Physical Properties of Hydrocarbons

PART 33–Methylamines

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IN THE PAST 20 YEARS, the methylamines have grown from a semi-commercial status to major products with production of about 100 million pounds per year. Dimethylamine (DMA) accounts for the majority of this production. The methylamines are largely used as intermediates in the production of surface active agents, agricultural chemicals, and pharmaceuticals.

The most common manufacturing method for the methylamines is to react methanol and ammonia in the presence of alumina at high temperature and pressure.

The physical properties of all three methylamines have been studied in depth. Because methylamine is often encountered as an aqueous solution, the physical properties of the water solutions are also included in this article.

Critical Properties and Vapor Pressure. The critical properties and the vapor pressures from the freezing point to the critical point have been experimentally determined.[1,2,3]

Figs. 33-2, 33-3 and 33-4 present the vapor pressure of aqueous solutions of the methylamines.[2] The boiling points at atmospheric pressure for the aqueous solutions from 0 - 100 percent are shown in Fig. 33-5.[1]

Heat of Vaporization. Aston and co-workers have measured the heat of vaporization at the boiling point.[4,5,6] These data were extended over a wide temperature range by the Kharbanda nomograph, with a probable error of only a few percent.[7]

Heat Capacity. Kobe and Harrison have calculated the vapor heat capacities of all three compounds from spectroscopic data.[8] Aston and Doty measured the vapor heat capacity from 0 - 50°C.[9] The two methods agree closely.

The liquid heat capacities have been measured from the melting point to the boiling point.[5,6,10] These data were extended to 80°C by use of the equation: density times heat capacity equals a constant. The error should be only a few percent.

Density. Experimental data are available for methylamine from −82° to +60°C, for dimethylamine from −10 to +60°C, and for trimethylamine from −10 to +60°C.[1,2,10,11,12,13] The data have been extended to the critical point by the Othmer method in the literature.[2]

Figs. 33-10, 33-11 and 33-12 present the aqueous densities of methylamines from 0-50°C.[1,2,10]

Viscosity. The vapor viscosities were calculated by the equation proposed by Bromley and Wilke, with a probable error of 2 - 5 percent.

The liquid viscosities of dimethylamine and trimethylamine have been measured from −33°C to +35°C.[15,16] Only the viscosity at 0°C has been measured for methylamine.[15] The viscosities from −40°C to +60°C were calculated by the method of Thomas.[17] His equation relates viscosity to the density, reduced temperature, and a vis-

TABLE 33-1—Physical Properties of Methylamines

Compound	Abbreviation	Boiling Point	Freezing Point	Molecular Weight	Critical Properties		
					T_c °C	P_c psia	d_c g/ml
Methylamine......	MMA	-6.45	−92.5	31.06	156.9	1080	0.216
Dimethylamine....	DMA	6.88	−92.2	45.09	164.6	760	0.256
Trimethylamine...	TMA	2.87	−117.3	59.11	160.2	591	0.233

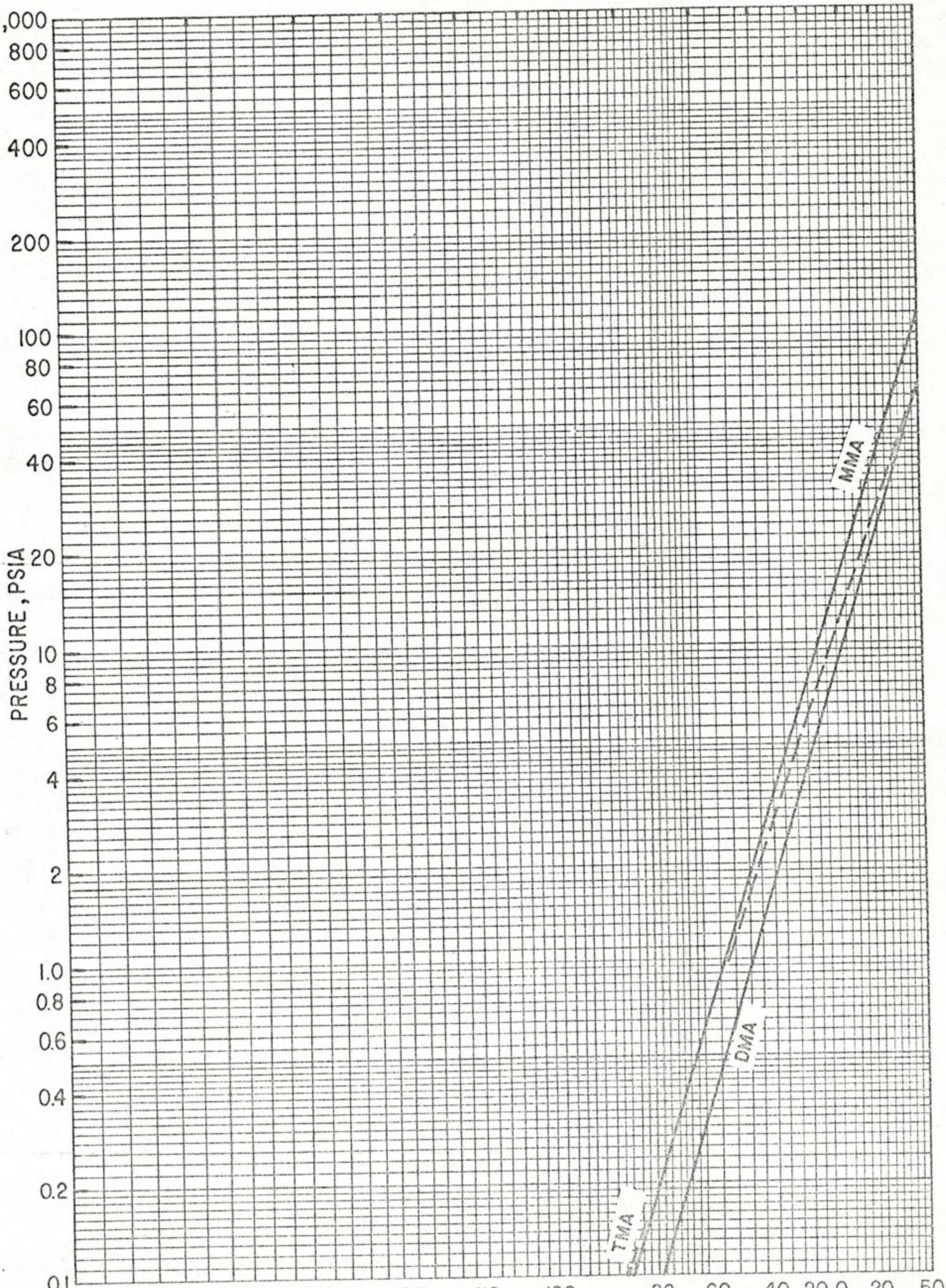


Fig. 33-1—Vapor pressure of methylamines from −80° C to +50° C.

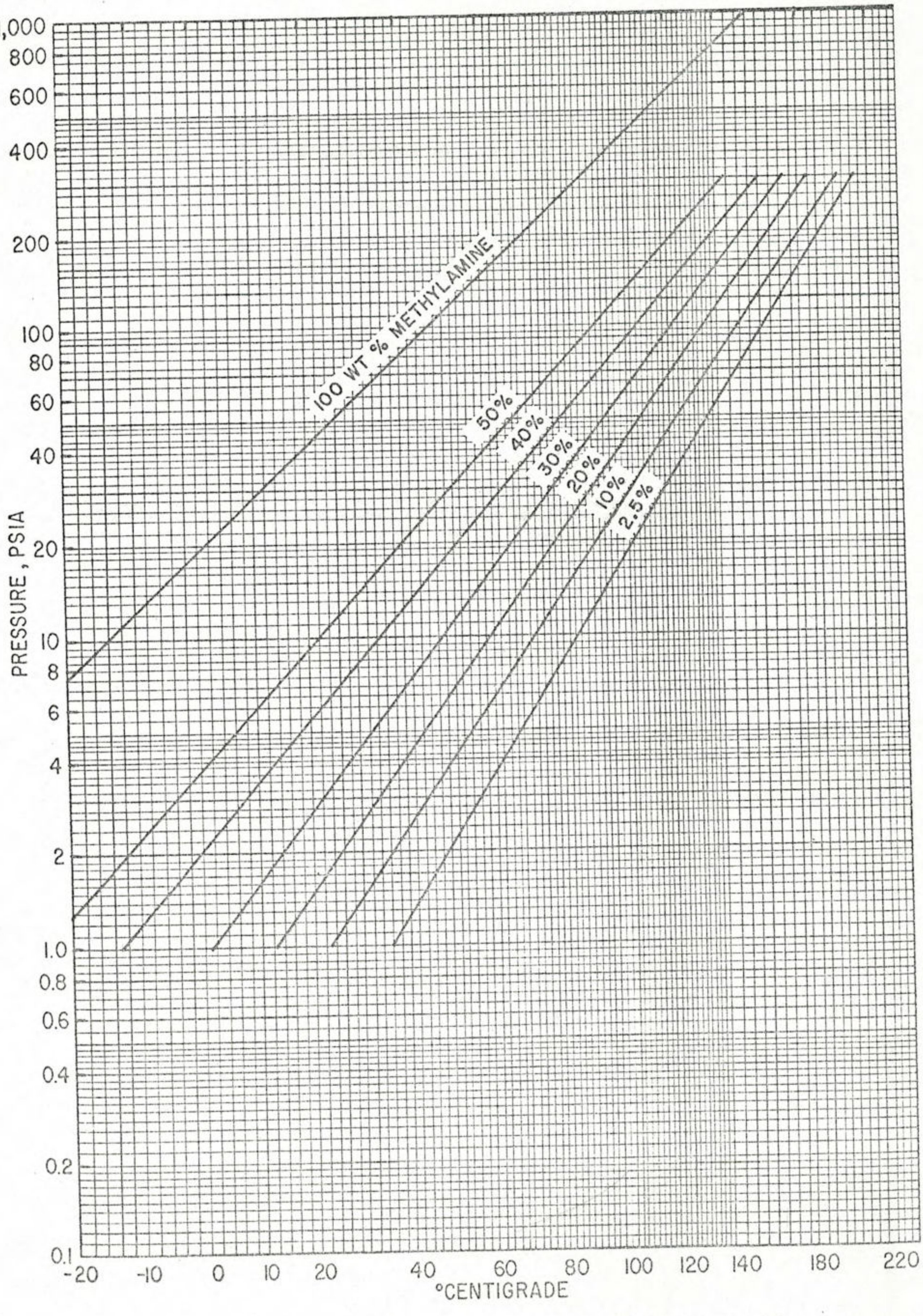


Fig. 33-2—Vapor pressure of aqueous methylamine from −20° C to +220° C.

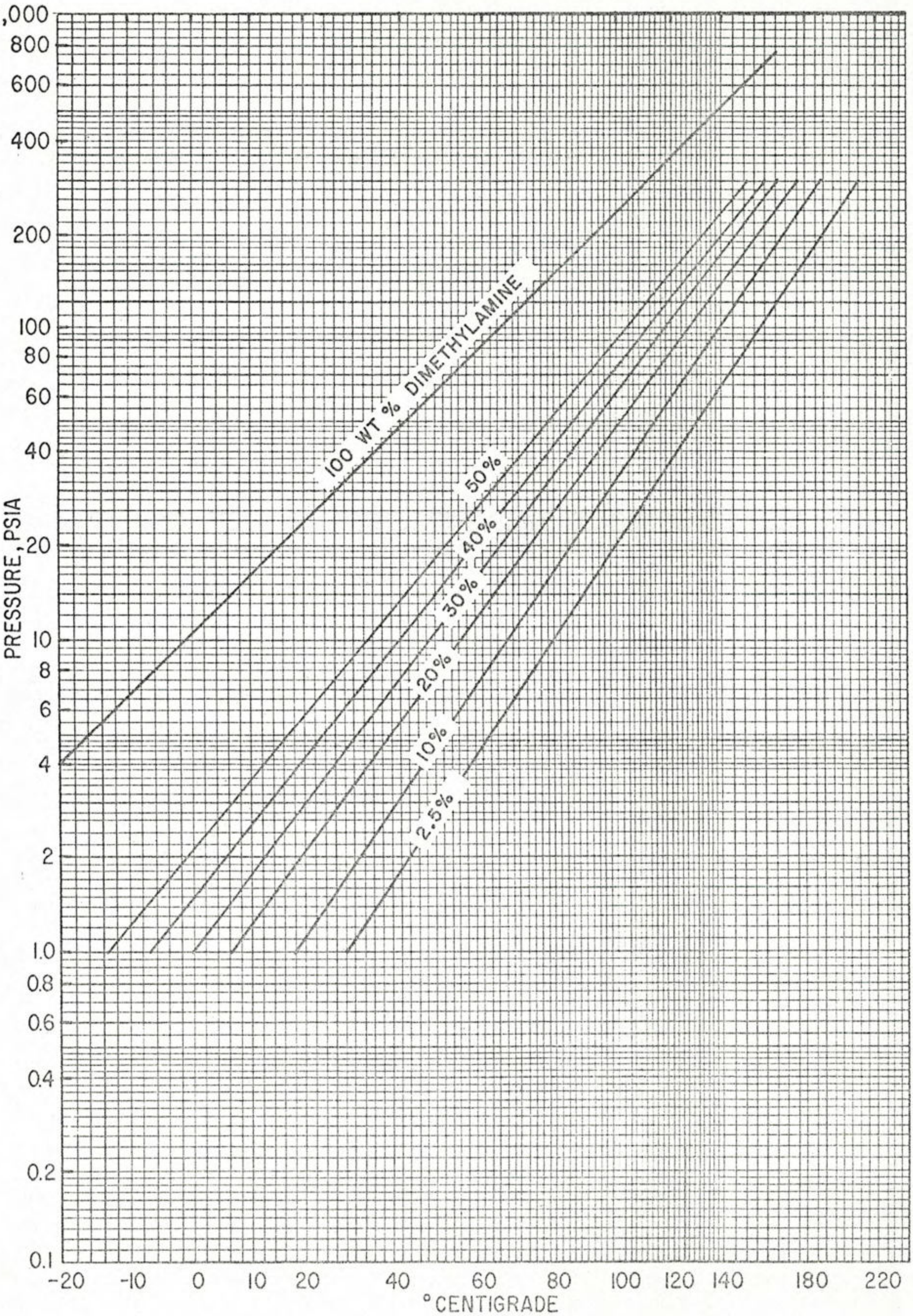


Fig. 33-3—Vapor pressure of aqueous dimethylamine from —20° C to +210° C.

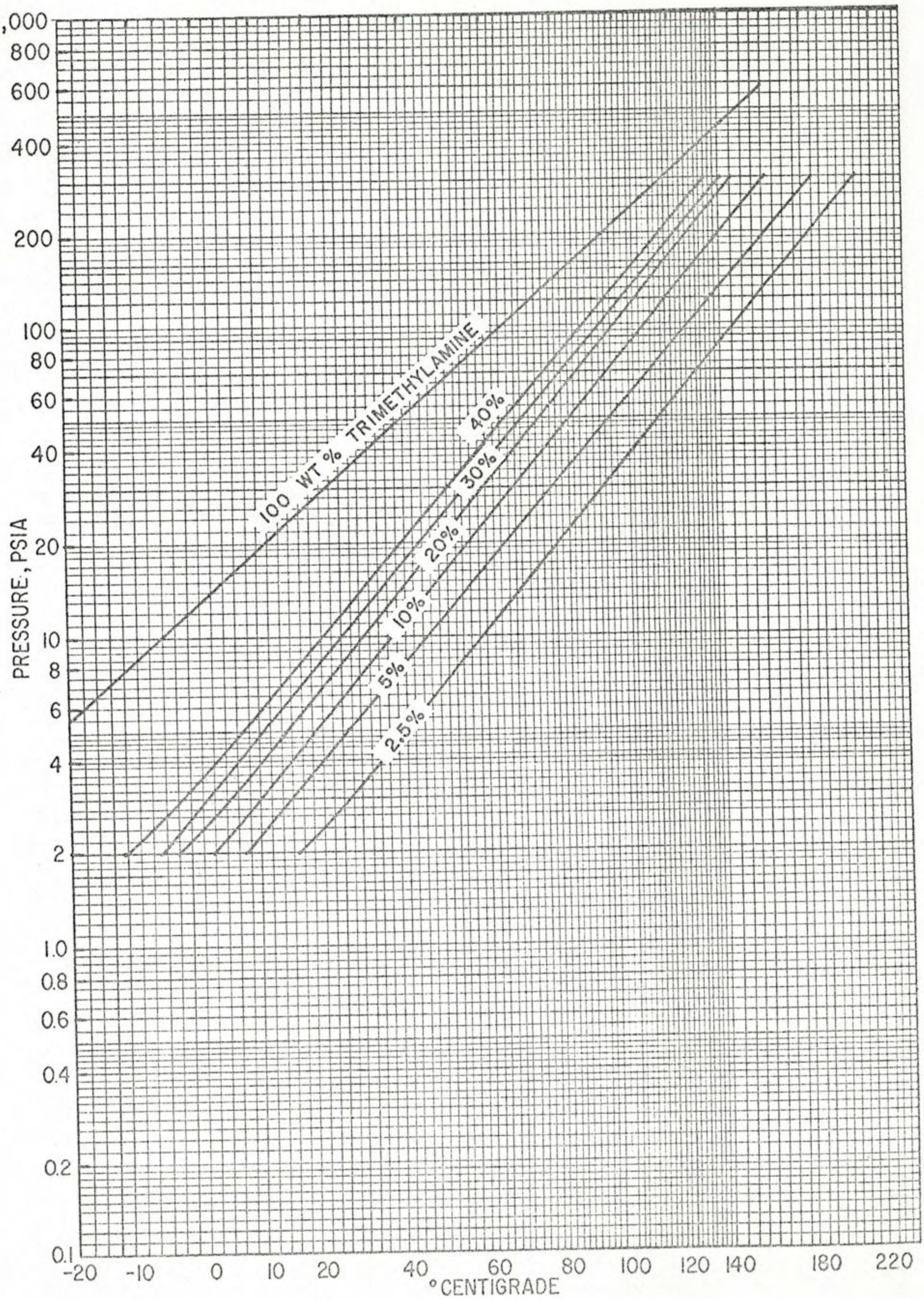


Fig. 33-4—Vapor pressure of aqueous trimethylamine from −20° C to +210° C.

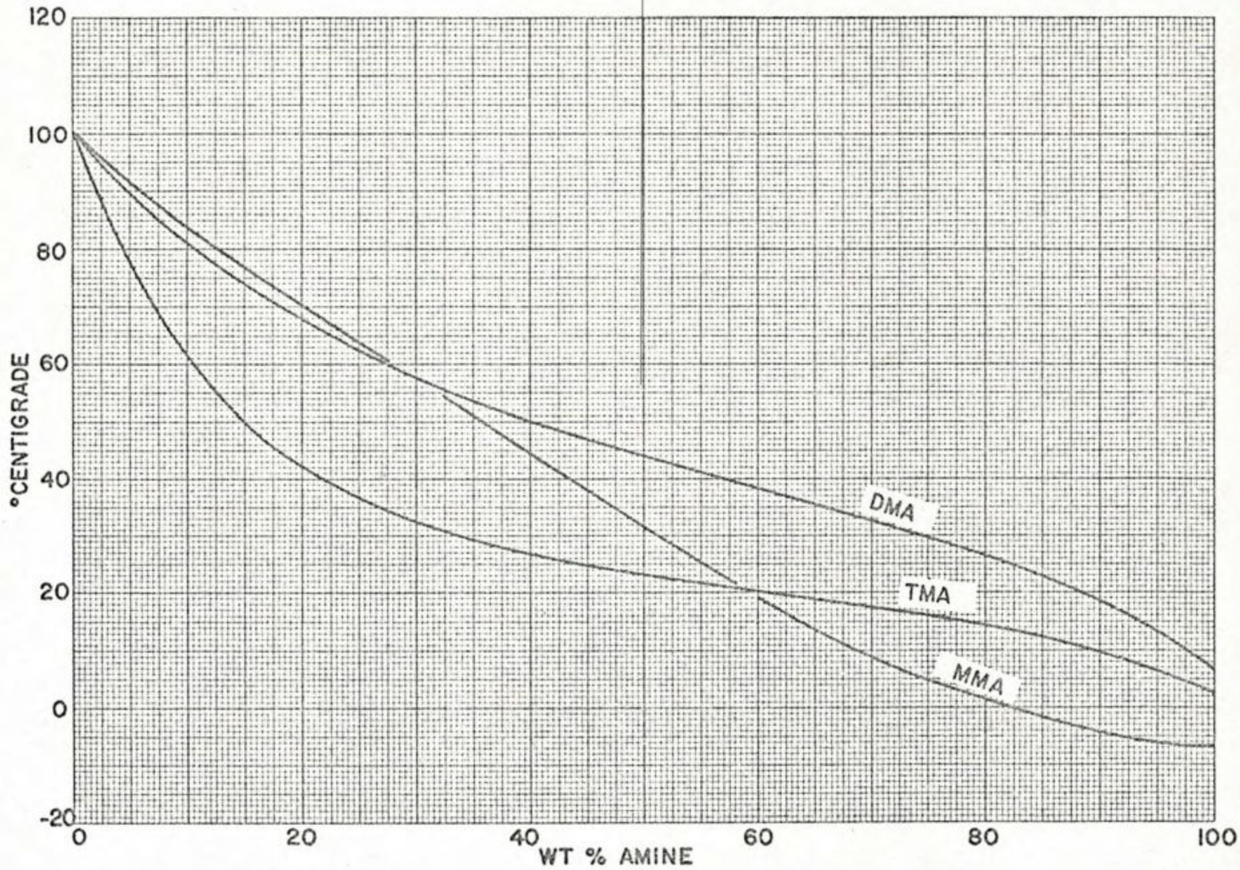


Fig. 33-5—Boiling points of aqueous methylamines at atmospheric pressure.

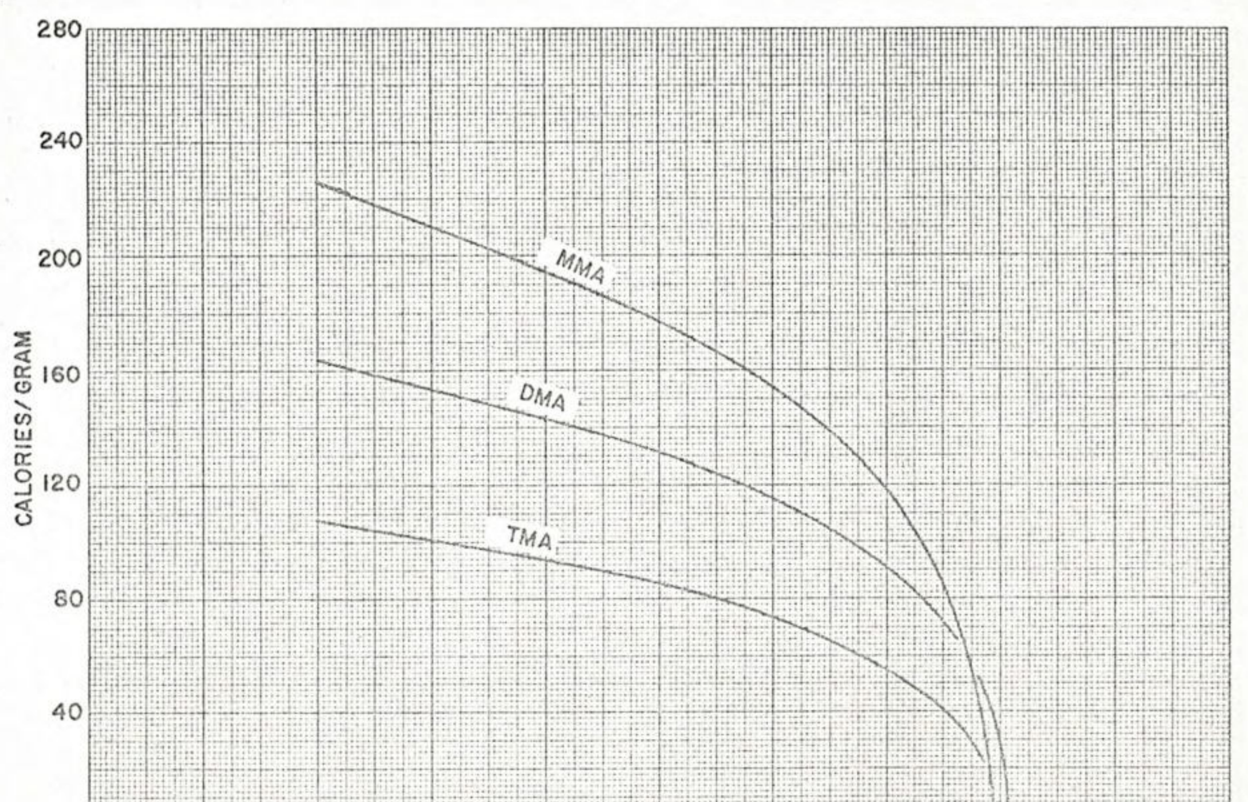


Fig. 33-6—Heat of vaporization of methylamines from −80° C to +160° C.

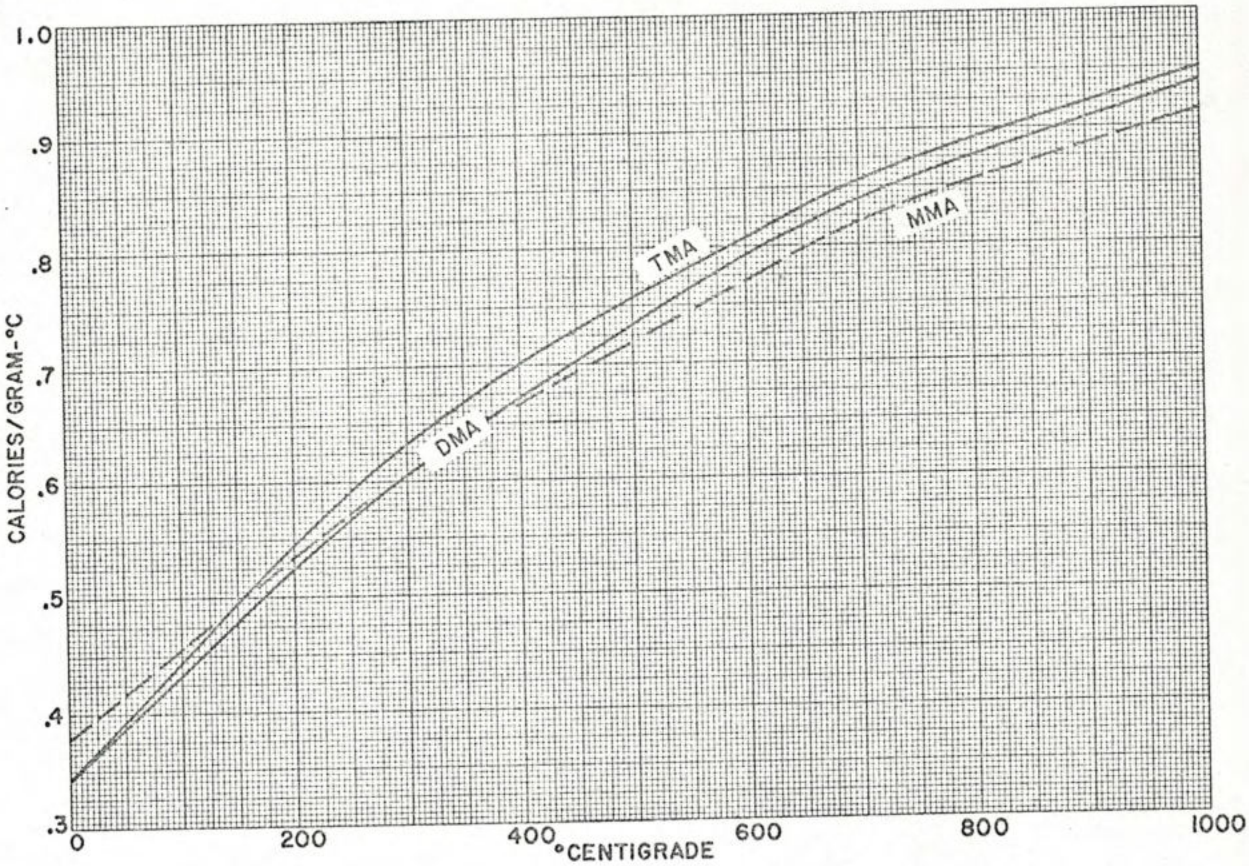


Fig. 33-7—Vapor heat capacity of methylamines from 0° C to 1,000° C.

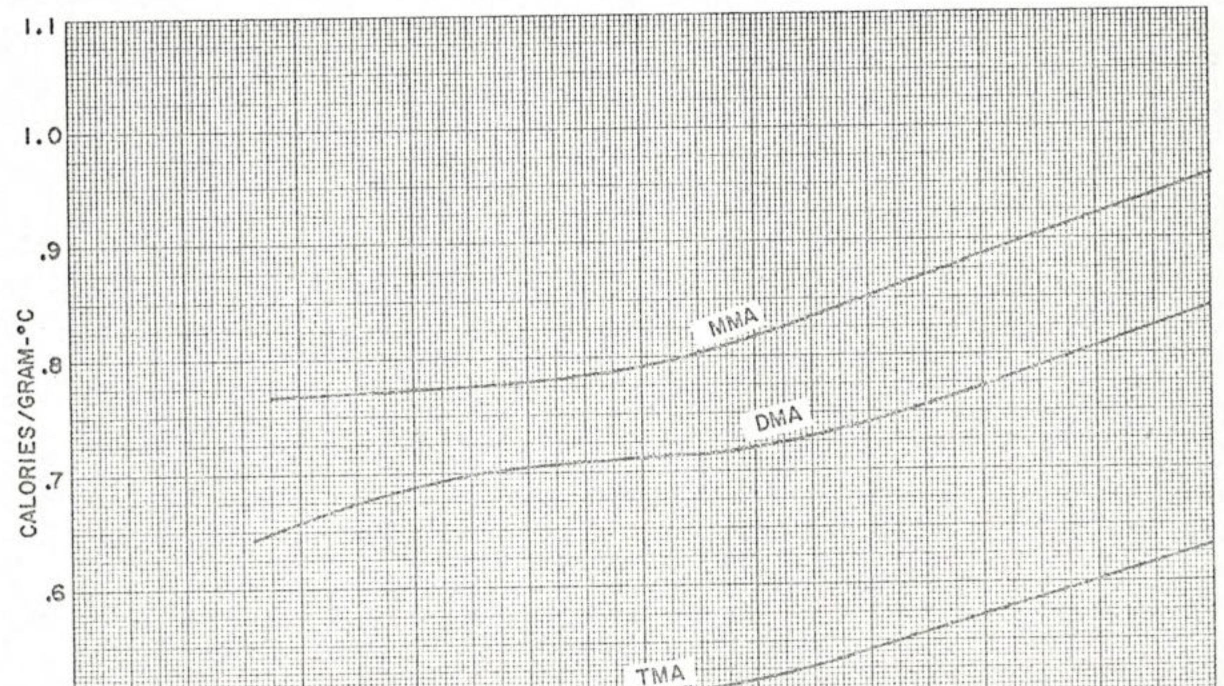


Fig. 33-8—Liquid heat capacity of methylamines from −110° C to +80° C.

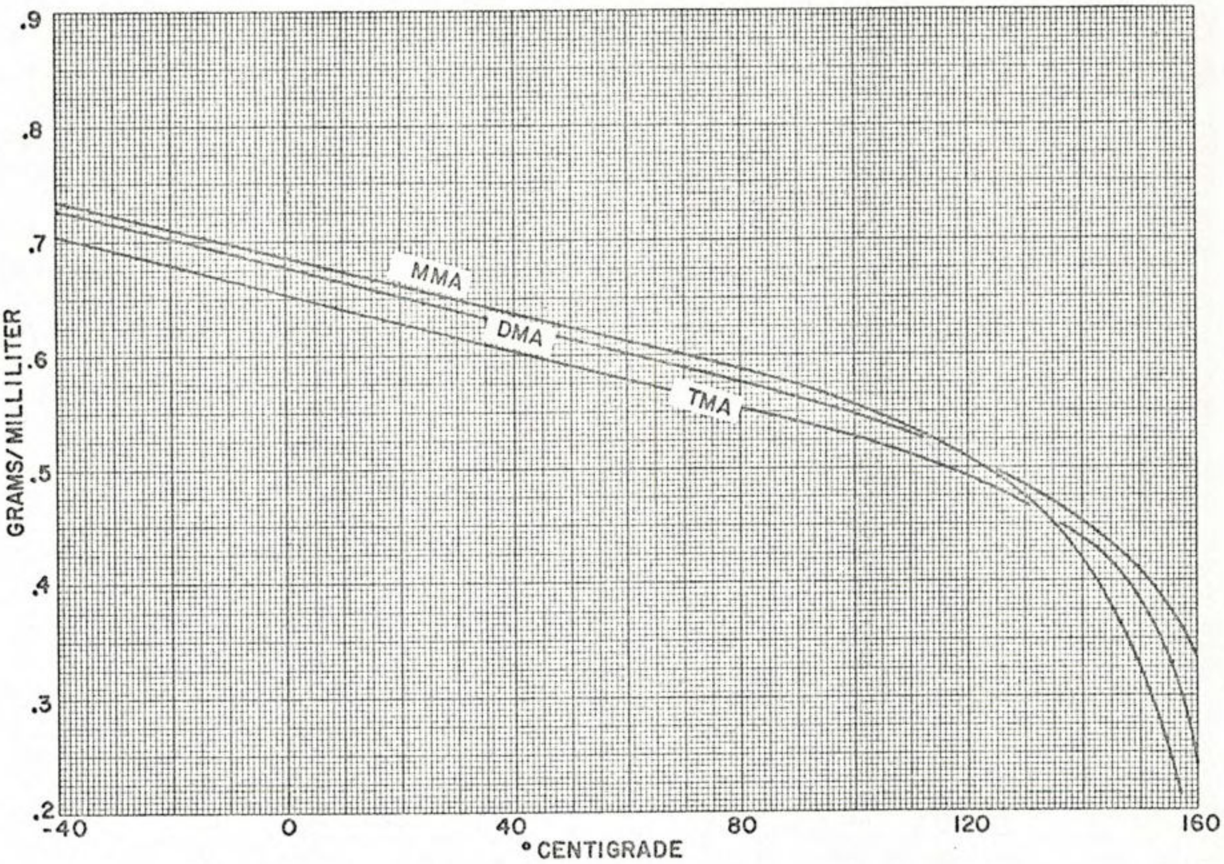


Fig. 33-9—Liquid density of methylamines from −40° C to +160° C.

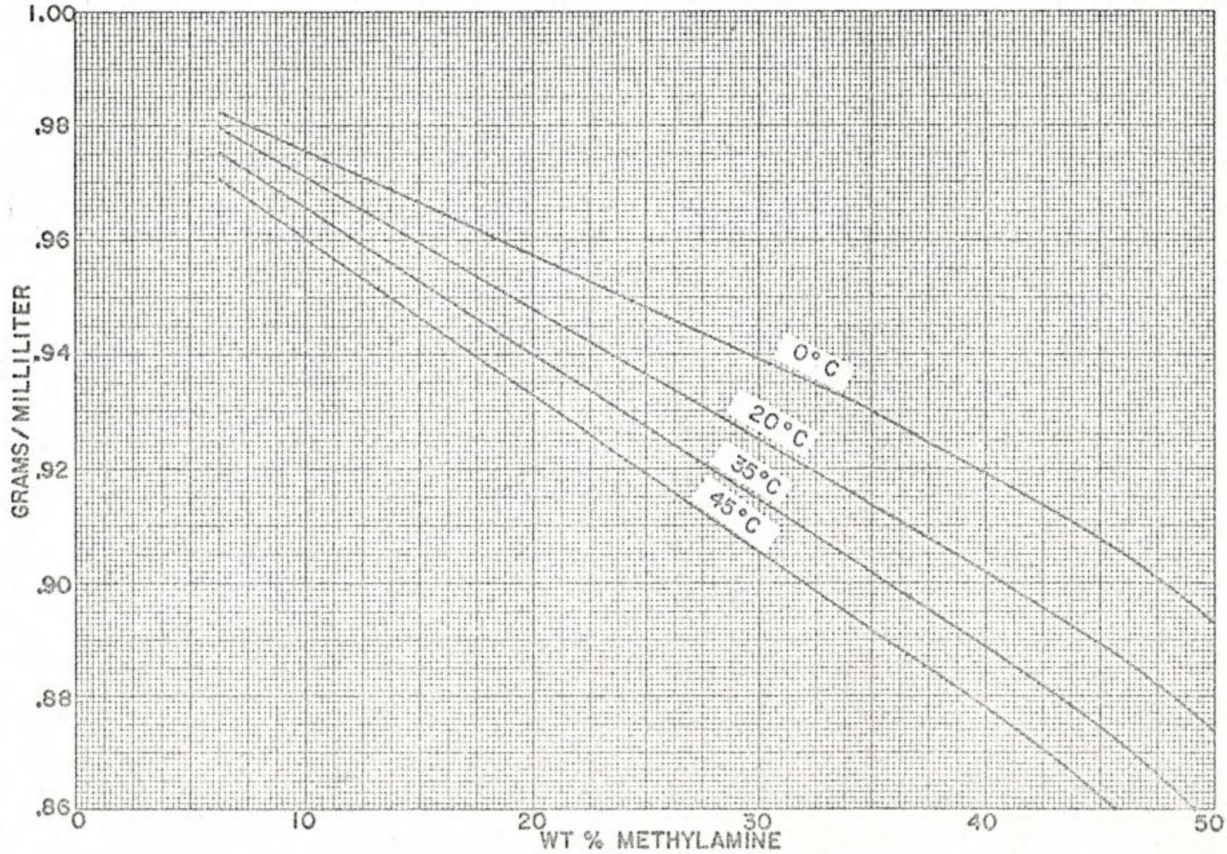


Fig. 33-10—Density of aqueous methylamine from 0° C to 50° C.

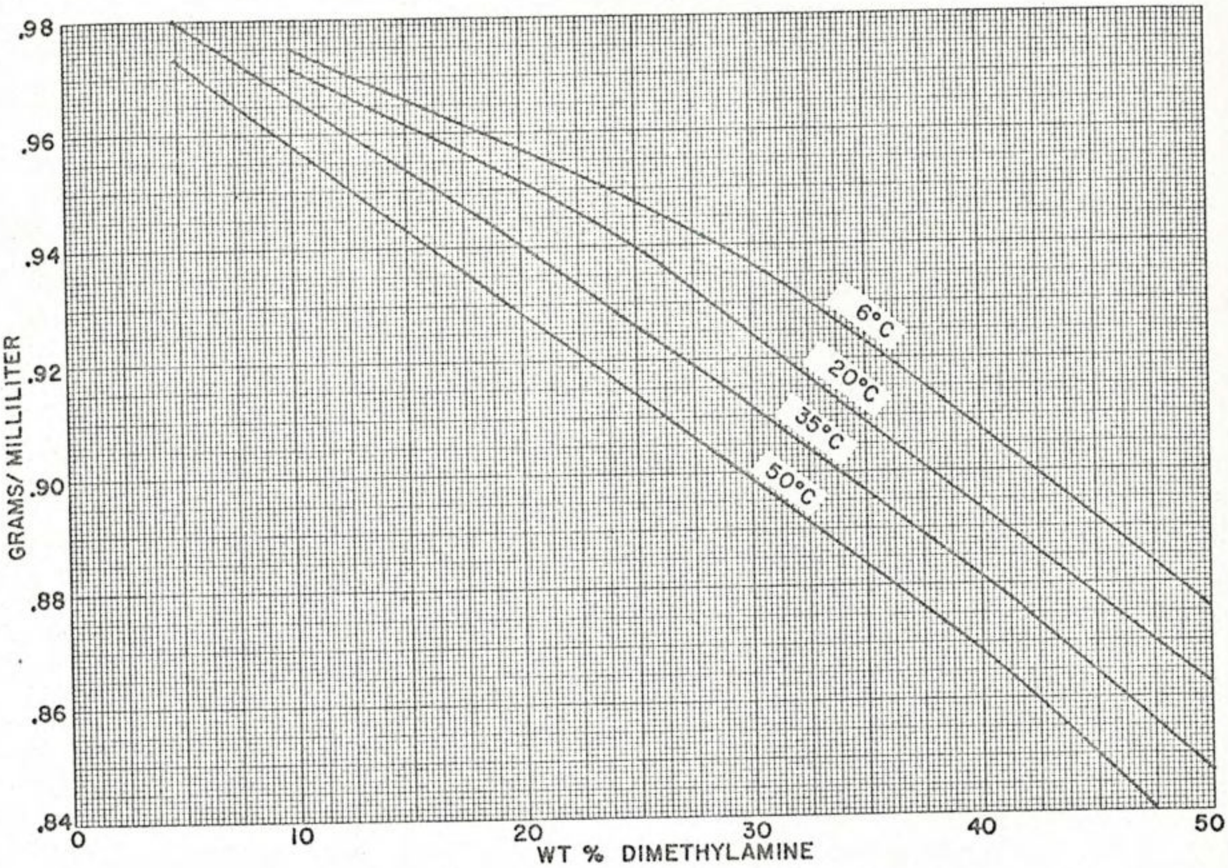


Fig. 33-11—Density of aqueous dimethylamine from 0° C to 50° C.

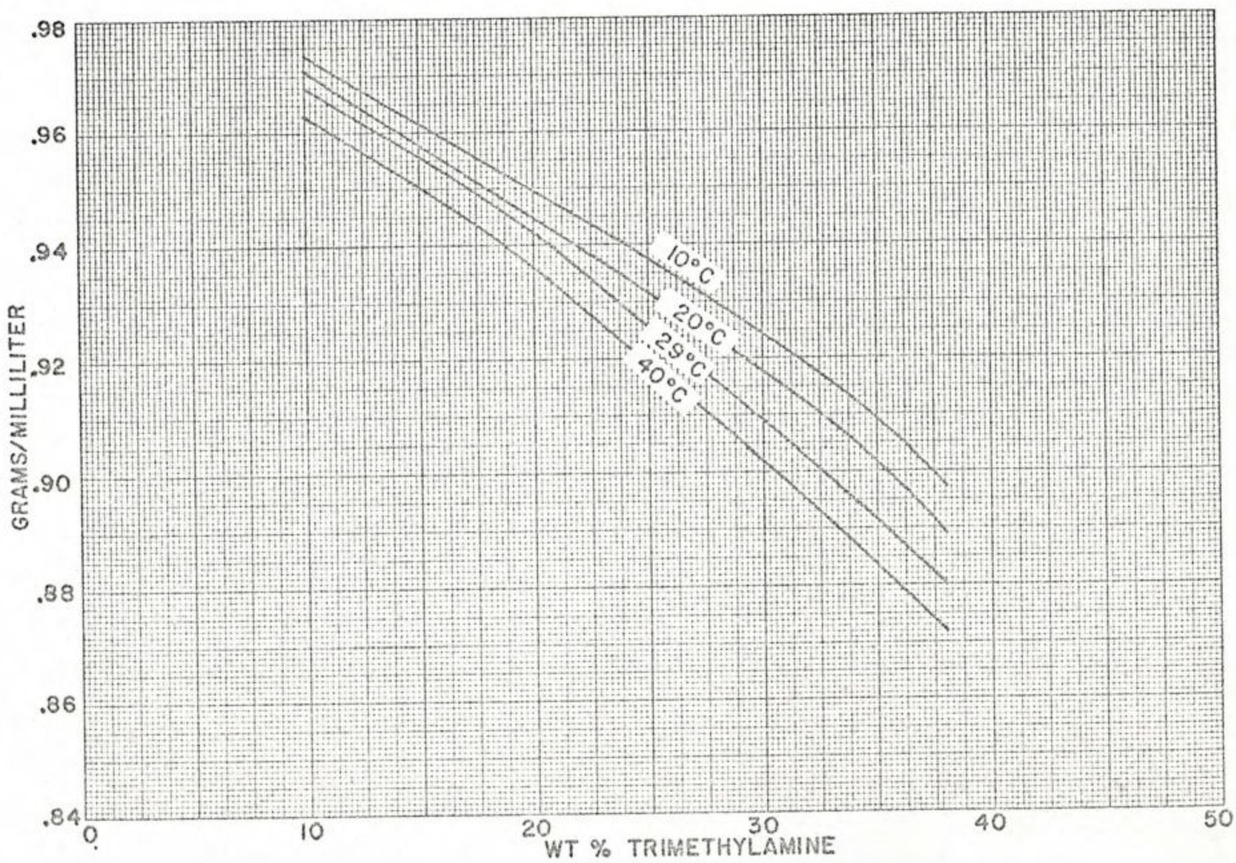


Fig. 33-12—Density of aqueous trimethylamine from 10° C to 40° C.

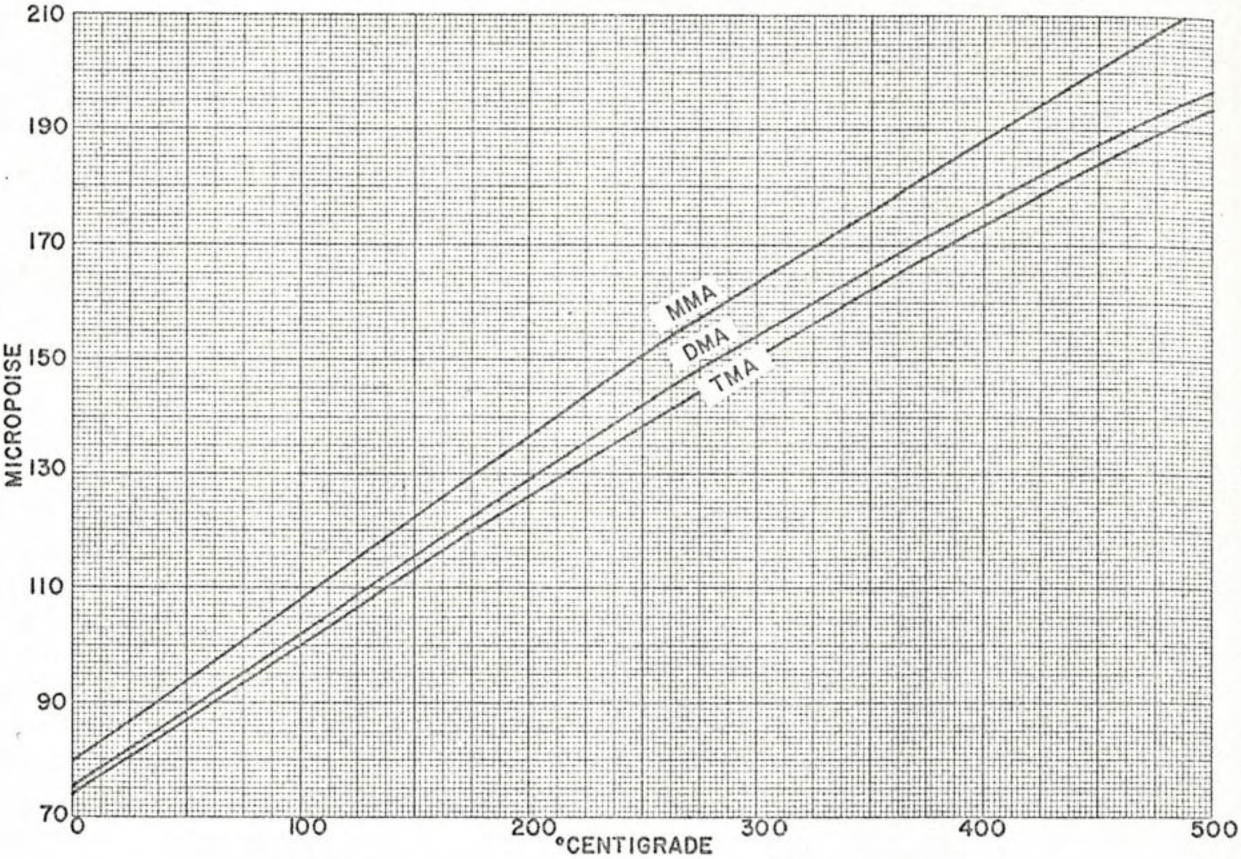


Fig. 33-13—Vapor viscosity of methylamines from 0° C to 500° C.

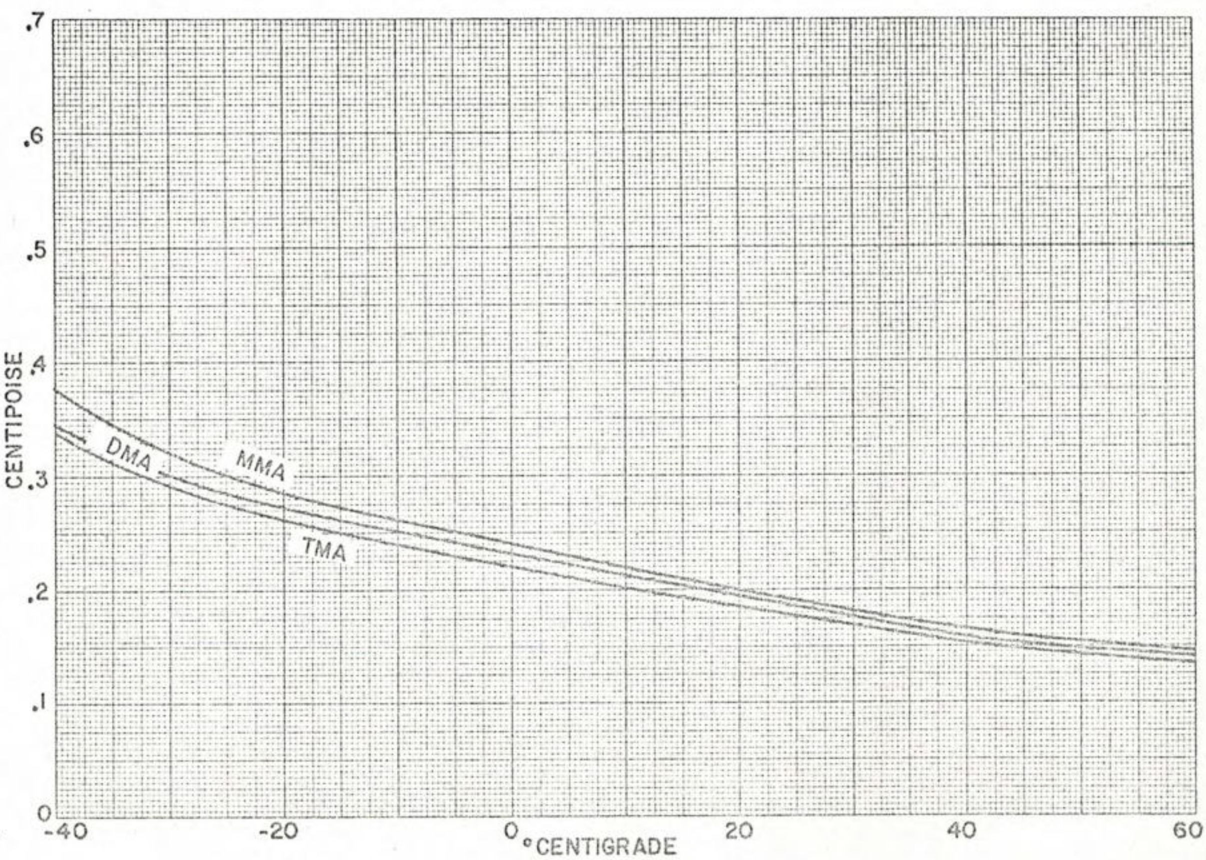


Fig. 33-14—Liquid viscosity of methylamines from —40° C to +60° C.

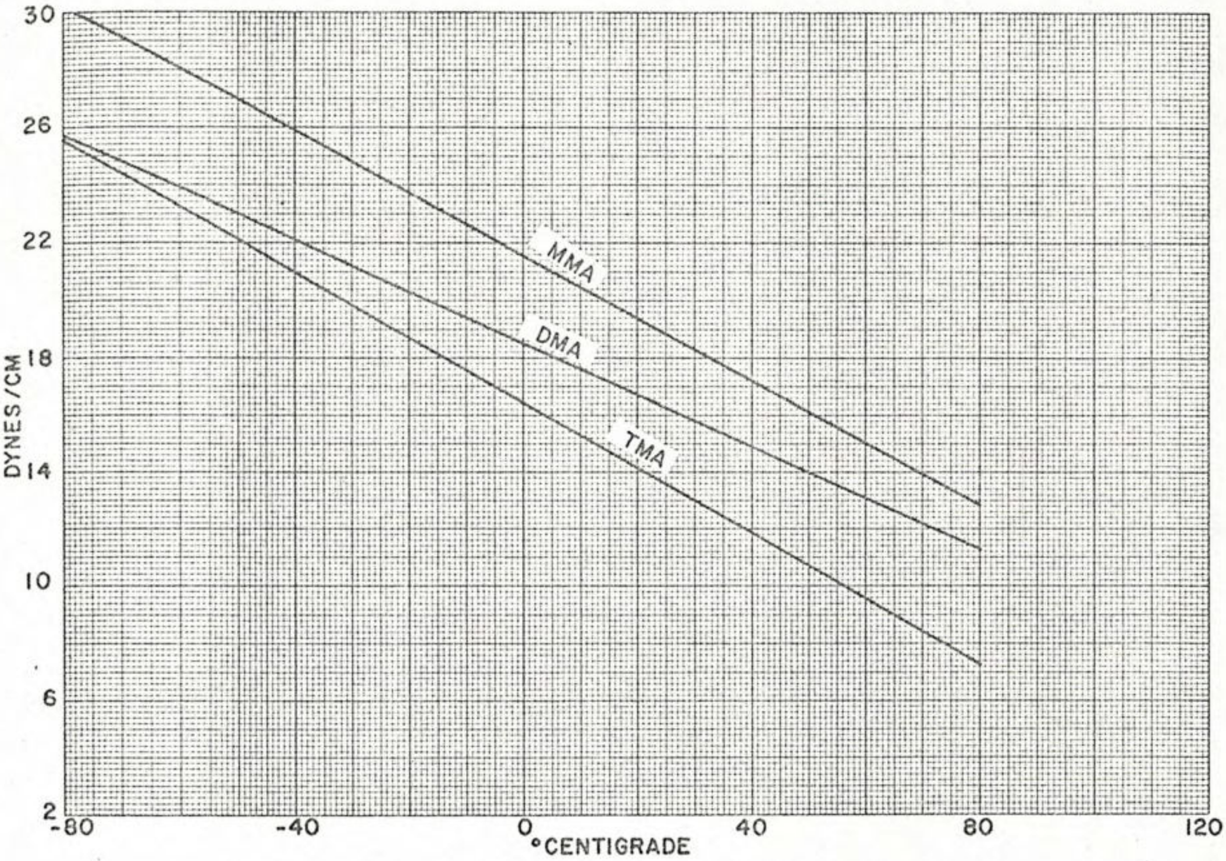


Fig. 33-15—Surface tension of methylamines from −80° C to +80° C.

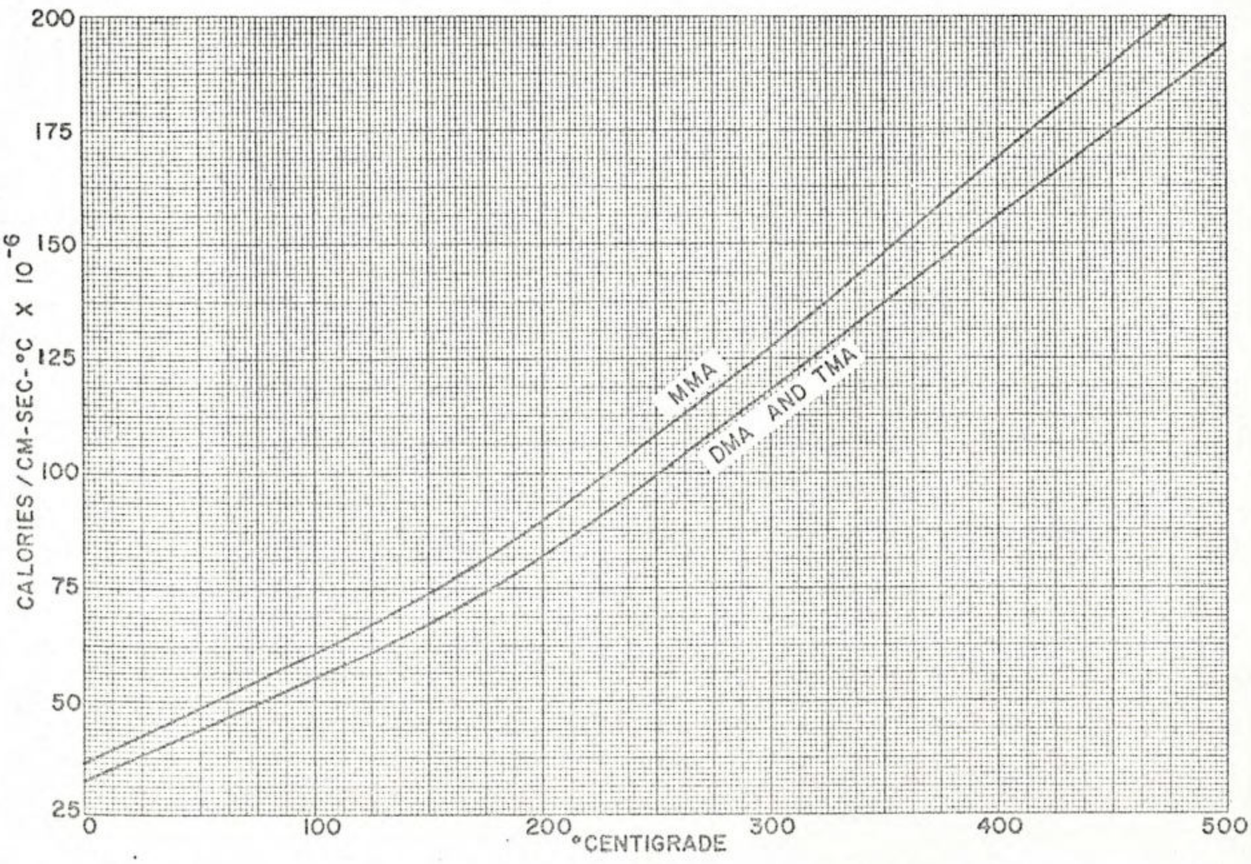


Fig. 33-16—Vapor thermal conductivity of methylamines from 0° C to 500° C.

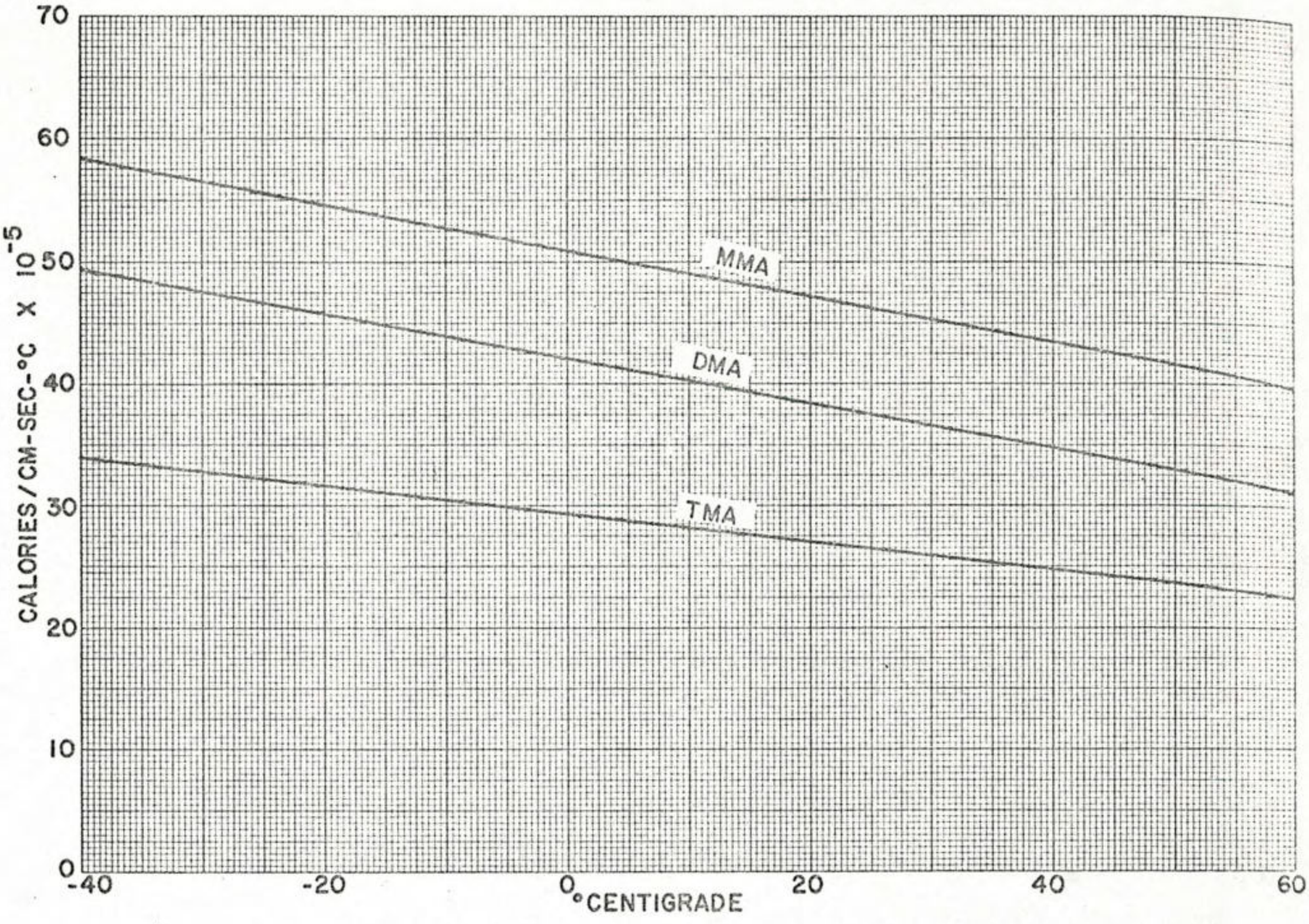
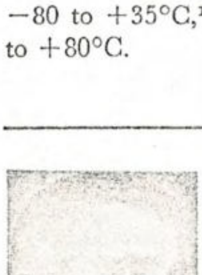


Fig. 33-17—Liquid thermal conductivity of methylamines from −40° C to +60° C.

cosity-constitutional constant which is calculated from the molecular structure. Since his data do not include any atomic contributions for amine compounds, the constant was determined by using one experimental data point to calculate the constant. When compared to four other experimental values at various temperatures, this technique gave an average error of only 1.8 percent.

Surface Tension. The experimental data, available from −80 to +35°C,[15,18] were extrapolated as a straight line to +80°C.



About the author

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Thermal Conductivity. The vapor and liquid thermal conductivities have been estimated by the methods used in previous articles.[19,20]

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Indexing Terms: Computations-4, Dimethylamine-9, Heat-7, Liquid Phase-5, Methylamine-9, Physical Properties-7, Pressure-6, Properties/Characteristics-7, Temperature-6, Trimethylamine-9, Vapor Phase-5.

Part 34, "Ethylamines," will appear in an early issue.