Physical Properties of Hydrocarbons

Part 23—Brominated Hydrocarbons

R. W. Gallant,
The Dow Chemical Co., Plaquemine, La.

THE BROMINATED HYDROCARBONS do not approach the chlorinated and fluorinated hydrocarbons in terms of volume usage but their unique properties have made them indispensible to the chemical industry. Total volume of the brominated hydrocarbons is probably less than 200 million pounds and ethylene dibromide alone accounts for over 75 percent of this total. Although many efforts have been made to replace ethylene dibromide as an essential anti-knock additive in gasoline, ethylene dibromide will probably remain in gasoline for many years yet.

Methyl bromide is the anchor compound of a growing number of valuable brominated agricultural chemicals. Bromotrifluoromethane is used in refrigerant, aerosol spray, and fire extinguishing applications. Ethyl bromide has a variety of specialty uses. The use of brominated compounds for imparting fire retardant properties to plastics could represent a major new market for brominated hydrocarbons.

Because these compounds have been well-known for many years, the physical properties have been extensively studied.

Vapor Pressure and Critical Properties. The critical properties and vapor pressures are available from the literature,[1,2,3] except for the critical density of methyl bromide which was estimated by the method of Vowles.[4]

Heat of Vaporization. The heat of vaporization has been determined at the boiling point for all four compounds.[2,3,5] Other data are available over a fairly wide temperature range for methyl bromide, ethyl bromide, and ethylene dibromide.[2] The data have been extended to the critical point by the Kharbanda nomograph,[6] with an average error of about 3 percent.

TABLE 23-1—Physical Properties of Brominated Hydrocarbons

	Boiling Point °C	Melting Point °C	Molecular Weight	Critical Properties T_c °C	P_c PSIA	d_c g/ml
Methyl Bromide	3.6	− 93	94.95	194	757	0.61*
Bromotrifluoromethane	−57.8	−168	148.93	67	575	0.745
Ethyl Bromide	38.4	−118	108.98	230.7	904	0.507
Ethylene Dibromide	131.5	9.8	187.88	309.8	1,038	0.776

* Estimated.

Heat Capacity. Gelles and Pitzer[7] have determined the vapor heat capacity of methyl bromide and bromotrifluoromethane from −200° C to +1200° C. Their data agree closely with the results of Spencer and Flanagan for methyl bromide[8] and McGee[9] for bromotrifluoromethane. The vapor heat capacities of ethyl bromide and ethylene dibromide have been calculated by the method of Rihani and Doraiswamy,[10] with an expected error of less than 2 percent.

Experimental liquid heat capacity data are available from −93° C to +7° C for methyl bromide,[5,11] −100° C to +20° C for ethyl bromide,[12] and +14° C to +52° C for ethylene dibromide.[13,14] Only the 25° C point is available on bromotrifluoromethane.[3] The data were extended over the −80° C to +120° C range by the method described in the previous two parts. When compared to 10 experimental points, the method gave an average error of 0.4 percent and a maximum error of 1.5 percent.

Density. Except for data on ethyl bromide which cover the −112° C to +30° C range,[14] the only data available are at room temperature.[2,3] Consequently, the method of Lyderson, Greenkorn, and Hougan[4] has been used to estimate the liquid density over the entire temperature range. For ethyl bromide, the average error was 0.2 percent. Experience with similar compounds indicates that the error on the other compounds should be 1 percent or less.

Viscosity. A limited amount of experimental vapor viscosity data are reported for methyl bromide[12,15] and bromotrifluoromethane.[15,16] The method of Bromley and

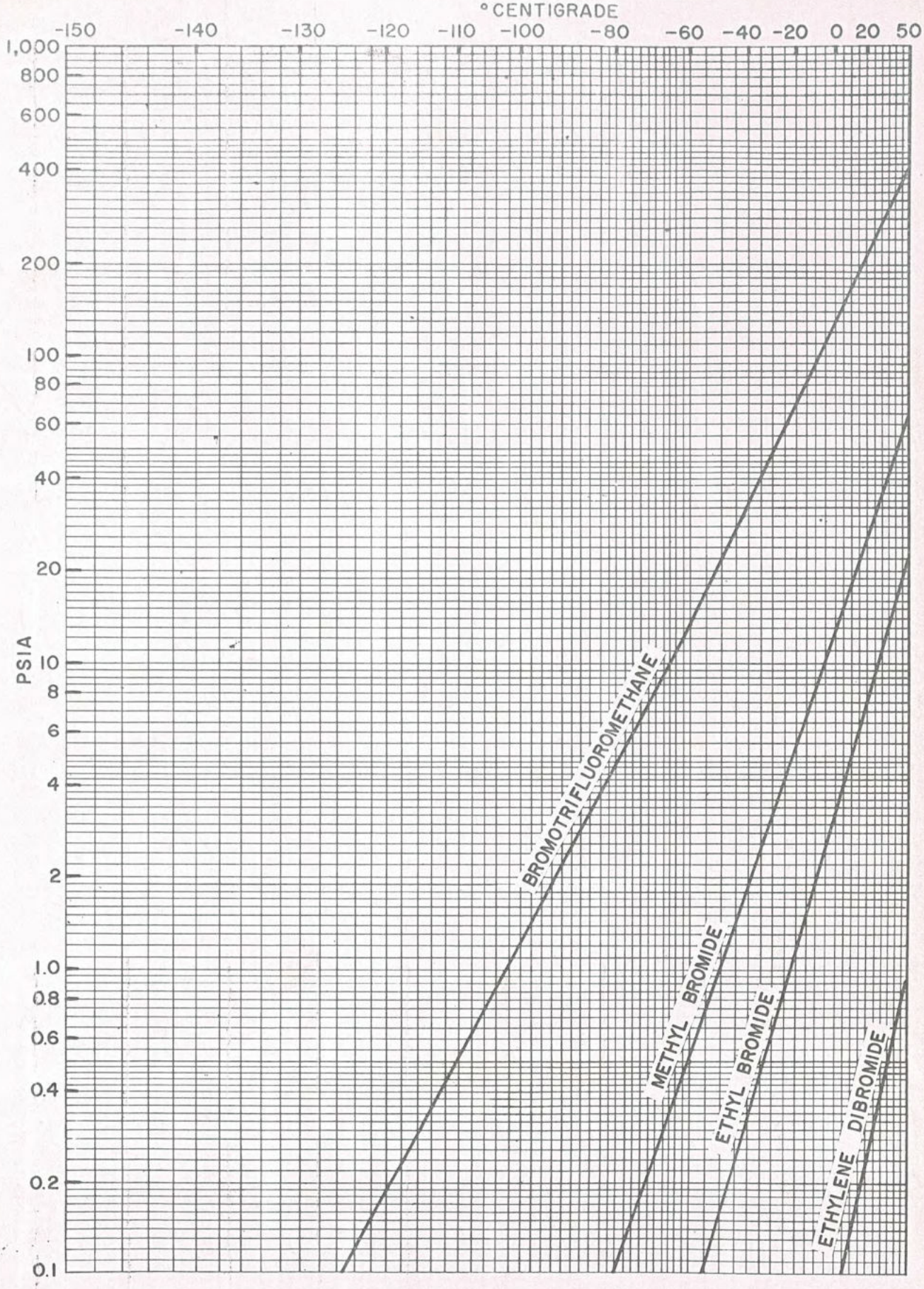

Fig. 23-1—Gives vapor pressure of brominated hydrocarbons from −150° C to +50° C.

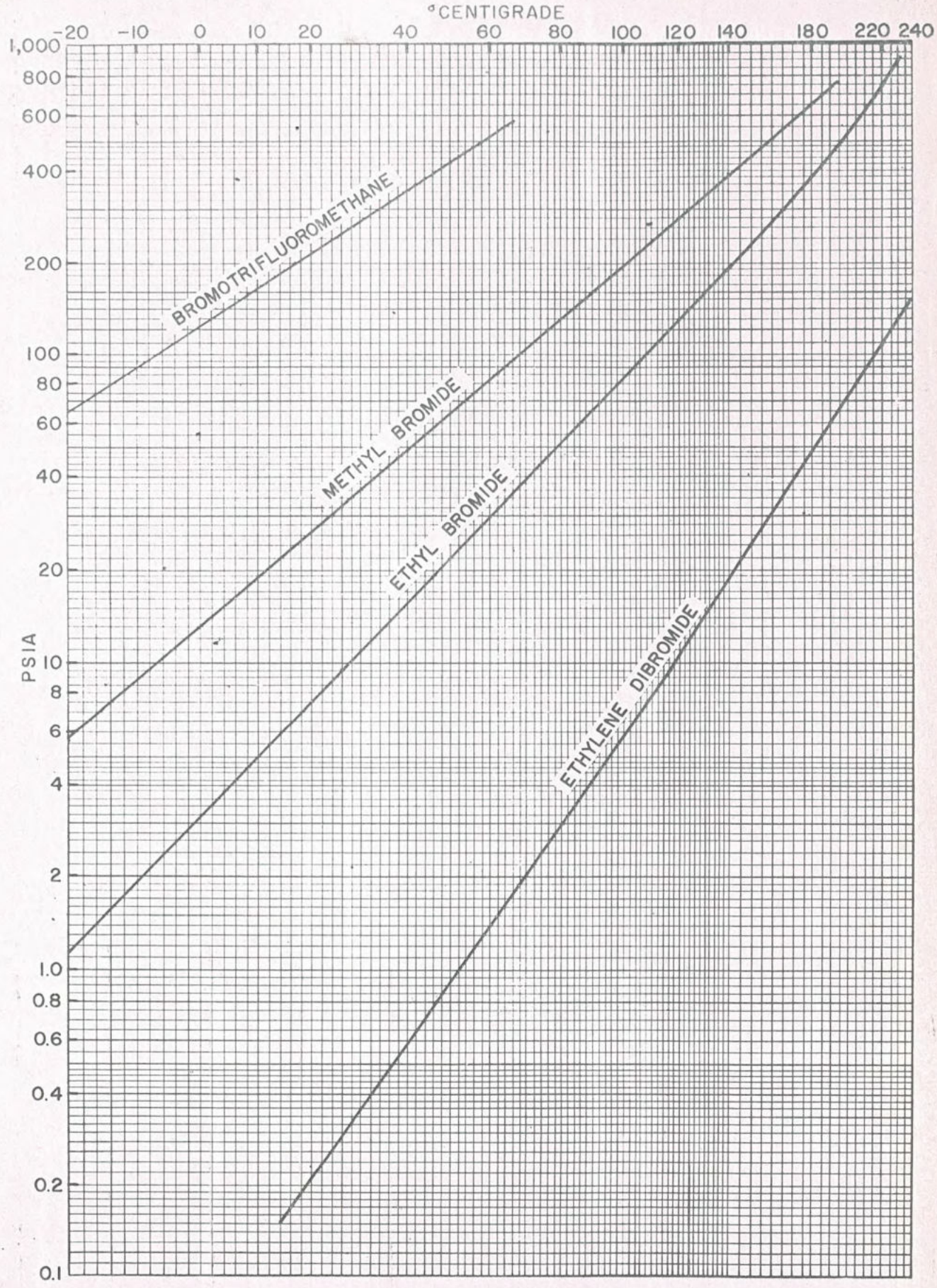

Fig. 23-2—Gives vapor pressure of brominated hydrocarbons from −20° C to +240° C.

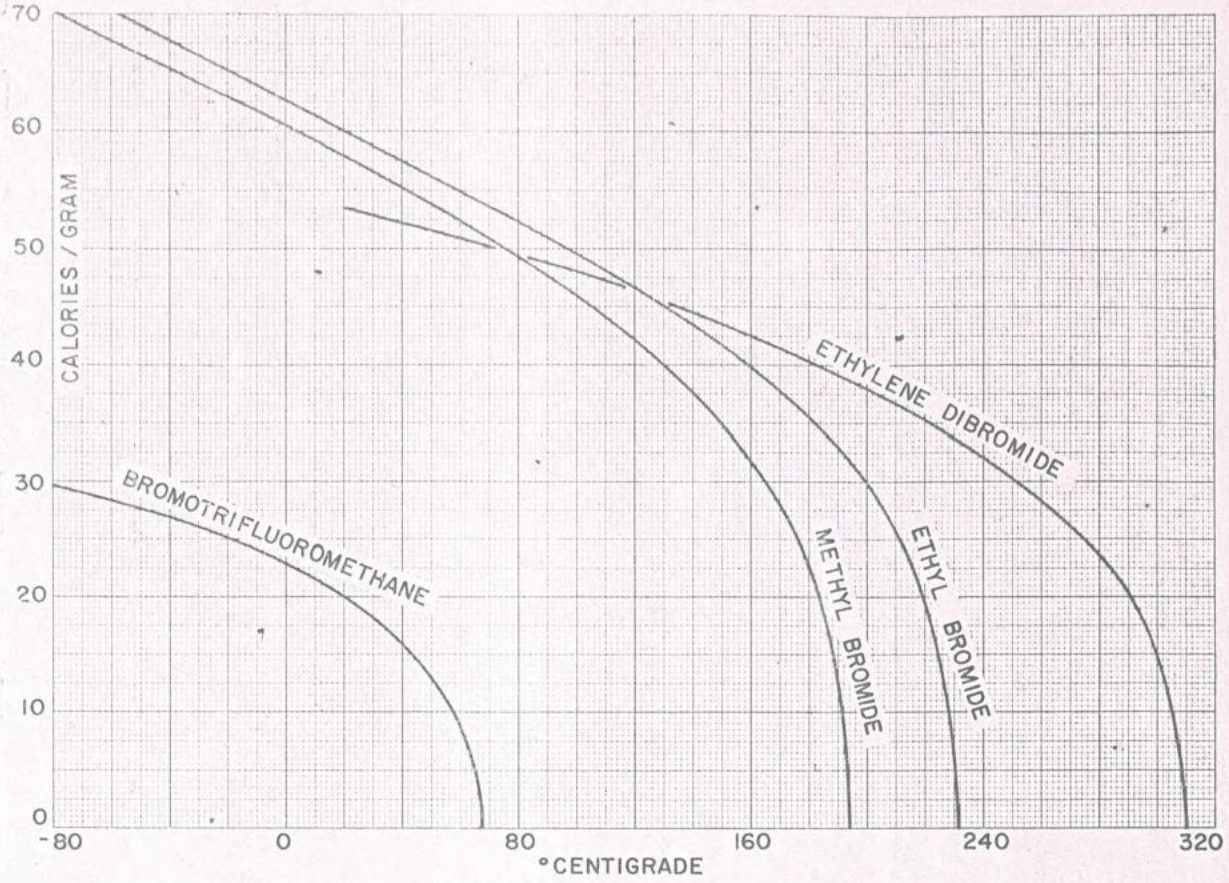

Fig. 23-3.—Gives heat of vaporization of brominated hydrocarbons from —80° C to +310° C.

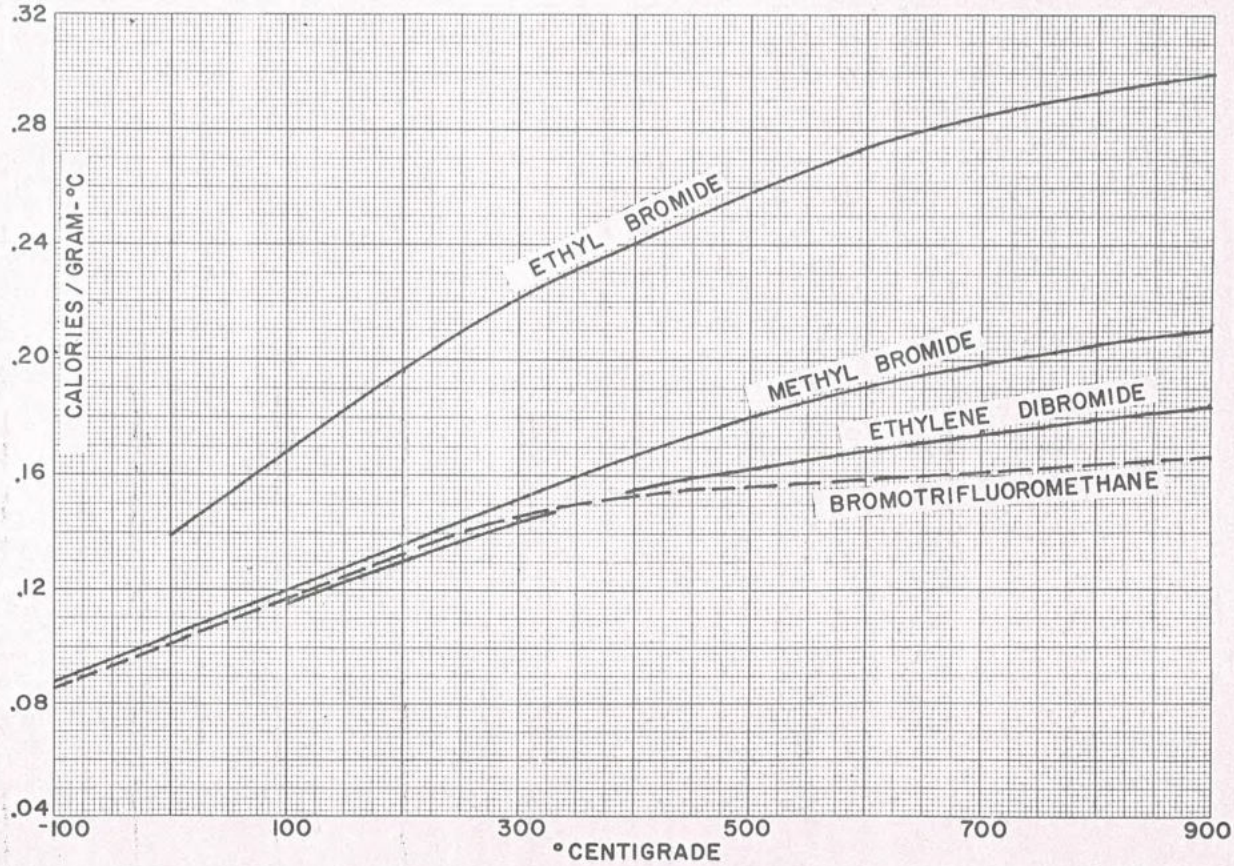

Fig. 23-4—Gives vapor heat capacity for brominated hydrocarbons from —100° C to +800° C.

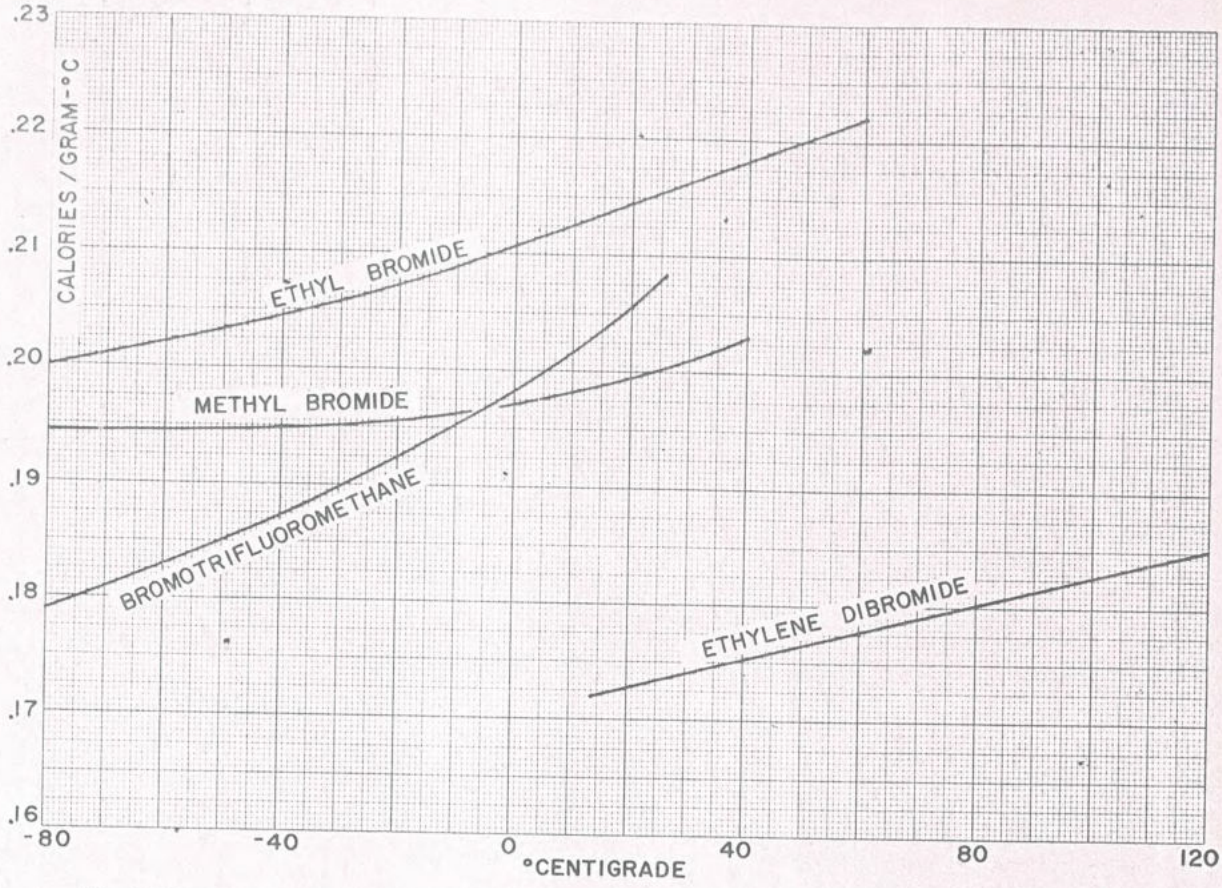

Fig. 23-5—Gives liquid heat capacity for brominated hydrocarbons from —80° C to +120° C.

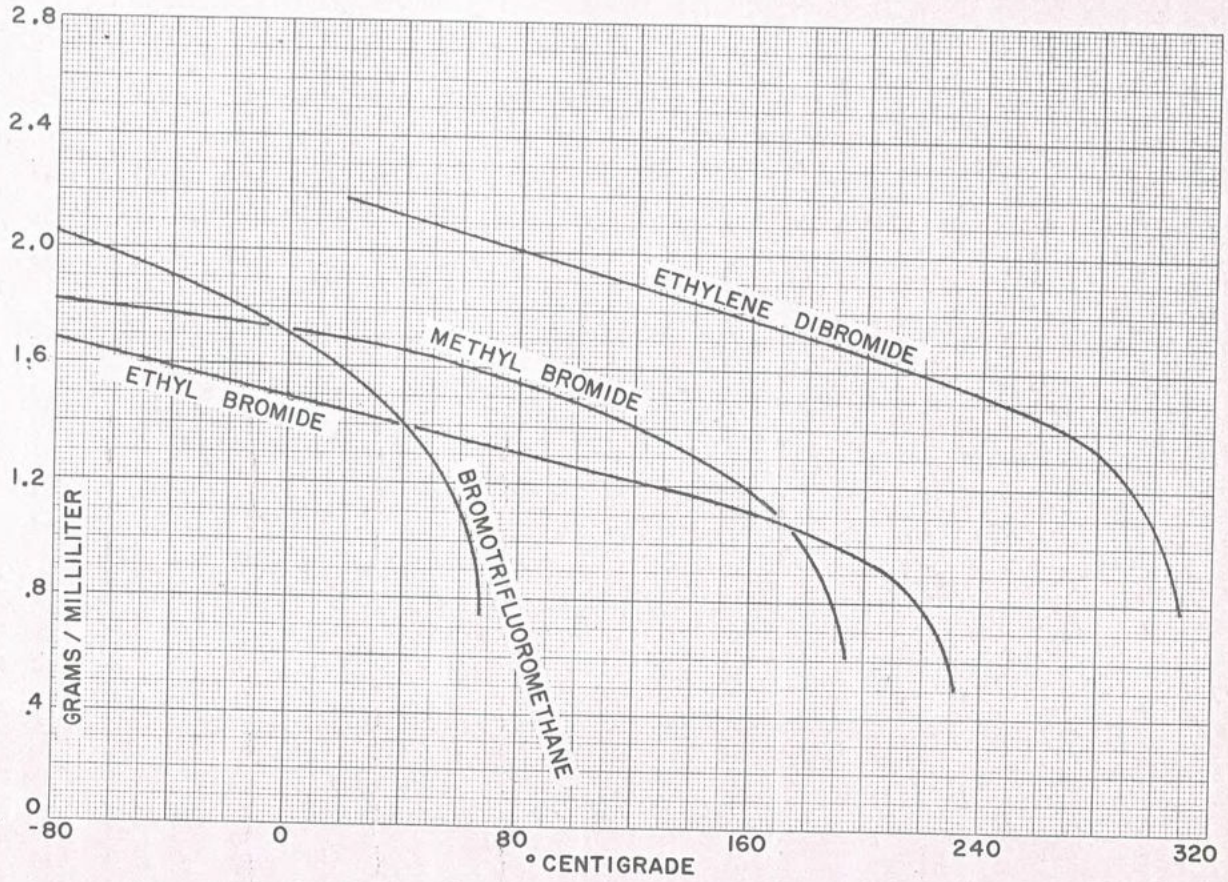

Fig. 23-6—Gives liquid density of brominated hydrocarbons from —80° C to +320° C.

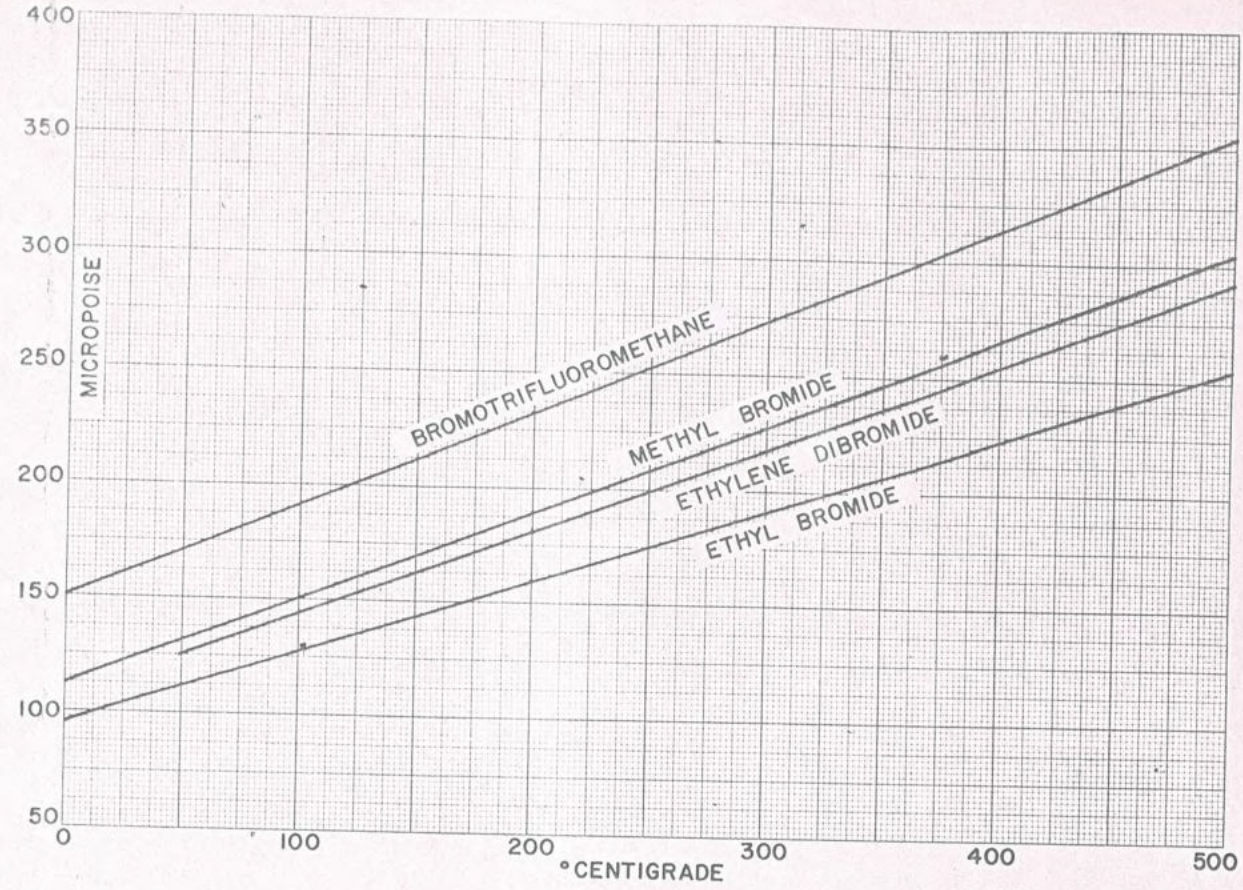

Fig. 23-7—Gives vapor viscosity of brominated hydrocarbons from 0° C to 500° C.

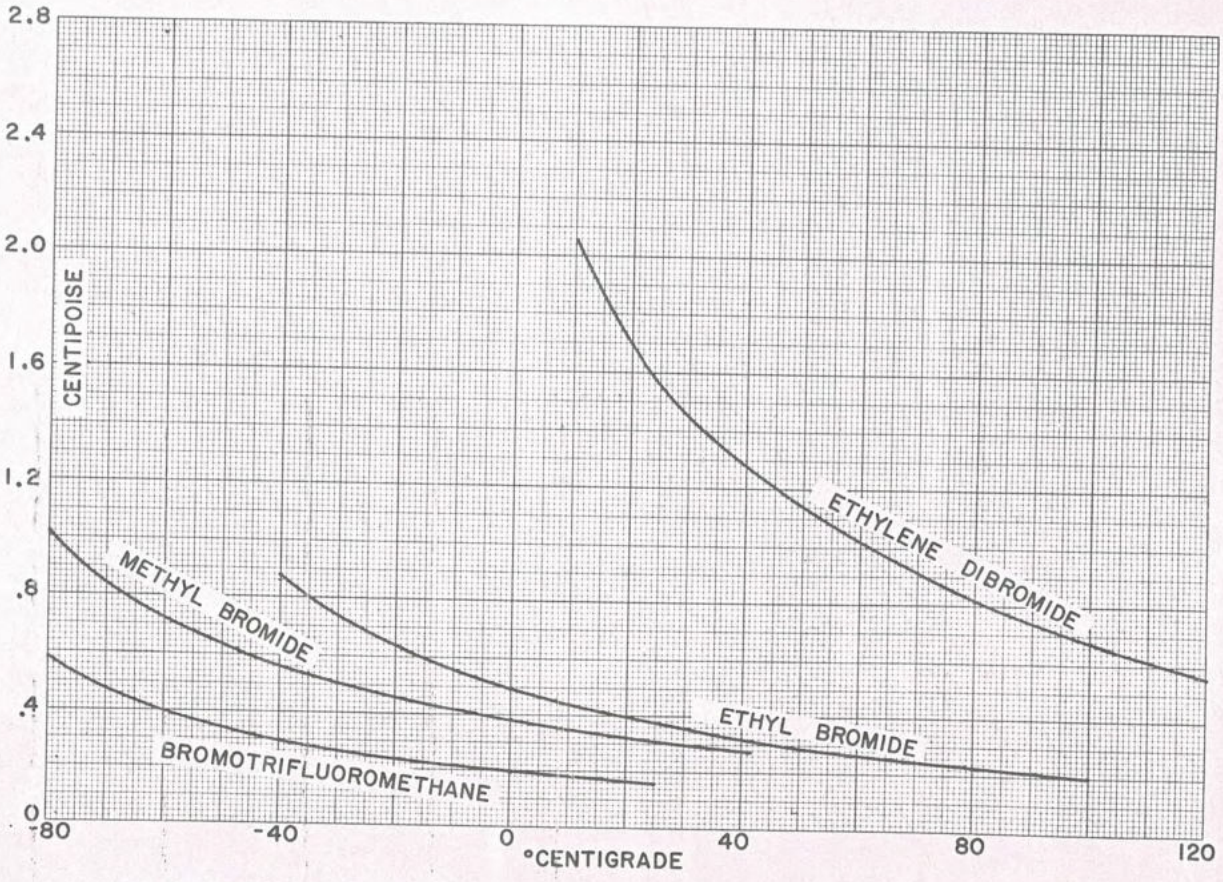

Fig. 23-8—Gives liquid viscosity of brominated hydrocarbons from −80° C to +120° C.

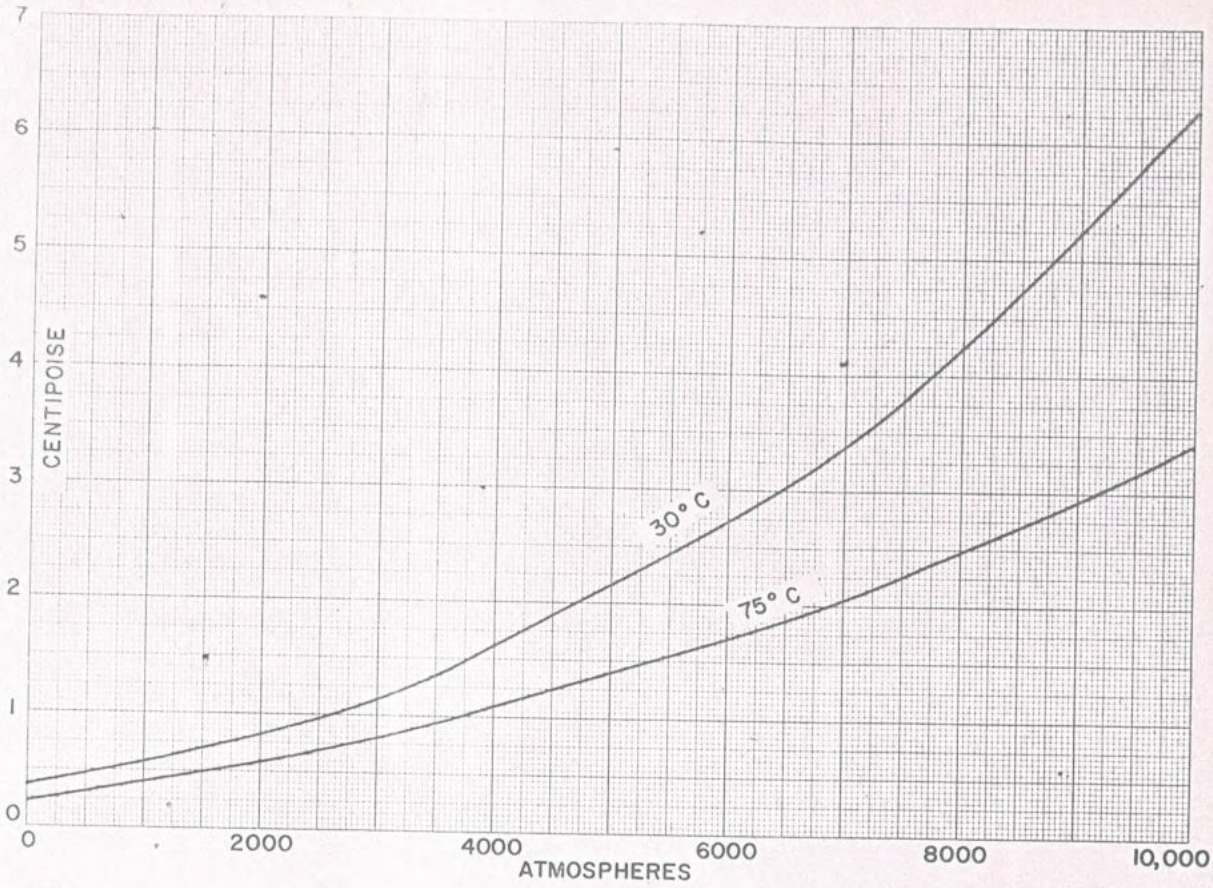

Fig. 23-9—Gives pressure effect on liquid viscosity of ethyl bromide from 0 atmospheres to 10,000 atmospheres.

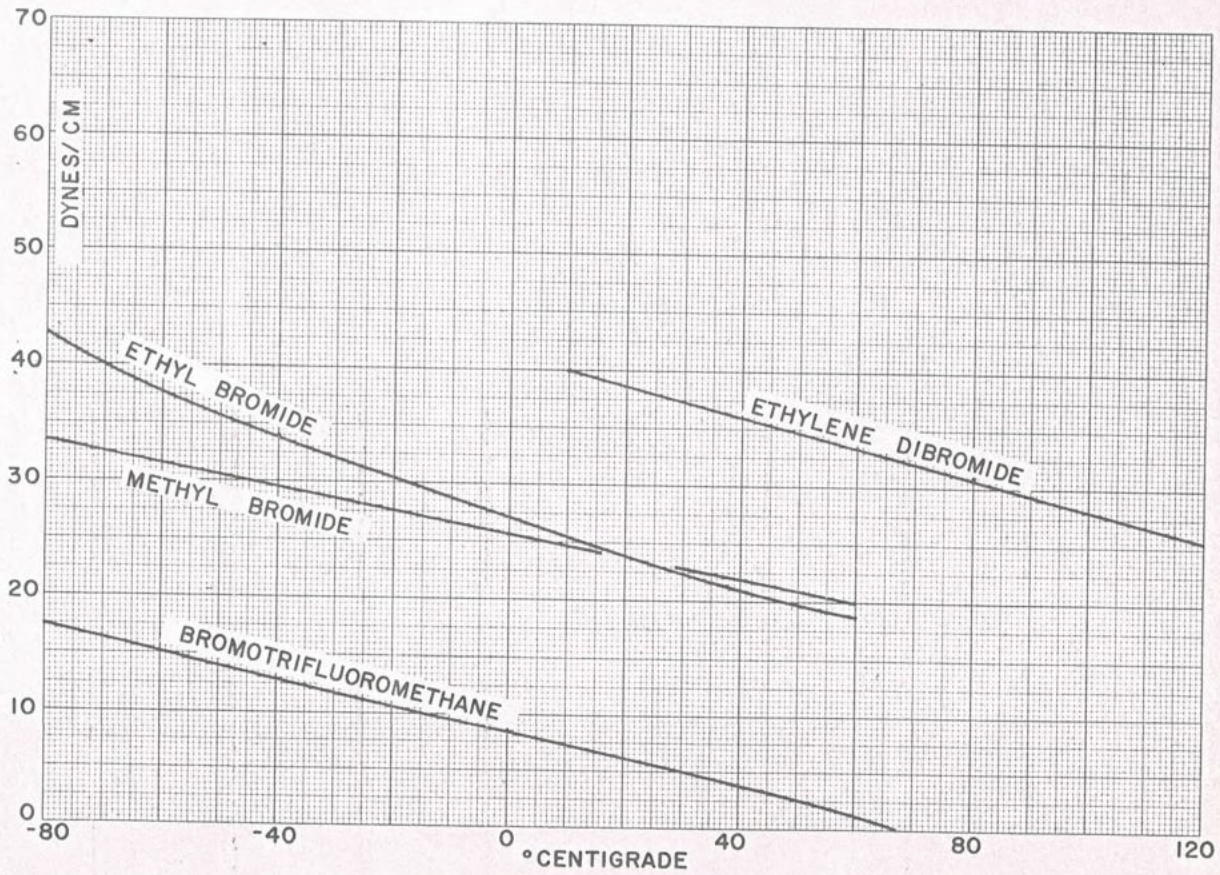

Fig. 23-10—Gives surface tension of brominated hydrocarbons from −80° C to +120° C.

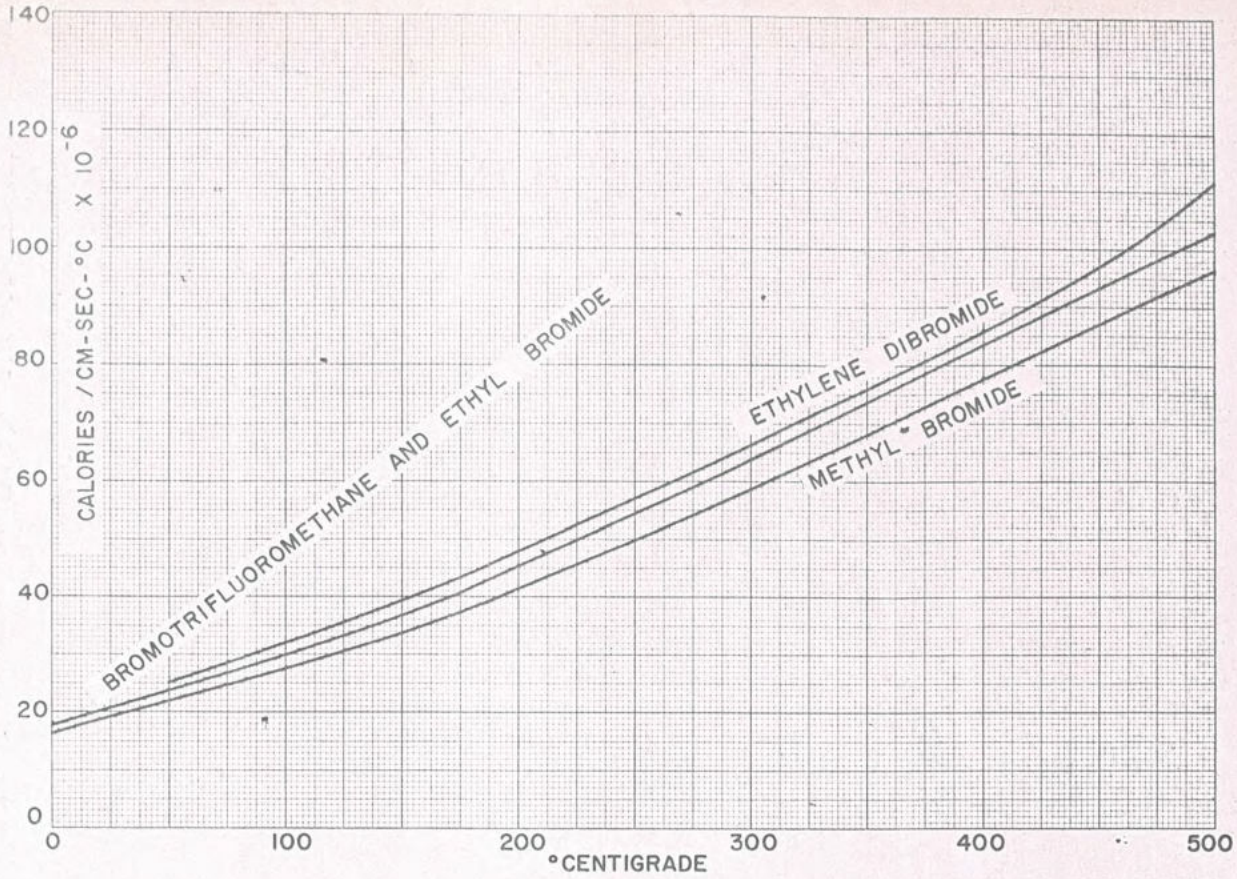

Fig. 23-11—Gives vapor thermal conductivity for brominated hydrocarbons from 0° C to 500° C.

Wilke,[17] with a somewhat lower constant to allow for the lower vapor viscosities of halogenated hydrocarbons, has been used to estimate the vapor viscosities of all four compounds. The error should be less than 5 percent.

The liquid viscosities of ethyl bromide[2,11,12,18,19] and ethylene dibromide[2,12,19] have been measured over a wide temperature range. The more limited data on methyl bromide[2] and bromotrifluoromethane[3,16] have been extended by plotting the logarithm of the viscosity against the reciprocal of the absolute temperature. The error should be less than 5 percent.

Graph 23-9 presents experimental data on the effect of pressure on the liquid viscosity of ethyl bromide.[12]

Surface Tension. The surface tension of ethylene dibromide has been determined from 10° C to 130° C.[12] Only room temperature data are available for bromotrifluoromethane[3] and ethyl bromide.[2,11,12] There are no data for methyl bromide. Consequently, the surface tensions of all but ethylene dibromide have been estimated by the previously described method that relates surface tension to parachlor, density, and molecular weight.[4] When compared with nine experimental points, the method gave an average error of 8 percent.

Thermal Conductivity. Masia and Alvarez report the vapor thermal conductivity of bromotrifluoromethane at

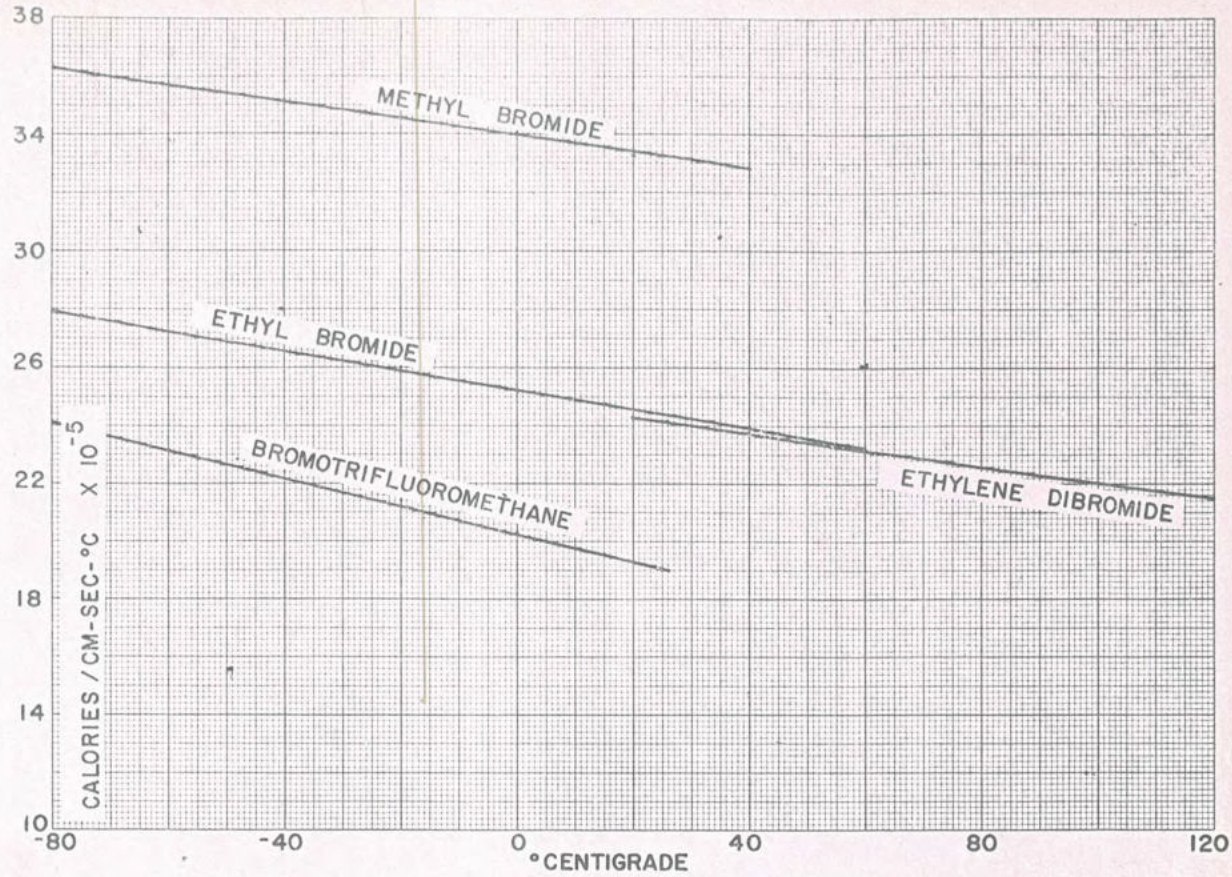

Fig. 23-12—Gives liquid thermal conductivity of brominated hydrocarbons from —80° C to +120° C.

5° C and 134° C.[20] With no other data available, the vapor thermal conductivities of the four compounds have been calculated by the method proposed by Owens and Thodos.[21] Because the quasicritical thermal conductivities had to be estimated, the error is probably about 10 percent.

The liquid thermal conductivities of ethyl bromide[22] and ethylene dibromide[23] have been measured at room temperature. The method of Robbins and Kingrea[23] has been used to calculate the thermal conductivities for all four compounds, with a probable error of 5-10 percent.

LITERATURE CITED

[1] Stull, D. R., *Industrial and Engineering Chemistry* 39, pp. 517-50 (April 1947).
[2] Dreisbach, R. R., "Physical Properties of Chemical Compounds, Volume II." Advances in Chemistry Series No. 22, American Chemical Society (1959).
[3] "Freon Fluorocarbons," Technical Bulletin B-2, E. I. du Pont de Nemours & Co.
[4] Reid, R. G., and Sherwood, T. K., The Properties of Gases and Liquids. McGraw-Hill Book Company, New York (1958).
[5] Egan, C. J. and Kemp, J. D., *Journal of the American Chemical Society* 60, pp. 2097-2101 (1938).
[6] Kharbanda, P. O., *The Industrial Chemist*, pp. 124-7 (March, 1955).
[7] Gelles, E. and Pitzer, K. S., *Journal of the American Chemical Society* 75, pp. 5259-67 (1953).
[8] Spencer, H. M. and Flannagan, G. M. *Ibid.* 64, pp. 2511-13 (1942).
[9] McGee, P. R., *et al.*, *Journal of Chemical Physics* 21, pp. 242-6 (1953).
[10] Rihani, D. N., and Doraiswamy, L. K., *Industrial and Engineering Chemistry Fundamentals* 4 (1), pp. 17-21 (1965).
[11] Timmermans, J., Physico-Chemical Constants of Pure Organic Compounds, Elsevier Publishing Company, Inc., New York (1950).
[12] International Critical Tables, McGraw-Hill Book Company, Inc. (1926).
[13] Railing, W. E., *Journal of the American Chemical Society* 61, pp. 3349-53 (1939).
[14] Pitzer, K. S., *Ibid.* 62 pp. 331-5 (1940).
[15] Reed, J. F., and Rabinovitch, B. S., *Journal of Chemical and Engineering Data* 2 (1), p. 75 (1957).
[16] Witzell, O. W., and Johnson, J. W., Paper presented at American Society of Heating, Refrigerating, and Air-Conditioning Engineers Semi-Annual Meeting (Jan., 1965).
[17] Bromley, L. A., and Wilkes, C. R., *Industrial and Engineering Chemistry* 43 (7), pp. 1641-8 (1951).
[18] Kimura, O., *Journal of the Chemical Society, Japan* 63, pp. 814-19 (1942).
[19] Heston, W. M., *et al.*, *Journal of the American Chemical Society* 72, pp. 2071-5 (1950).
[20] Masia, A. P., and Alvarez, M. D., U. S. Department of Commerce, Office of Technical Service, PB Report 147,614 (1961).
[21] Owens, E. J., and Thodos, G., *AIChE Journal* 6 (4), pp. 676-81 (1960).
[22] Venart, J. E. S., *Journal of Chemical and Engineering Data* 10 (3), pp. 239-41 (July 1965).
[23] Robbins, L. A., and Kingrea, C. L., *American Petroleum Institute, Division of Refining* 42 (III), pp. 52-61 (1962).

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.*

Indexing Terms: Brominated Hydrocarbons-9, Bromotrifluoromethane-9, Computations-4, Ethyl Bromide-9, Ethylene Dibromide-9, Halogenated Hydrocarbons-9, Heat-7, Liquid Phase-5, Methyl Bromide-9, Physical Properties-7, Pressure-6, Properties/Characteristics/-7, Temperature-6, Vapor Phase-5.

Part 24, C_1-C_4 Aldehydes, will appear in an early issue.