Physical Properties of Hydrocarbons

PART 43–Halogenated Aromatics

From charts you can get these properties of halogenated aromatics:

- Vapor pressure
- Heat of vaporization
- Heat capacity
- Density
- Viscosity
- Surface tension
- Thermal conductivity

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FOR MANY YEARS, chlorobenzene was the preferred intermediate for producing phenol. All new phenol production is now based on oxidation of either toluene or cumene. With phenol consuming over one-half of the total chlorobenzene and DDT accounting for 25 percent, chlorobenzene would appear to be in for slow, if any, growth from its present level of 600 million pounds/year.

Bromobenzene and fluorobenzene are largely used as solvents or intermediates for producing specialty products.

Benzyl chloride is enjoying a fast growth and should top 100 million pounds/year in 1970. The major use is in the production of butyl benzyl phthalate.

Vapor Pressure and Critical Properties. The critical properties have been experimentally measured for bromobenzene, chlorobenzene, and fluorobenzene.[1,2,3] Lydersen's method was used to calculate the critical properties of benzyl chloride.[4]

Literature data are reported for the vapor pressure of bromobenzene; chlorobenzene, and fluorobenzene up to the critical point.[1,3,5] Stull has compiled the vapor pressure data on benzyl chloride up to its boiling point.[3] The vapor pressure above the boiling point was estimated.[6]

Heat of Vaporization. The heat of vaporization at the boiling point was estimated for benzyl chloride by the Giacalone equation, with a probable error of a few percent.[4] The experimental data[1,5,7] for the other three compounds at their boiling points were extended over a wide temperature range by the Kharbanda nomograph.[8]

Heat Capacity. The vapor heat capacities of bromobenzene, chlorobenzene, and fluorobenzene have been reported in the literature.[5,9,10,11] The data for benzyl chloride were estimated from its molecular structure.[9] Above 500° C, the error should be less than 2 percent.

Timmermans records the liquid heat capacities of bromobenzene, chlorobenzene, and fluorobenzene from −23 to 47° C.[2] Scott and coworkers measured the heat capacity of fluorobenzene from −38 to 77° C.[5] The room temperature values are available for all four compounds.[1,7] The data were extended to 200° C by the equation, density times heat capacity equals a constant, with a probable error of 5 percent or less.

Density. Experimental data over the entire temperature range are available for all but benzyl chloride.[1,2,7] The room temperature data for benzyl chloride[2] was extended by Lydersen's method.[4] For the other compounds, the error averaged 0.4 percent when compared to eight experimental values.

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TABLE 43-1—Physical Properties of Halogenated Aromatics

	Boiling Point, °C	Melting Point, °C	Molecular Weight	Critical Properties		
				T_c, °C	P_c, psia	d_c, g/ml
Bromobenzene	156.2	−30.6	157.02	397	655	0.4859
Chlorobenzene	131.6	−45.2	112.56	359.2	655	0.3654
Fluorobenzene	84.8	−41.9	96.10	286.6	655	0.3541
Benzyl Chloride	179.4	−39.2	126.58	411*	567*	0.348*

* Estimated.

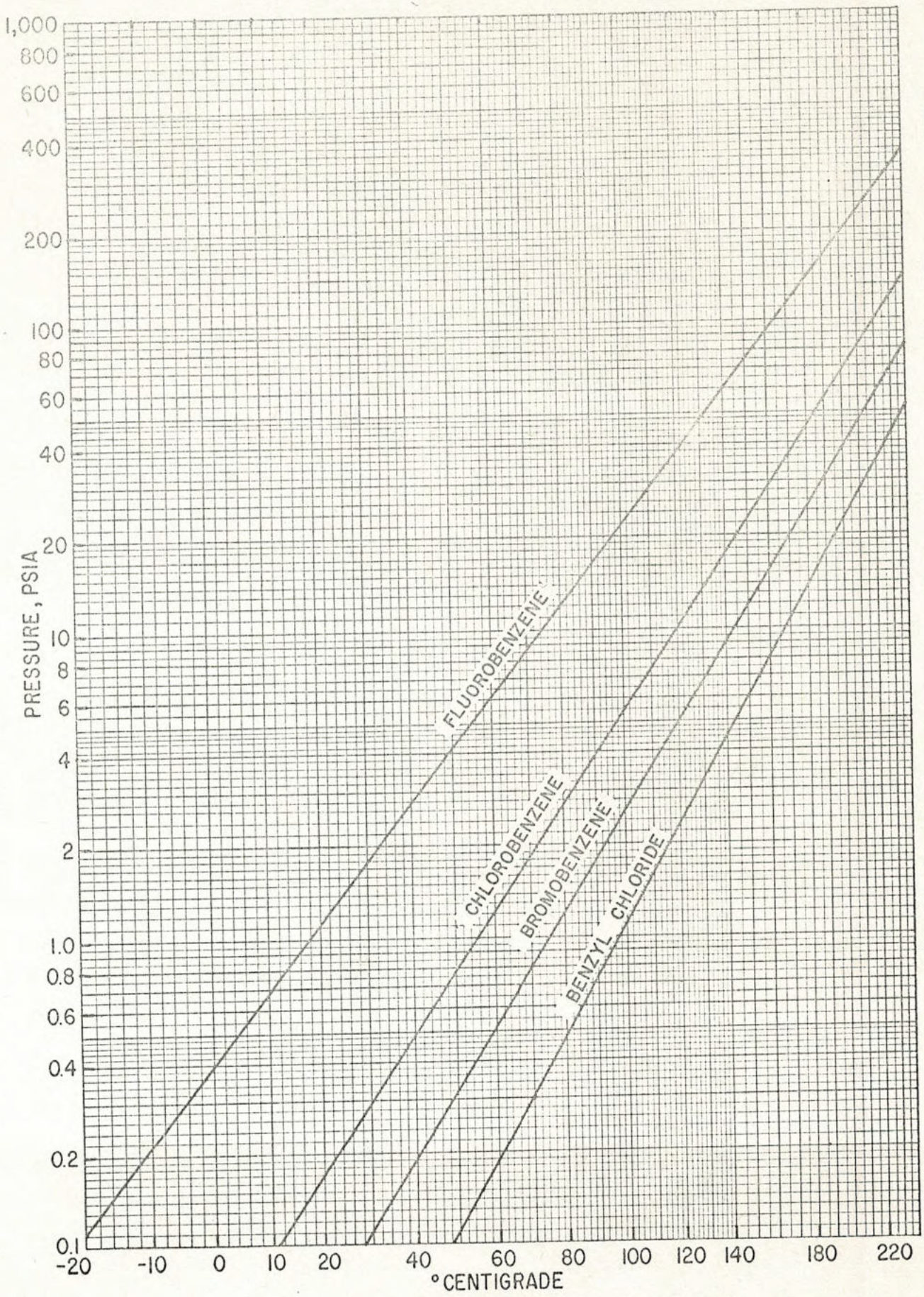

Fig. 43-1—Vapor pressure of halogenated aromatics from —20 to 240° C.

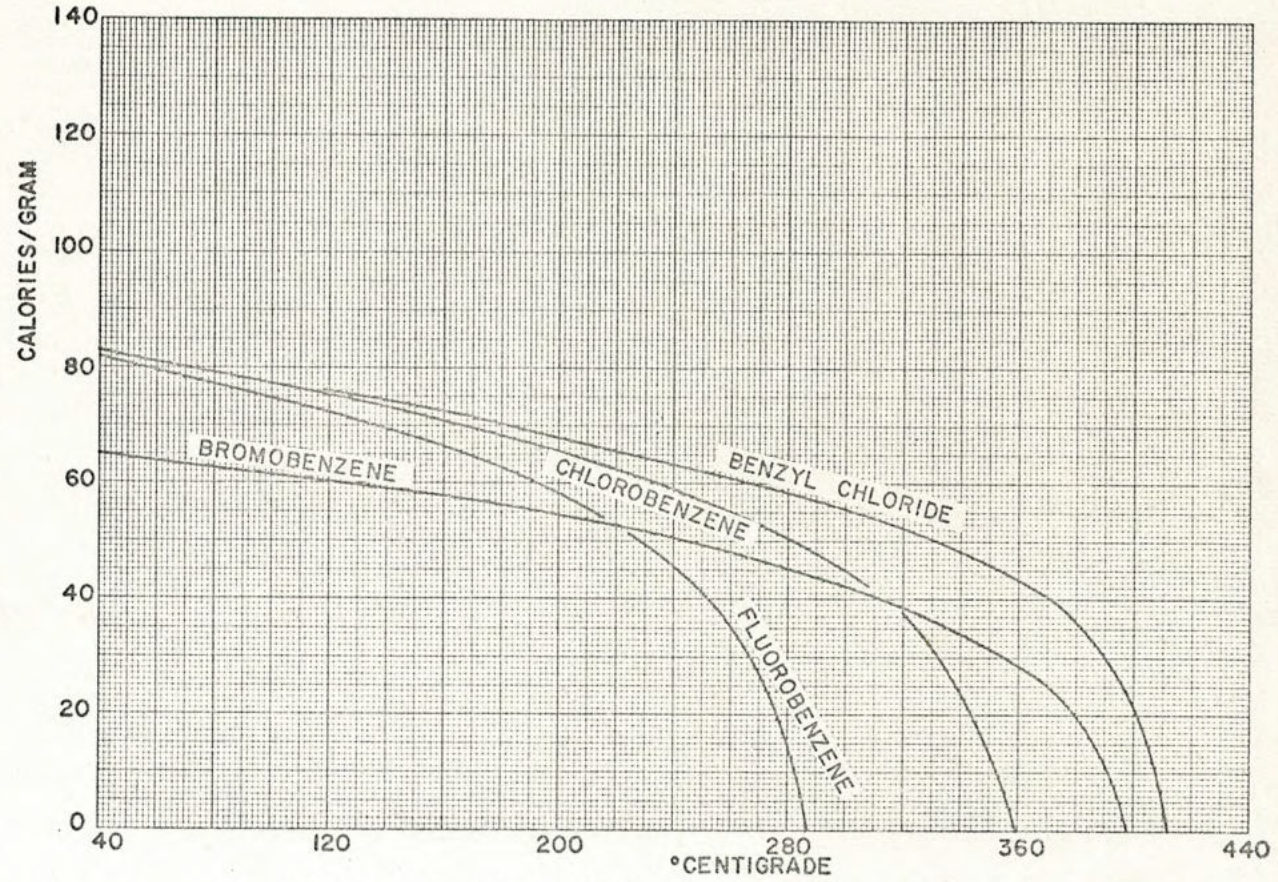

Fig. 43-2—Heat of vaporization of halogenated aromatics from 40 to 410° C.

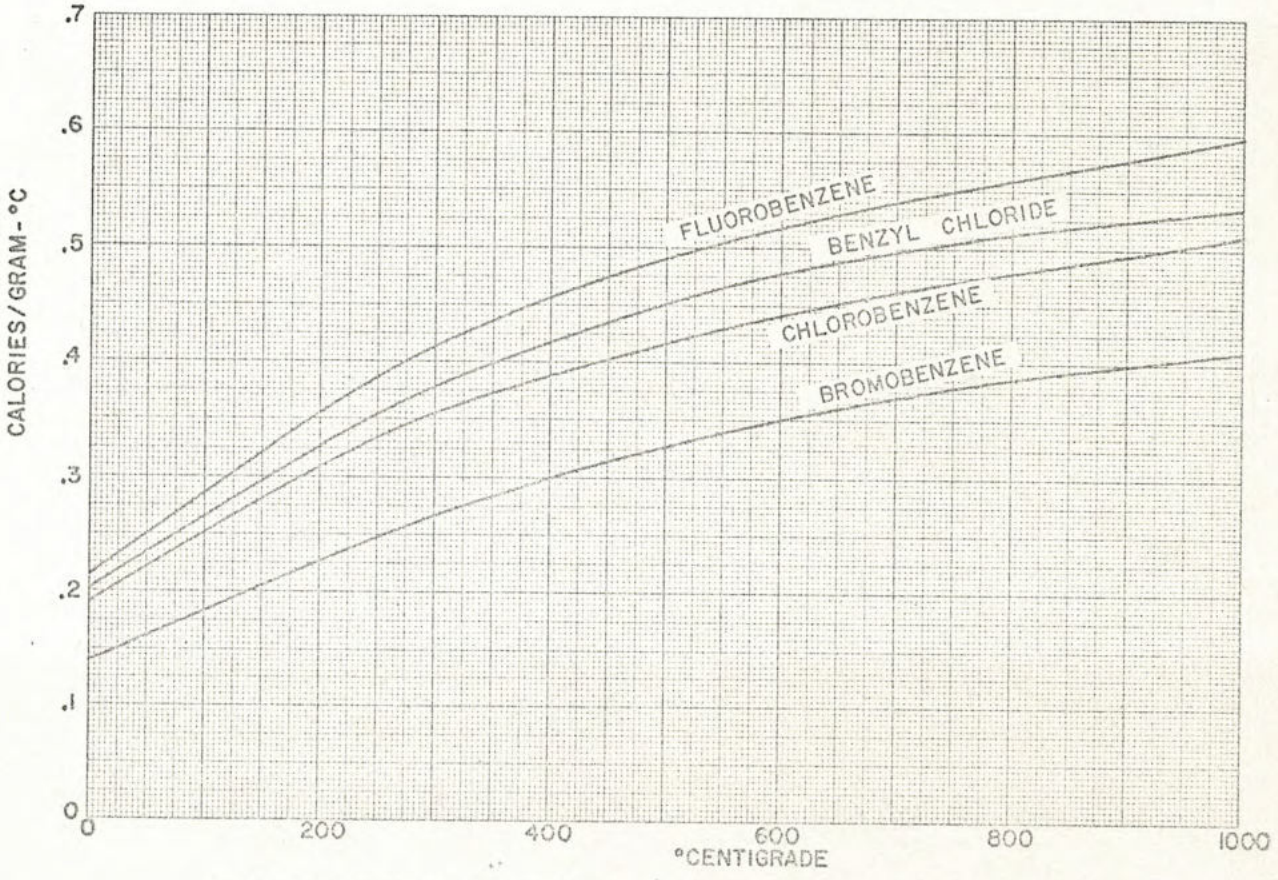

Fig. 43-3—Vapor heat capacity of halogenated aromatics from 0 to 1,000° C.

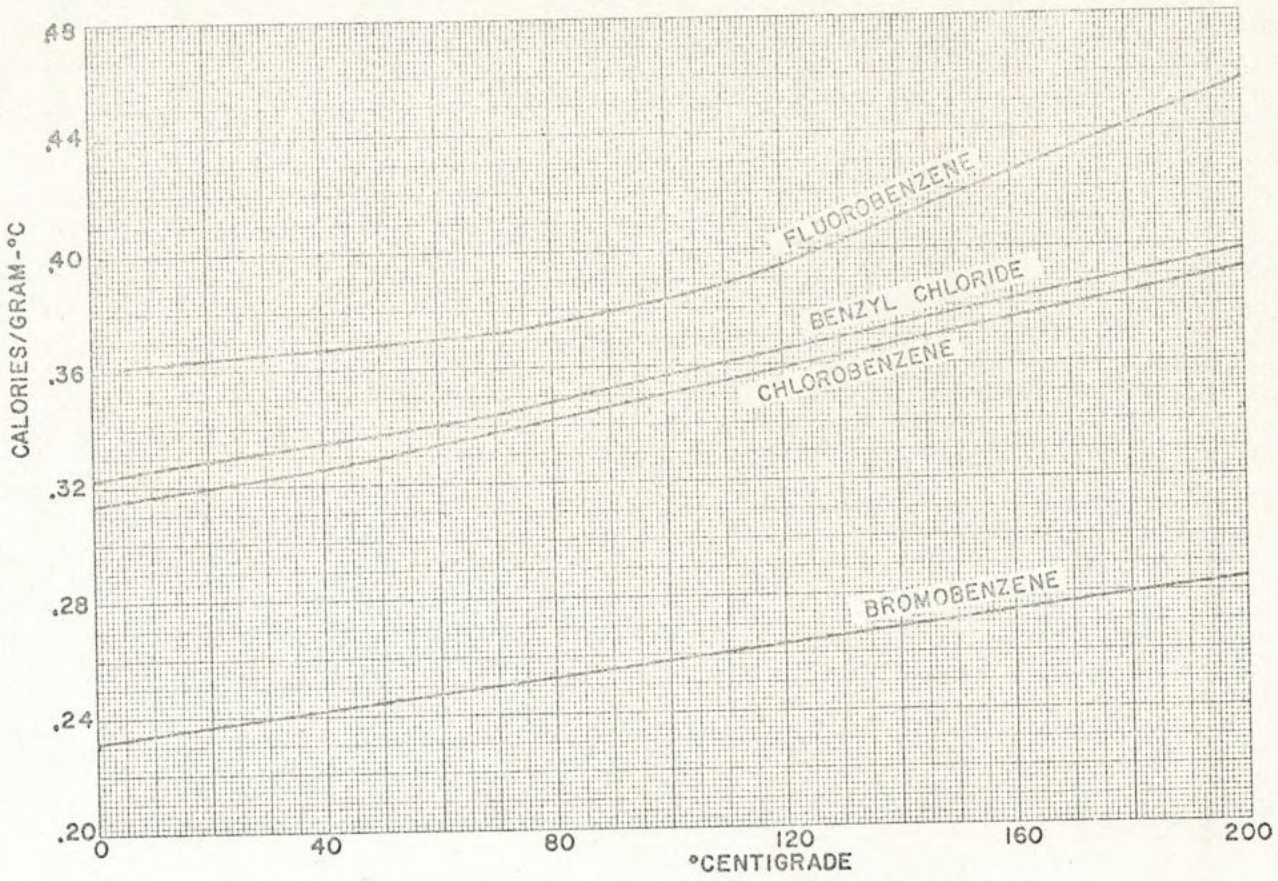

Fig. 43-4—Liquid heat capacity of halogenated aromatics from 0 to 200° C.

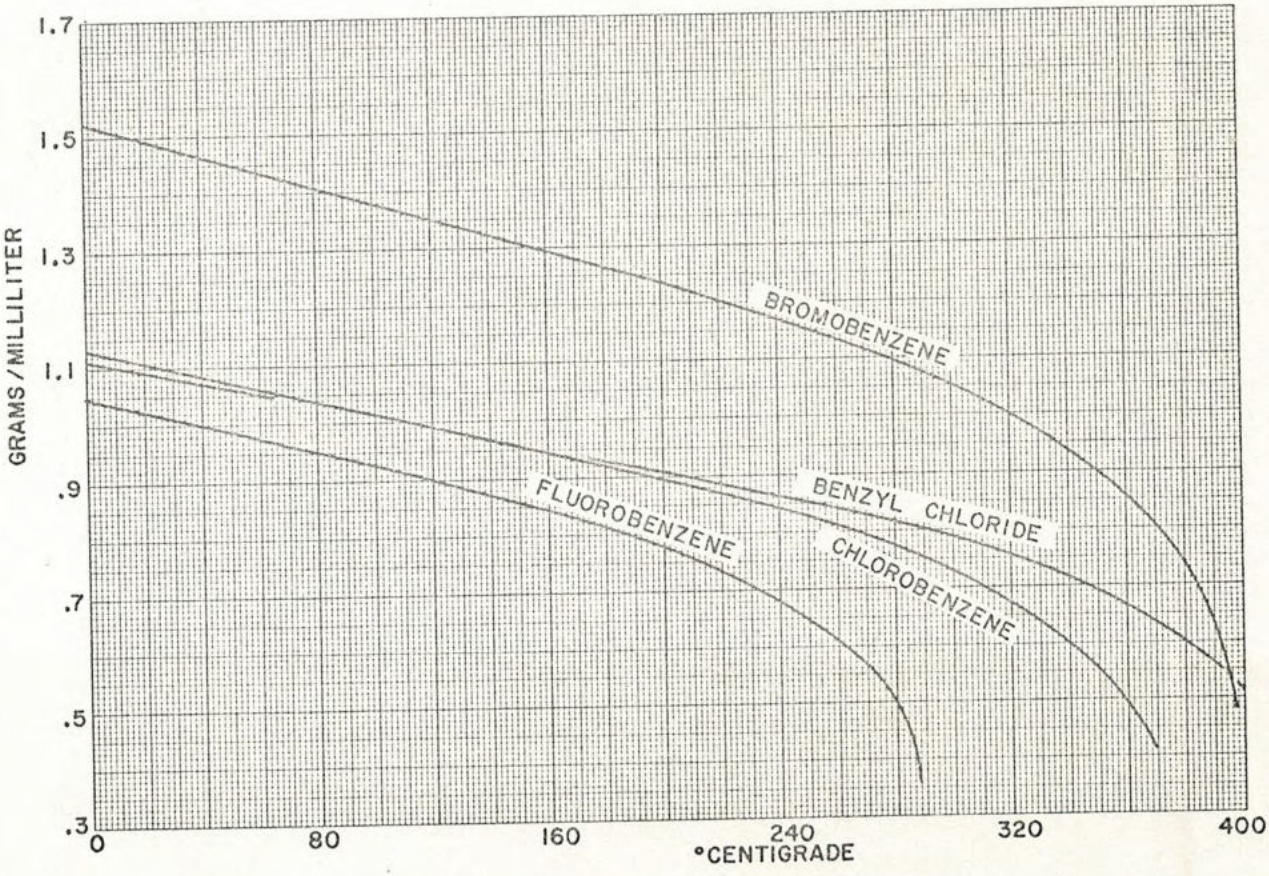

Fig. 43-5—Liquid density of halogenated aromatics from 0 to 400° C.

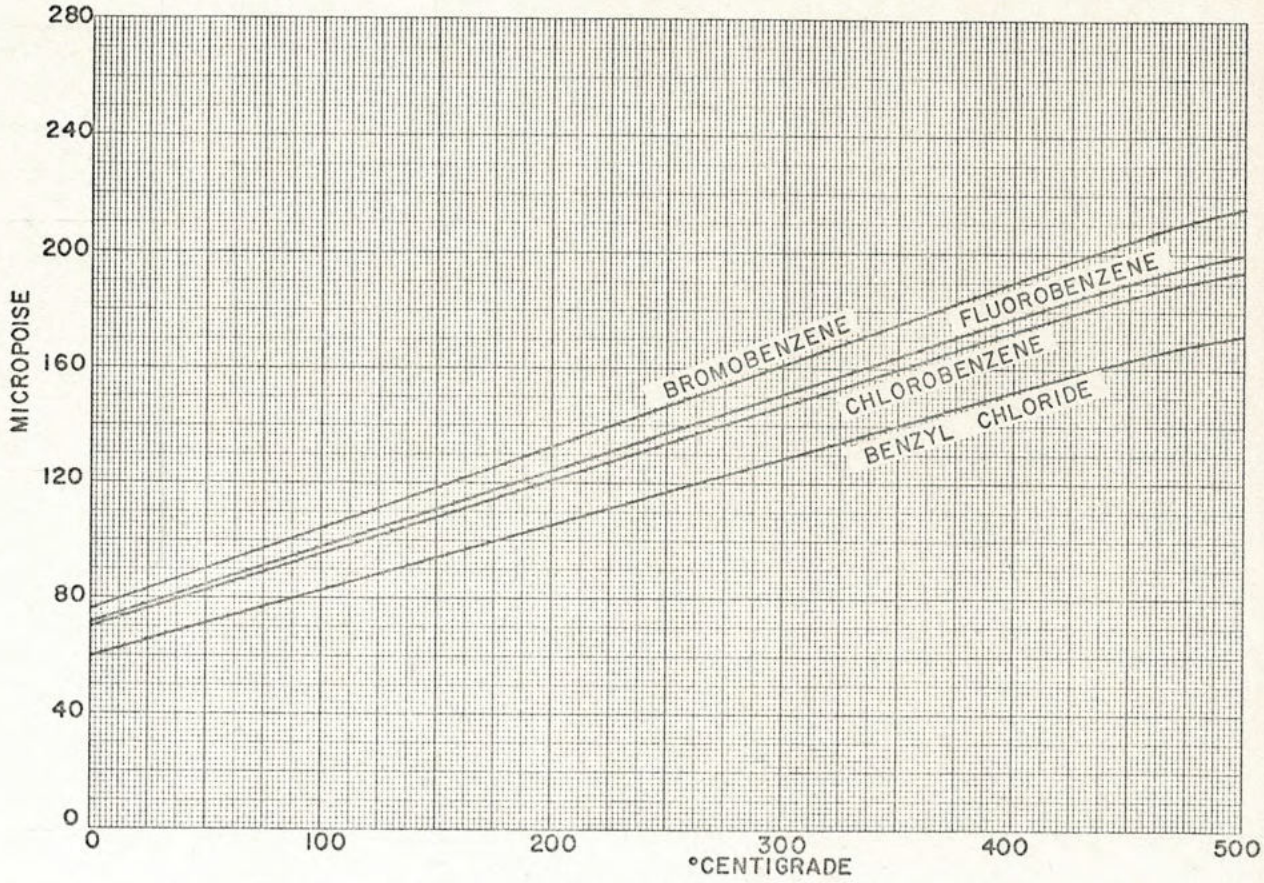

Fig. 43-6—Vapor viscosity of halogenated aromatics from 0 to 500° C.

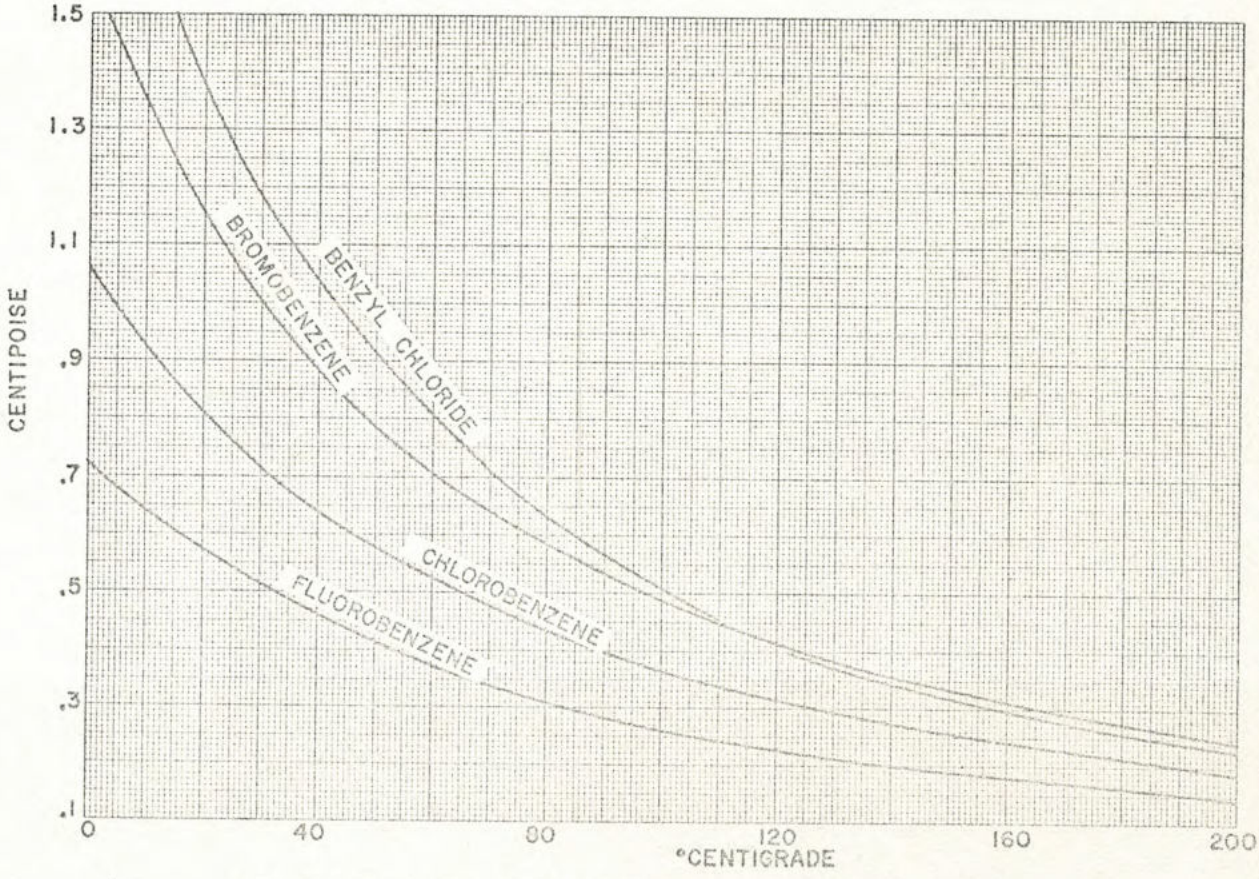

Fig. 43-7—Liquid viscosity of halogenated aromatics from 0 to 200° C.

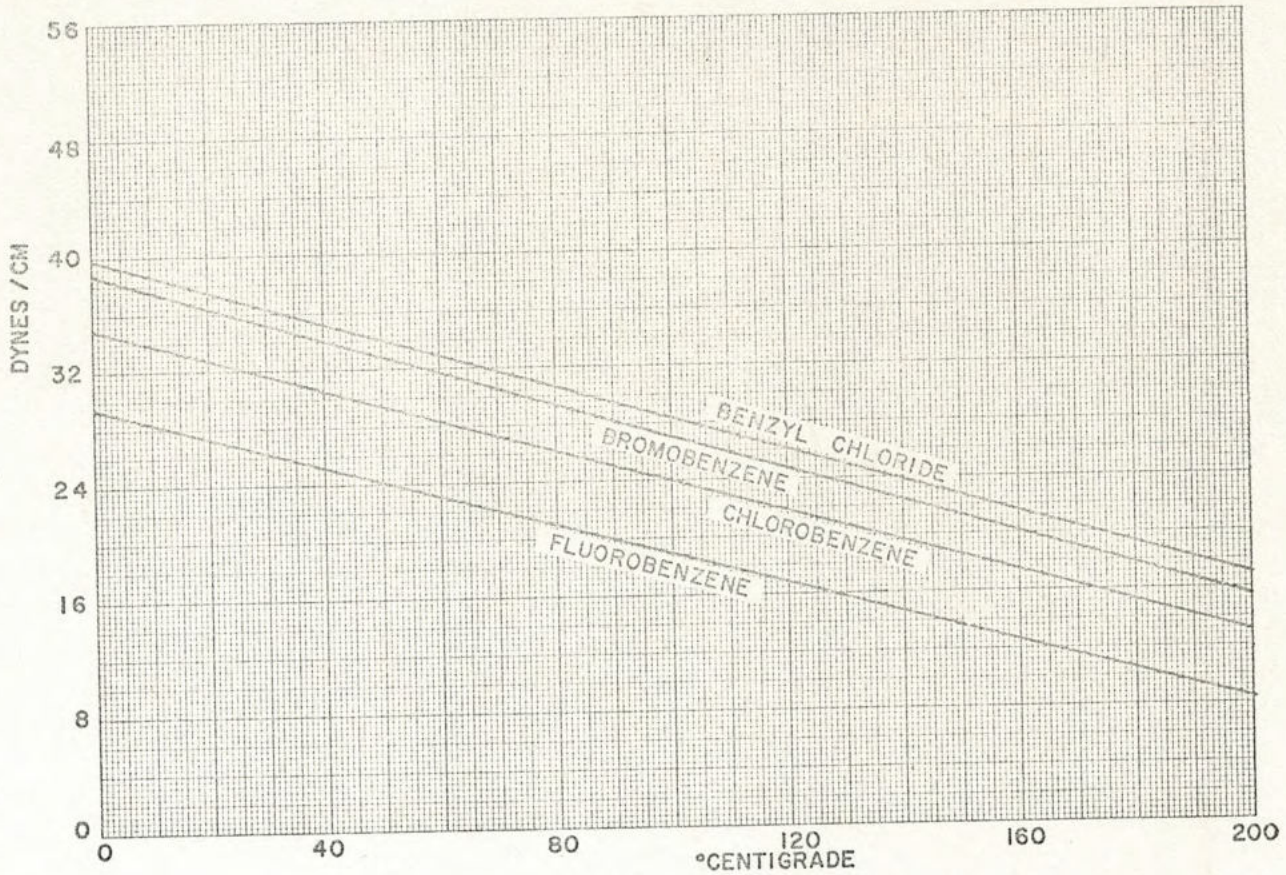

Fig. 43-8—Surface tension of halogenated aromatics from 0 to 200° C.

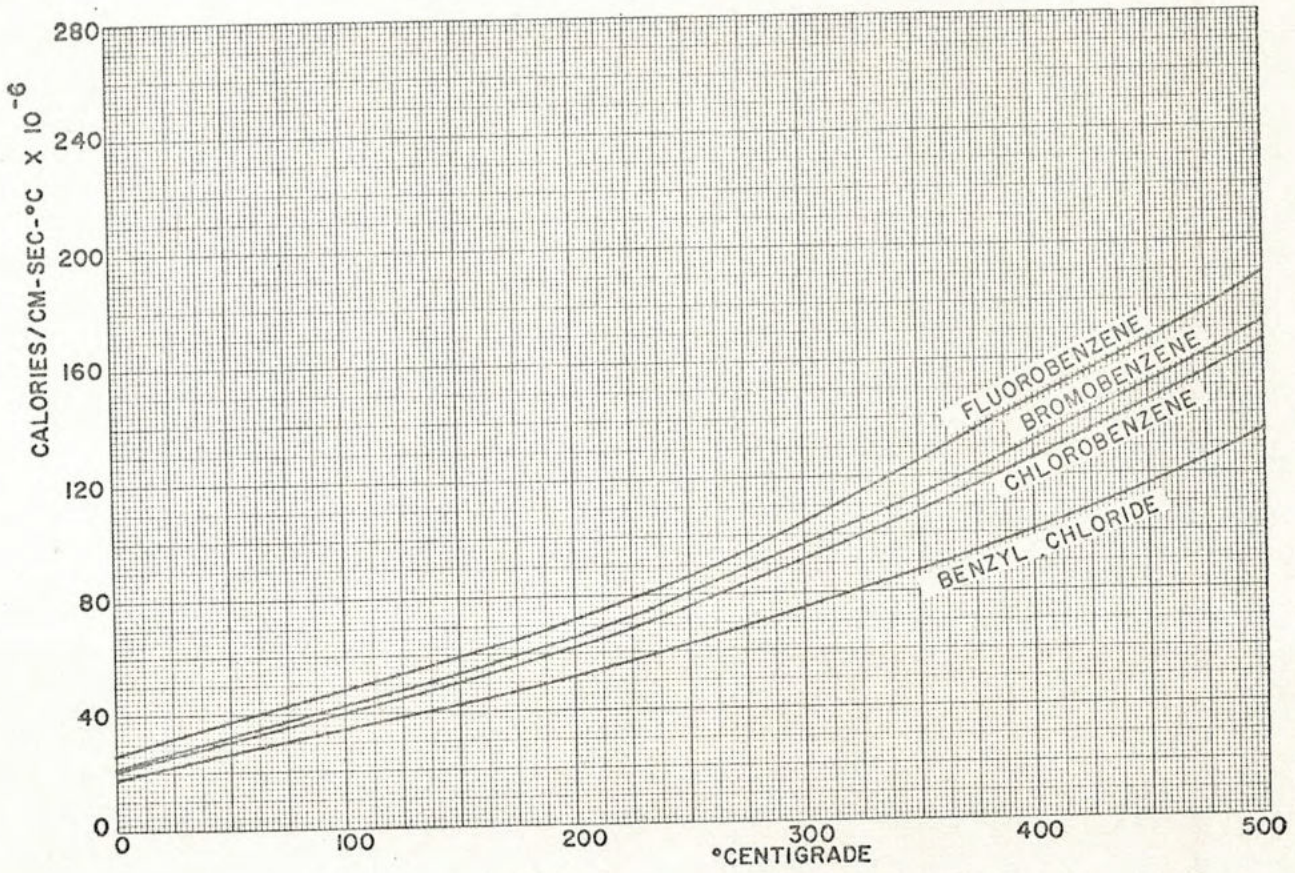

Fig. 43-9—Vapor thermal conductivity of halogenated aromatics from 0 to 500° C.

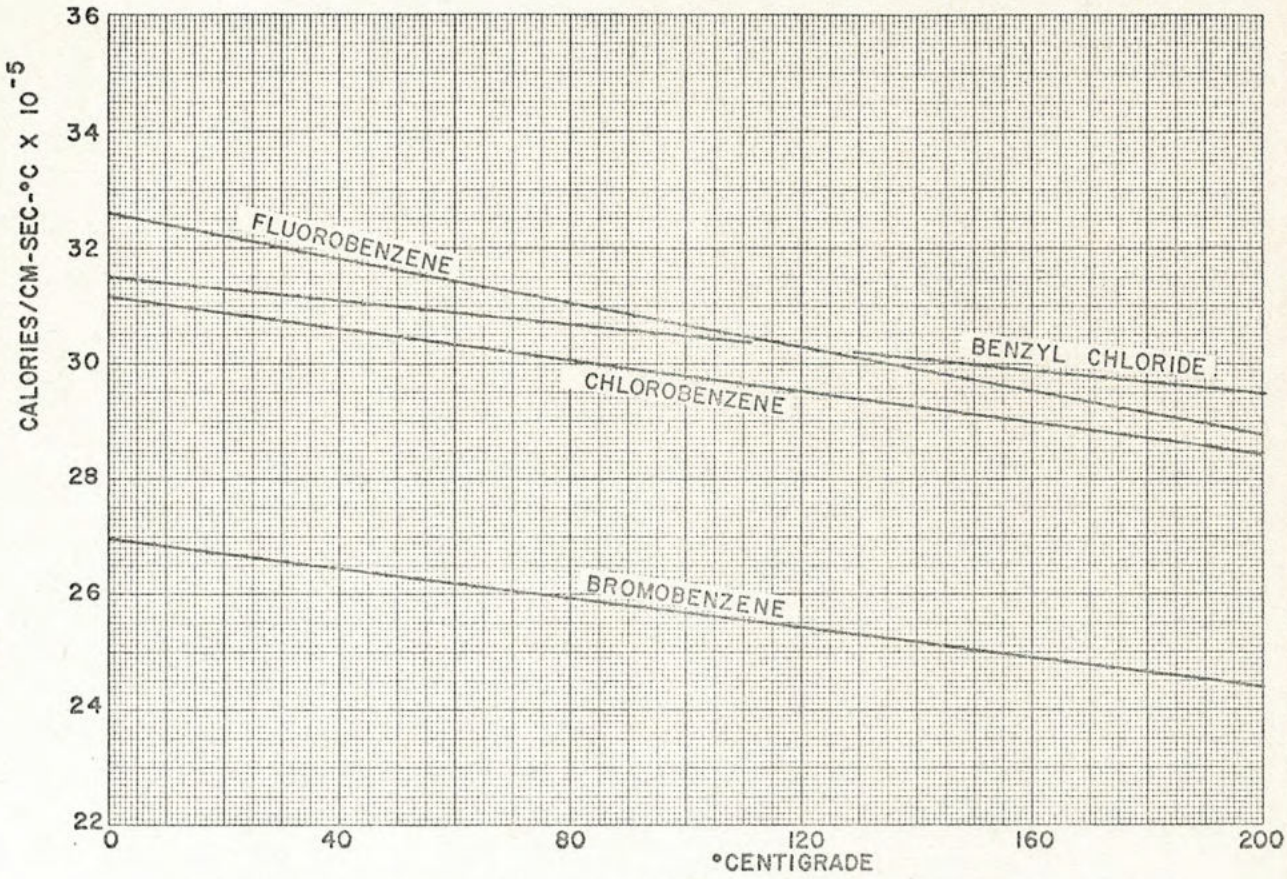

Fig. 43-10—Liquid thermal conductivity of halogenated aromatics from 0 to 200° C.

Viscosity. The procedure developed by Bromley and Wilke was used to estimate the vapor viscosities.[12]

Liquid viscosities have been measured from 0 to 150° C for bromobenzenes;[1,2,13] 0 to 240° C for chlorobenzene;[1,2,7,13] from 0 to 80° C for fluorobenzene;[1,2] and at room temperature for benzyl chloride.[2] Souder's method was used to extend the data to 200° C, with an expected error of 5 percent.

Surface Tension. Extensive surface tension data are reported for bromobenzene and chlorobenzene.[1,2] The room temperature values for fluorobenzene and benzyl chloride[1,2] were used to calculate the constant in Sugden's equation, which relates surface tension to the fourth power of the density. This equation was used to estimate the surface tension from 0 to 200° C for these two compounds. The error should be 2 to 5 percent.

Thermal Conductivity. Thodos' method was used to estimate the vapor conductivities.[14]

The procedure developed by Robbins and Kingrea was used to estimate the liquid thermal conductivities.[15] This method shows the thermal conductivity changing very slowly with temperature. The limited experimental data suggests the dropoff in thermal conductivity is more rapid with temperature.[15] The estimated values were used in plotting the graph but it is possible that the values are 10 to 15 percent low above 100° C.

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[15] Robbins, L. A. and C. L. Kingrea, *American Petroleum Institute, Division of Refining* 42 (III), pp. 52-61 (1962).

Indexing Terms: Benzyl Chloride-9, Bromobenzene-9, Chlorobenzene-9, Computations-4, Fluorobenzene-9, Halogens-9, Heat-7, Hydrocarbons-9, Liquid Phase-5, Physical Properties-7, Pressure-6, Properties/Characteristics/-7, Temperature-6, Vapor Phase-5.

PART 44—Sulfur-Containing Hydrocarbons, will appear in an early issue.