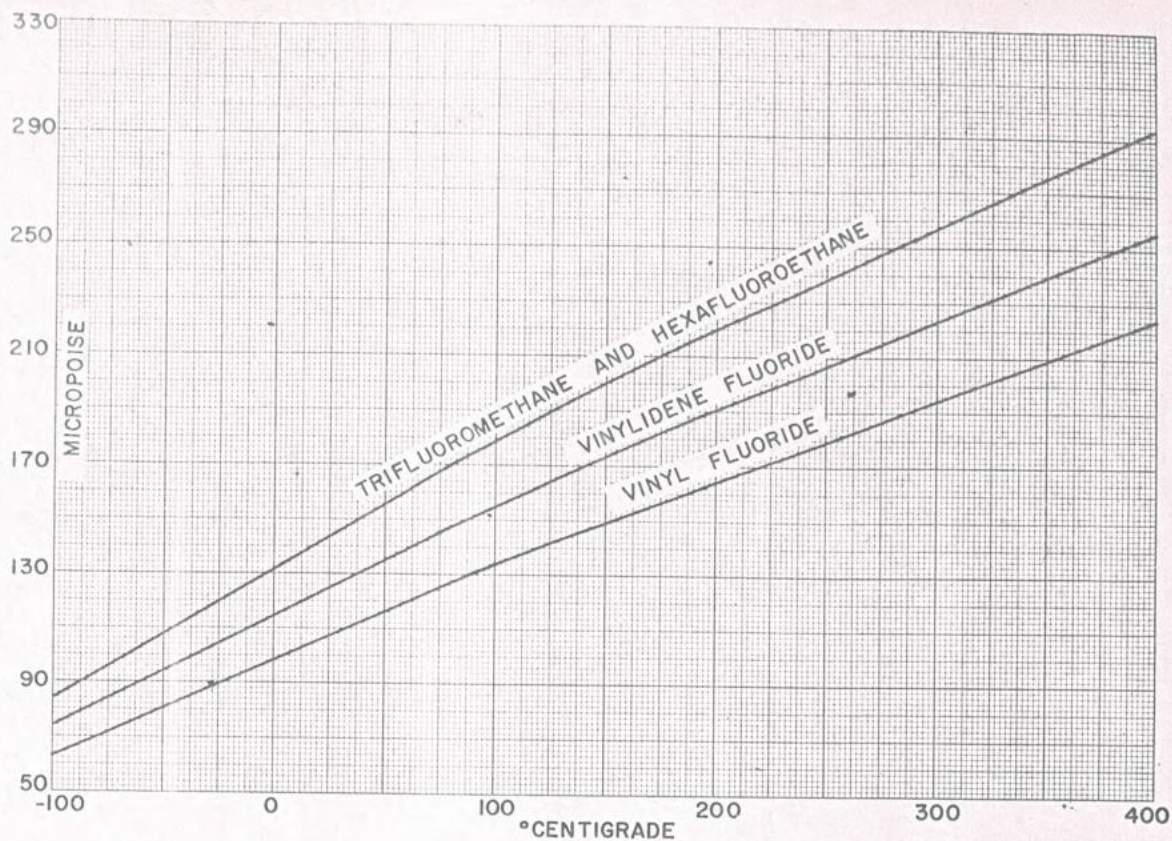


Fig. 22-6—Gives vapor viscosity of fluorinated hydrocarbons from  $-100^{\circ}\text{C}$  to  $+400^{\circ}\text{C}$ .

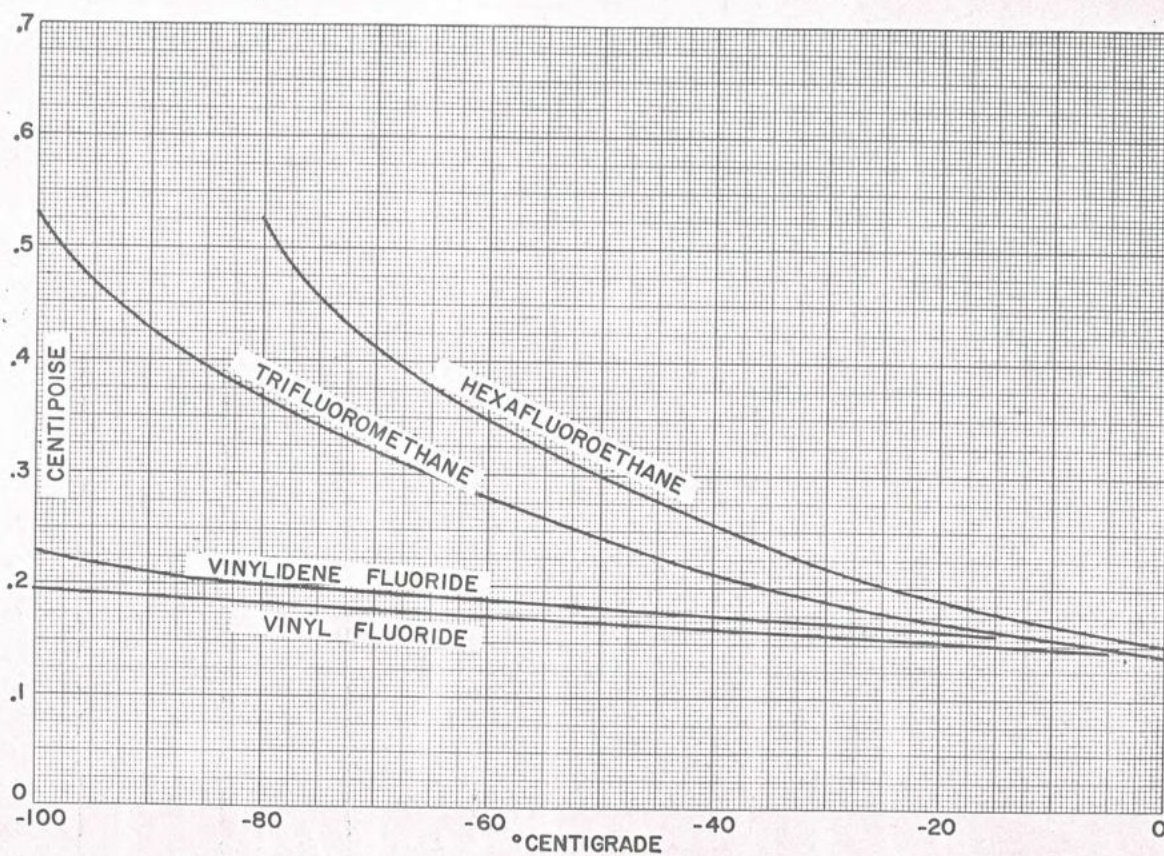


Fig. 22-7—Gives liquid viscosity of fluorinated hydrocarbons from  $-100^{\circ}\text{C}$  to  $+0^{\circ}\text{C}$ .



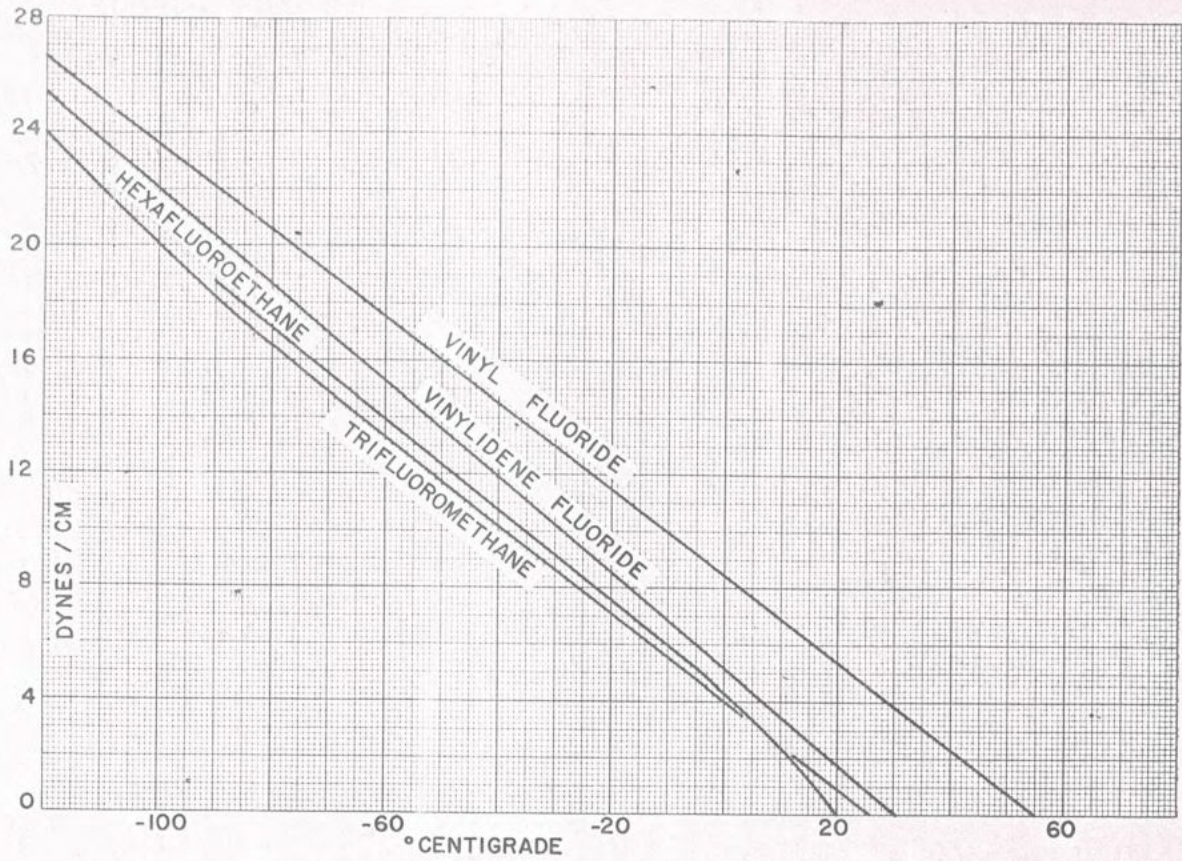


Fig. 22-8—Gives surface tension of fluorinated hydrocarbons from  $-120^{\circ}\text{C}$  to  $+55^{\circ}\text{C}$ .

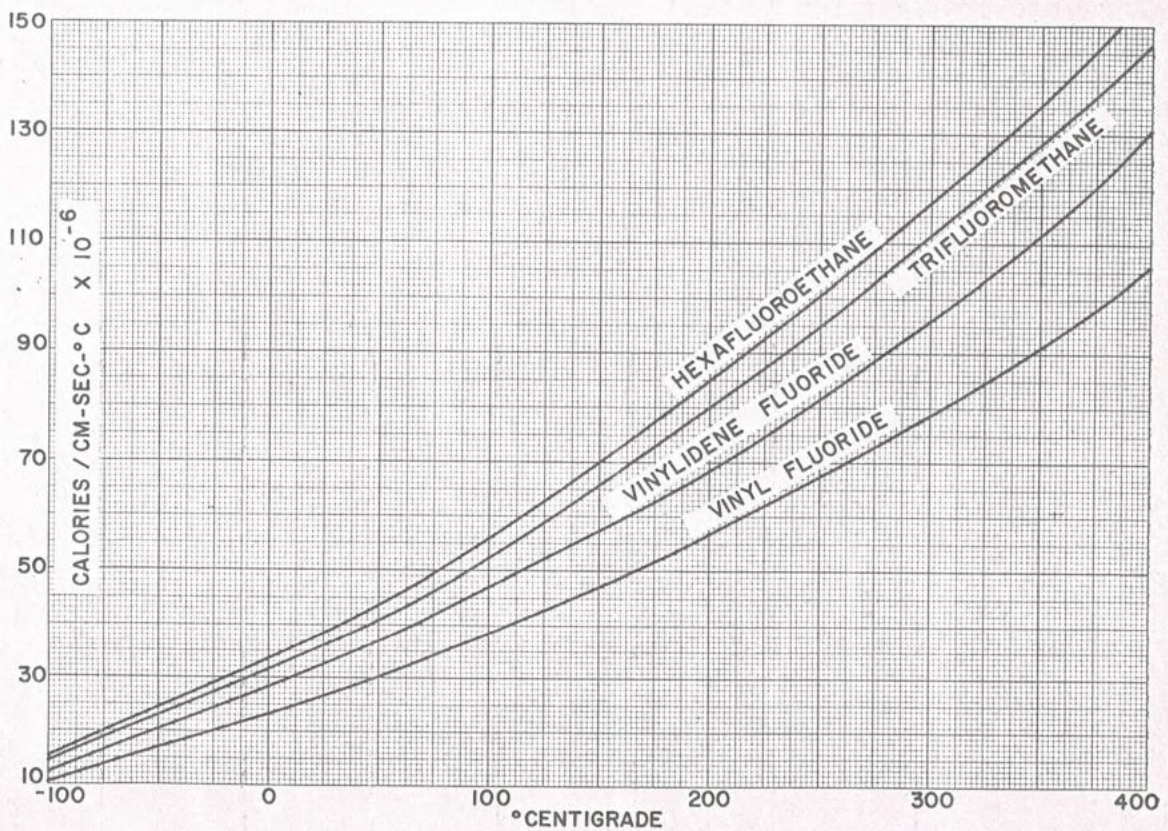


Fig. 22-9—Gives vapor thermal conductivity of fluorinated hydrocarbons from  $-100^{\circ}\text{C}$  to  $+400^{\circ}\text{C}$ .



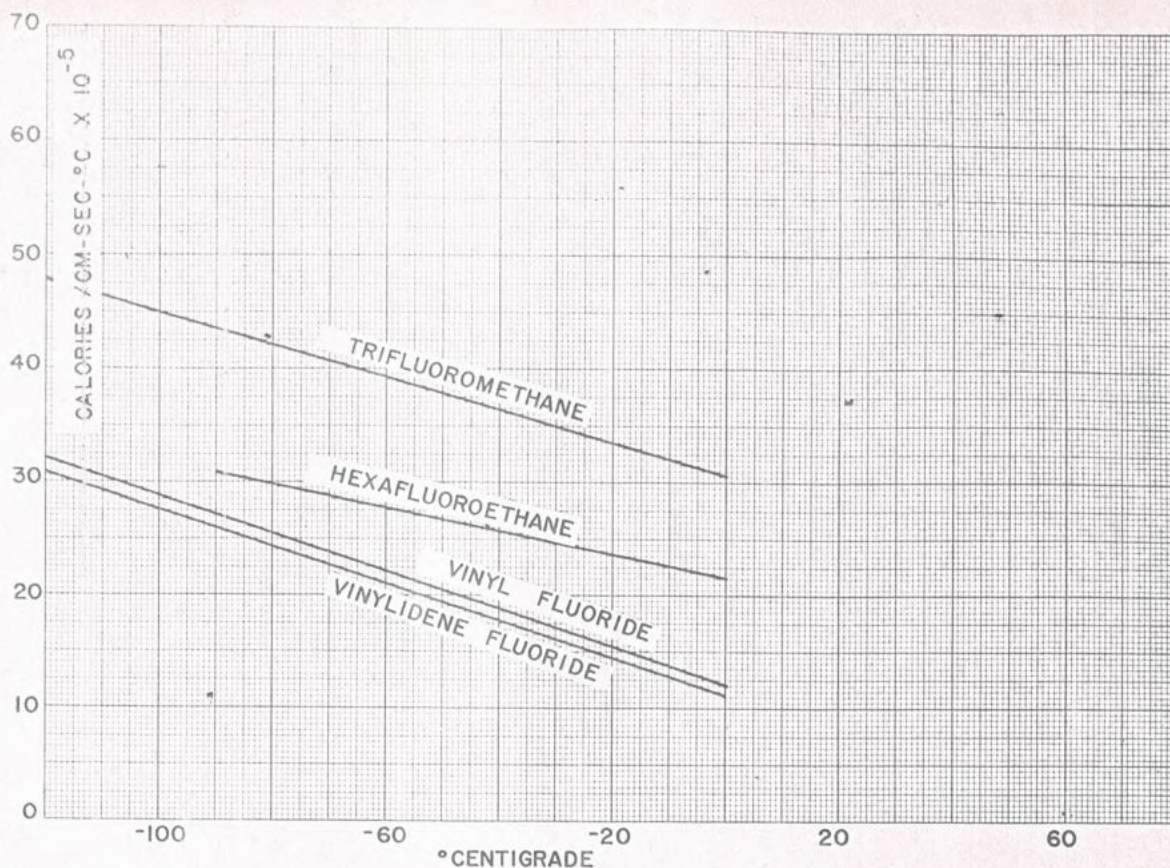


Fig. 22-10—Gives liquid thermal conductivity of fluorinated hydrocarbons from  $-120^{\circ}\text{C}$  to  $0^{\circ}\text{C}$ .

**Viscosity.** Witzell and Johnson<sup>10</sup> have measured the vapor viscosity of trifluoromethane from  $-37^{\circ}$  to  $+200^{\circ}\text{C}$ . No data are available for the other three compounds. The method of Bromley and Wilke<sup>11</sup> was used to calculate the viscosity over the range of  $-100^{\circ}$  to  $+400^{\circ}\text{C}$ , with an average error of 1.1 percent.

With no data available, the method of Thomas<sup>6</sup> has been used to estimate the liquid viscosities of the four compounds. The error is normally 10-20 percent.

**Surface Tension.** The only data available are for trifluoromethane and hexafluoroethane at  $-73^{\circ}\text{C}$ .<sup>1</sup> The surface tension has been estimated by the equation,

$$S = \frac{[P(d_l - d_v)]^4}{M}$$



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where

- $S$  = Surface tension, dynes/cm  
 $P$  = Parachor, calculated from molecular structure  
 $d_l$  = Density of the liquid, g/cc  
 $d_v$  = Density of the vapor, g/cc  
 $M$  = Molecular weight

The error is normally about  $\pm 10$  percent.

**Thermal Conductivity.** The thermal conductivities of the vapor and liquid have been calculated by methods previously described.<sup>12, 13</sup>

#### LITERATURE CITED

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**Indexing Terms:** Computations-4, Fluorinated Hydrocarbons-9, Halogenated Hydrocarbons-9, Heat-7, Hexafluoromethane-9, Liquid Phase-5, Physical Properties-7, Pressure-6, Properties/Characteristics-7, Temperature-6, Trifluoromethane-9, Vapor Phase-5, Vinylidene Fluoride-9, Vinyl Fluoride-9.

Part 23—"Brominated Hydrocarbons" will appear in an early issue.