Physical Properties of Hydrocarbons

PART 36–Nitriles

From charts you can get these properties for nitriles:

- **Vapor Pressure**
- **Heat of Vaporization**
- **Heat Capacity**
- **Density**
- **Viscosity**
- **Surface Tension**
- **Thermal Conductivity**

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HYDROGEN CYANIDE has been a major industrial chemical for many years. Although it has been replaced by ammonia as a raw material for producing acrylonitrile, hydrogen cyanide production still is about 400 million pounds per year. About half of this production is consumed in the manufacture of methyl methacrylate, adiponitrile and sodium cyanide. The preferred method of manufacturing hydrogen cyanide is to react methane, ammonia and air over a platinum catalyst at a temperature above 1,000° C.

Acetonitrile, propionitrile and butyronitrile are used as raw materials in the synthesis of specialty chemicals.

Vapor Pressure and Critical Properties. The critical properties of all four compounds have been reported in the literature.[1,2] The exception is the critical density of butyronitrile. This was estimated from the molecular structure by Vowles' method, with a probable error of one percent.[3]

Stull presents the vapor pressure of HCN from the freezing point to the critical temperature.[4] Data are available up to the boiling point for the other three nitriles.[1,2,4,5] The vapor pressures above 1 atmosphere were estimated by the method used in previous articles. This method gave an average error of 1.9 percent for HCN.

Heat of Vaporization. The heat of vaporization at the boiling point has been determined for HCN and acetonitrile.[2,3,5,6] The estimation technique of Giacalone was used to calculate the heat of vaporization of propionitrile and butyronitrile.[3] The boiling point data were extended over a wide temperature range by the Kharbanda nomograph.[7] The over-all error is probably 5 percent or less.

Heat Capacity. McBride and Gordon have calculated the vapor heat capacity of HCN.[8] Kobe and Long have used spectroscopic data to determine the vapor heat capacities of HCN and acetonitrile.[9] The heat capacities of the other two compounds were estimated, with a probable error of 1-2 percent.[10]

The liquid heat capacity of HCN has been experimentally measured from the freezing point to +30° C.[2,6] Room temperature data are available for acetonitrile[5] and propionitrile.[1] The room temperature value for butyronitrile was estimated by the method proposed by Johnson and Huang.[3] The heat capacities at other temperatures were estimated from the equation, density times heat capacity equals a constant.

Density. The orthobaric densities have been measured for HCN,[1] acetonitrile,[1,2] and propionitrile[1,2] up to the

TABLE 36-1—Physical Properties of C_1 - C_4 Nitriles

Compound	Boiling Point, °C	Freezing Point, °C	Molecular Weight	Critical Properties		
				T_c °C	P_c psia	d_c g/ml
Hydrogen Cyanide	25.7	− 13.3	27.03	183.5	733	0.20
Acetonitrile	81.8	− 45.7	41.05	274.7	700	0.237
Propionitrile	97.3	− 91.9	55.07	291.2	606	0.240
Butyronitrile	117.9	−112	69.10	309	549	0.242

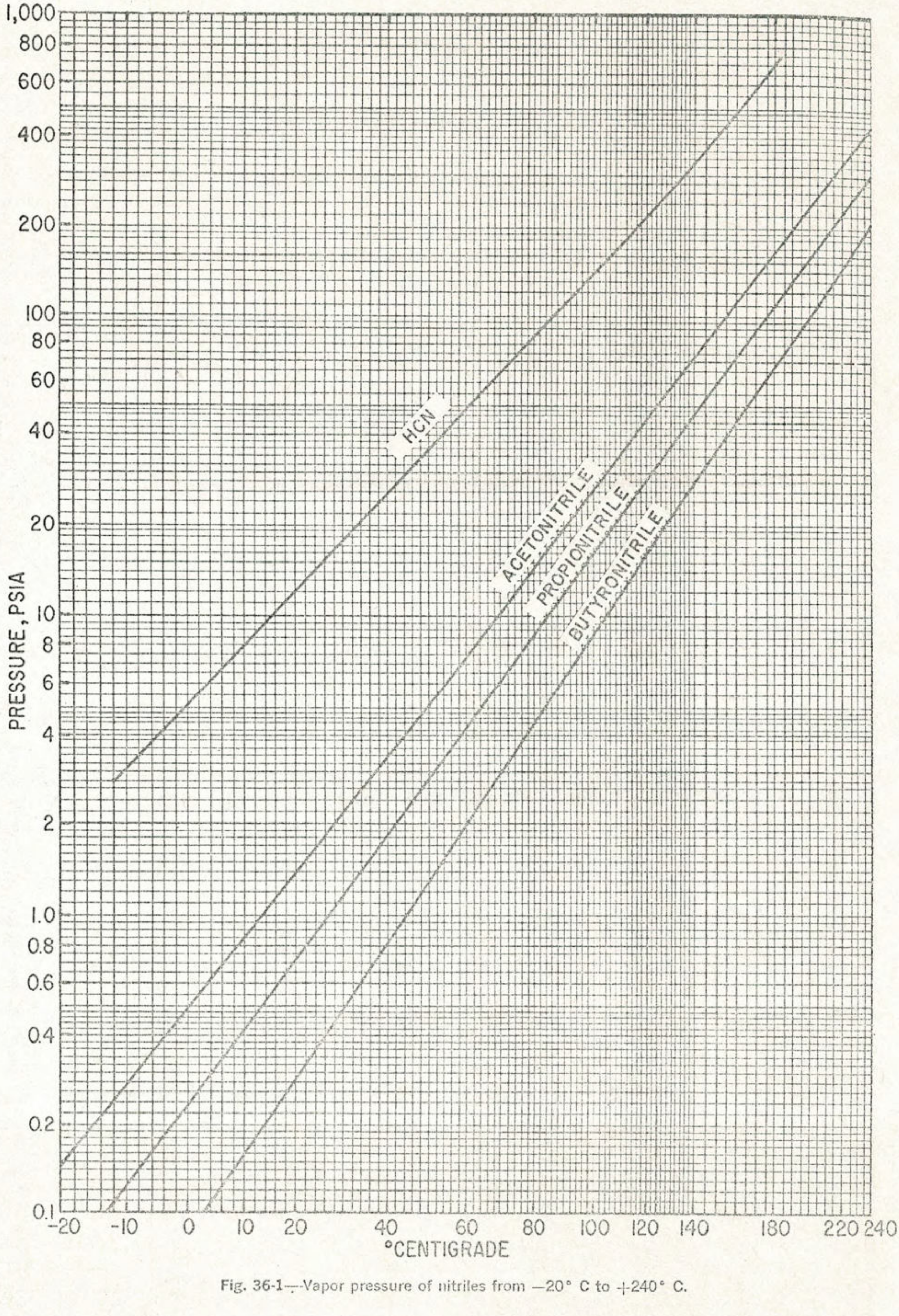

Fig. 36-1—Vapor pressure of nitriles from −20° C to +240° C.

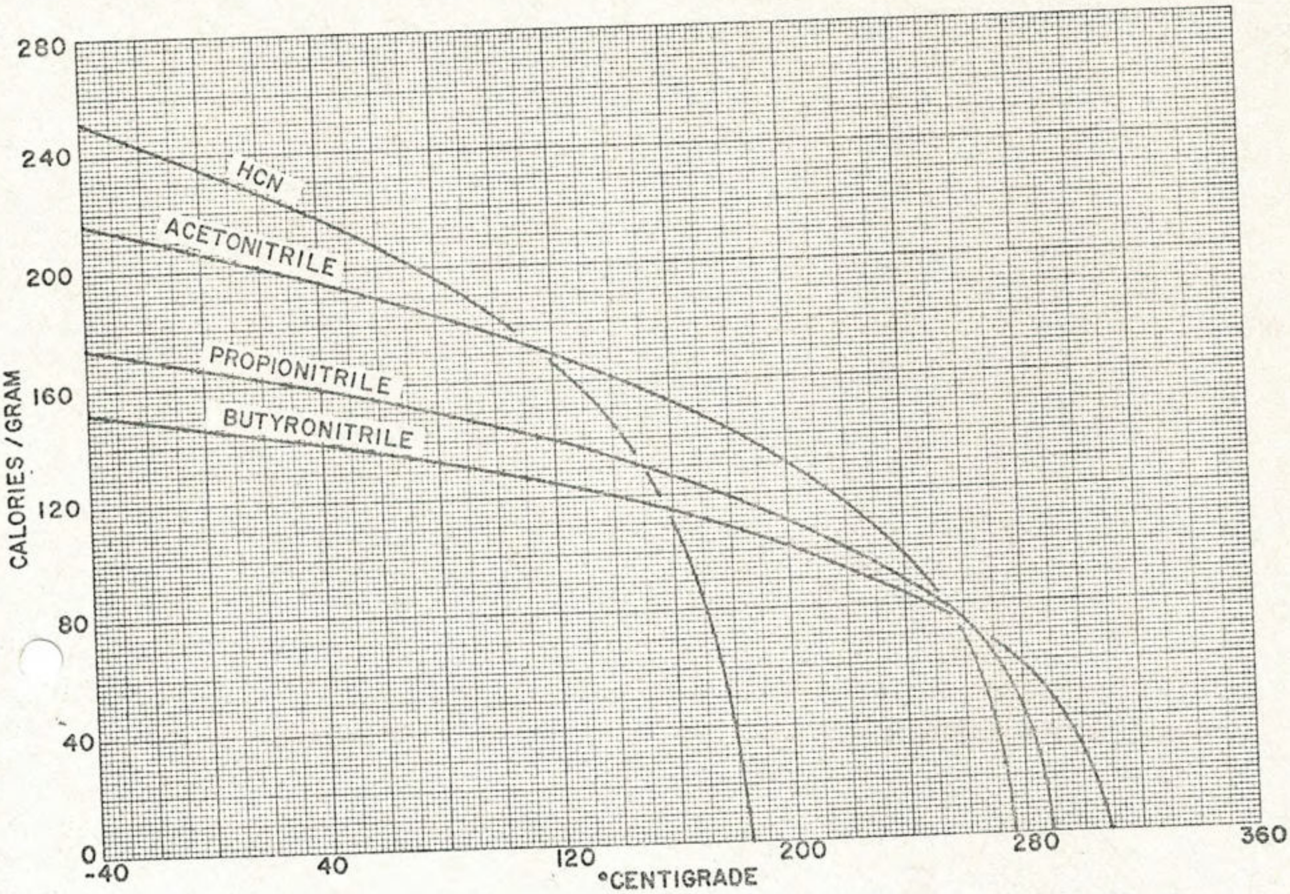

Fig. 36-2—Heat of vaporization of nitriles from −40° C to +310° C.

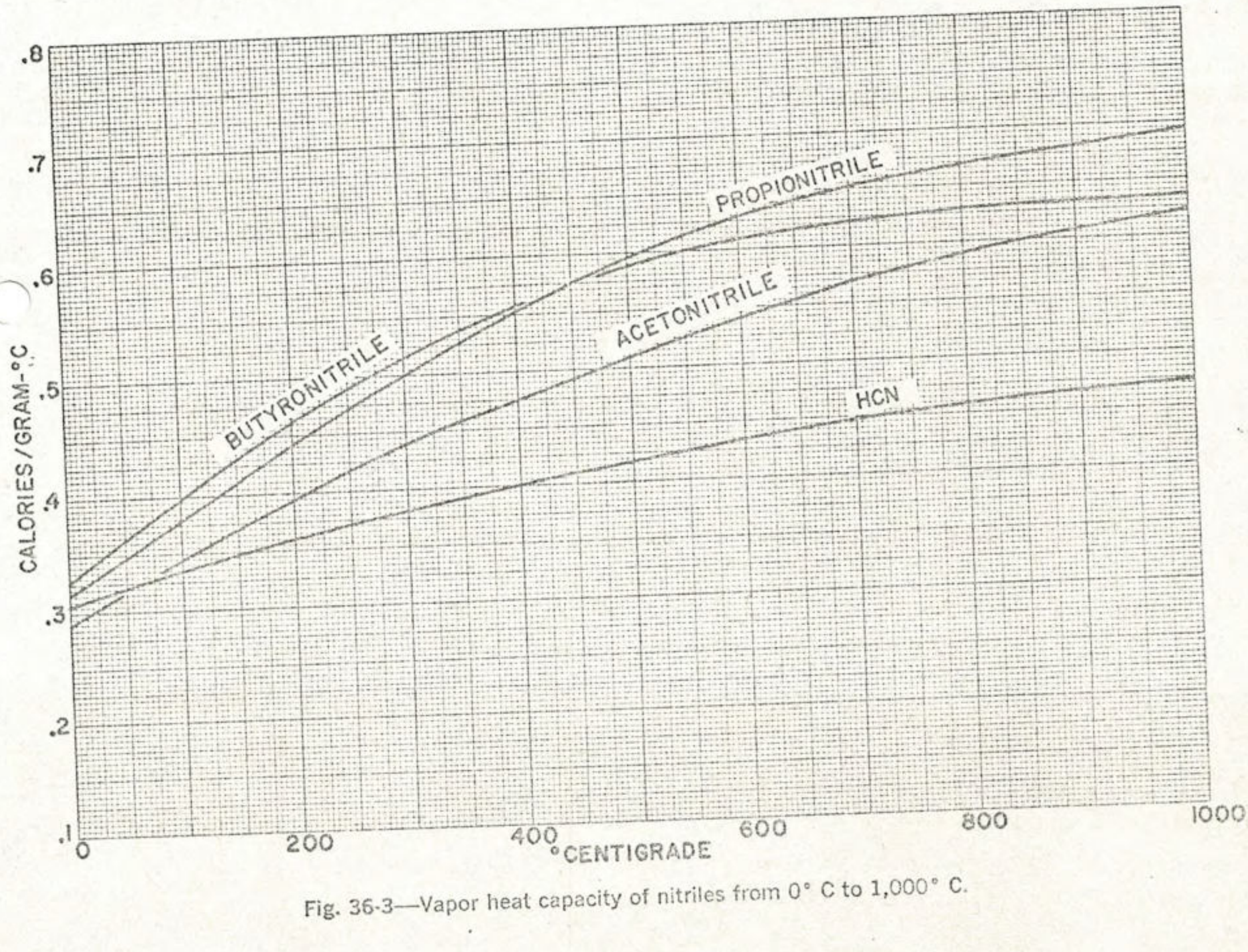

Fig. 36-3—Vapor heat capacity of nitriles from 0° C to 1,000° C.

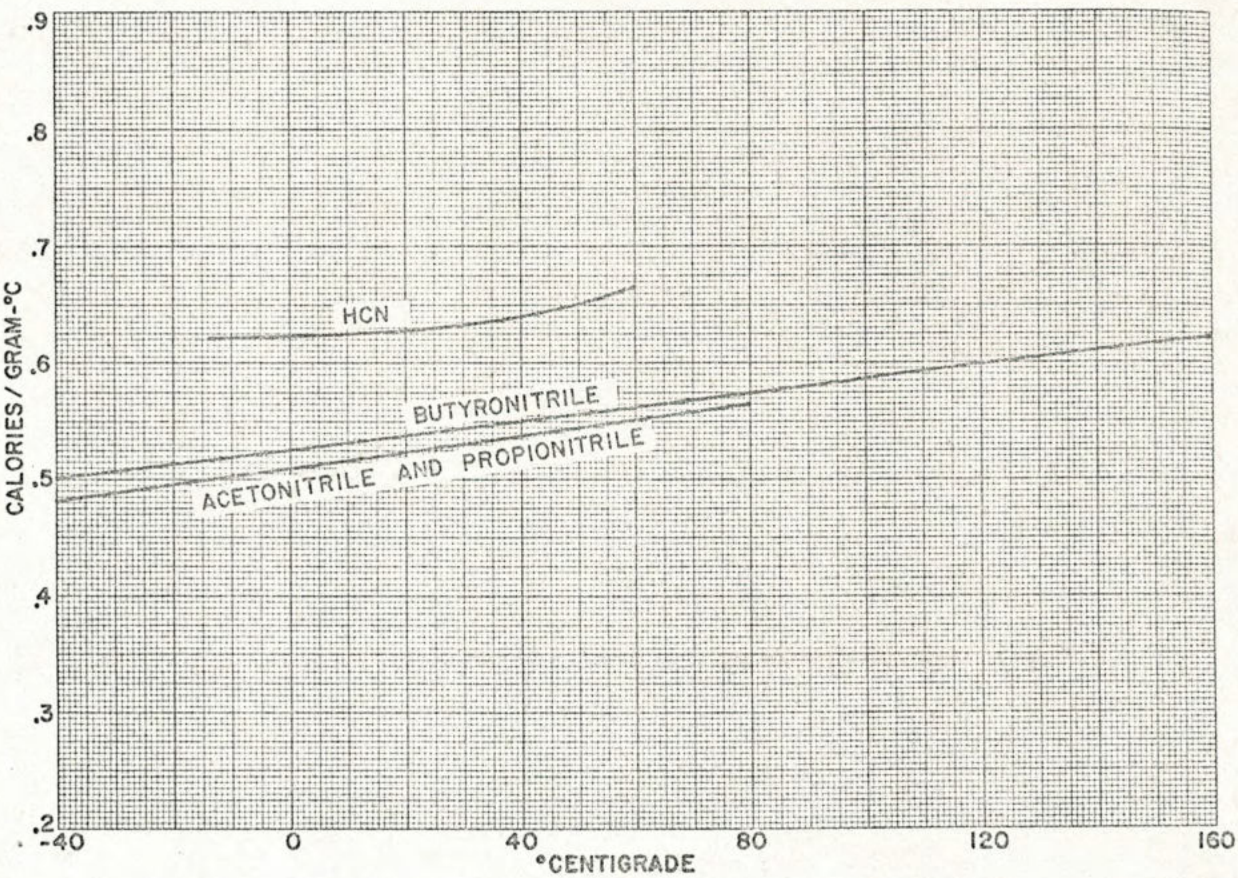

Fig. 36-4—Liquid heat capacity of nitriles from −40° C to +160° C.

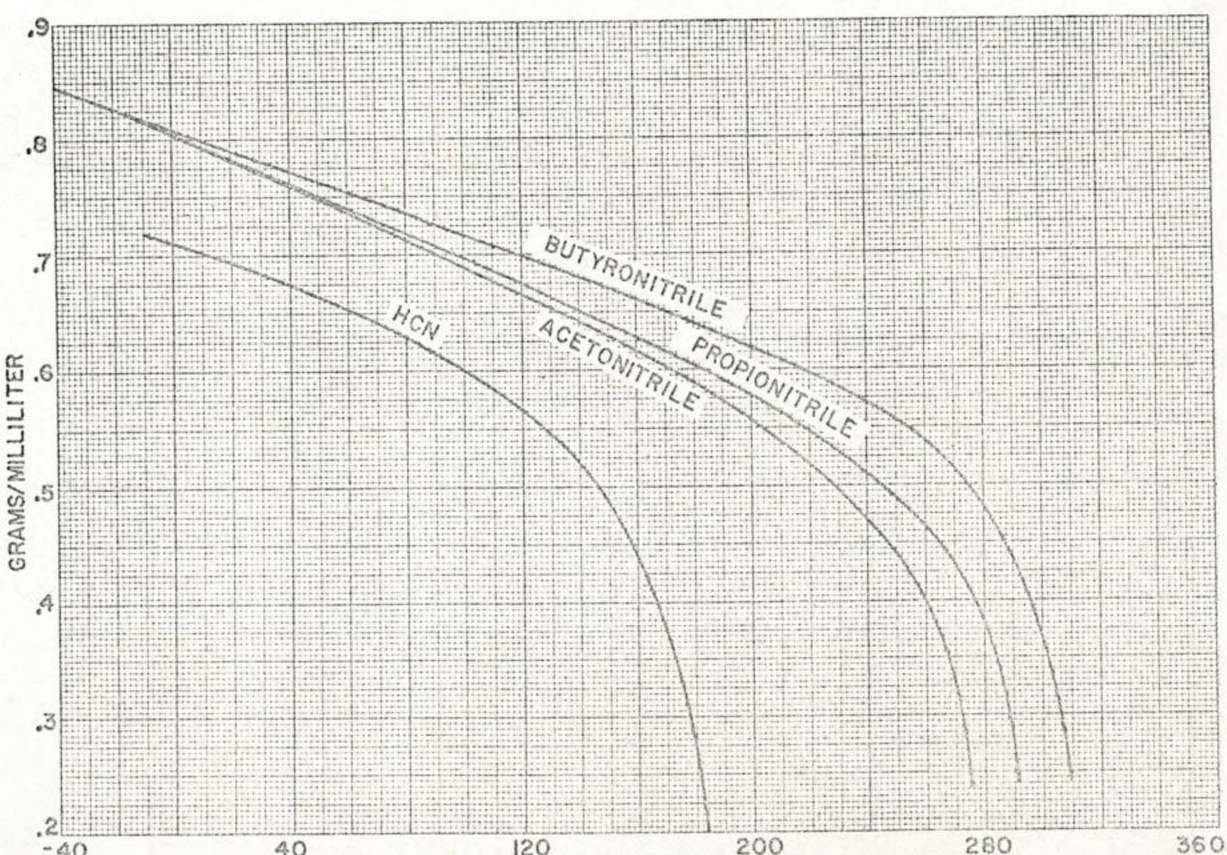

Fig. 36-5—Liquid density of nitriles from −40° C to +310° C.

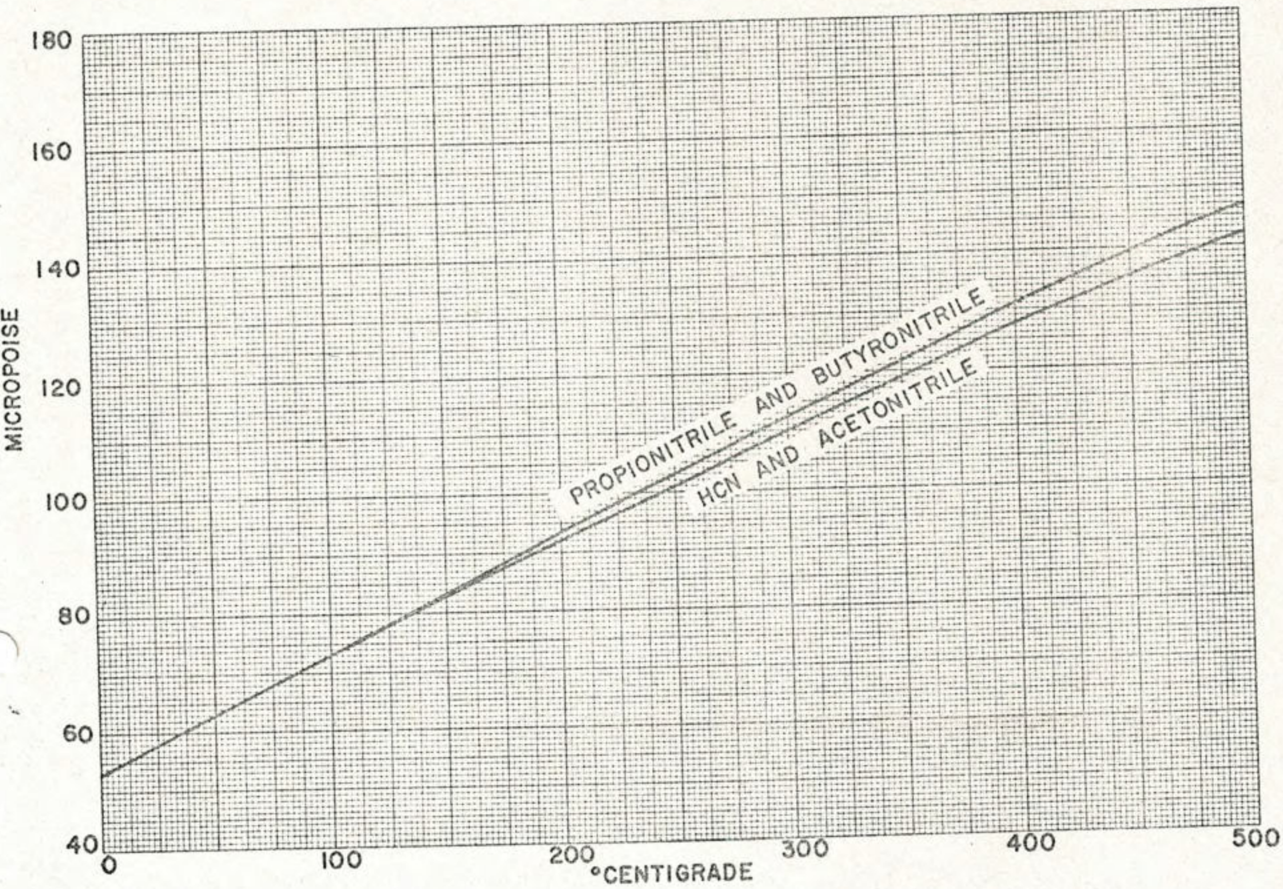

Fig. 36-6—Vapor viscosity of nitriles from 0° C to 500° C.

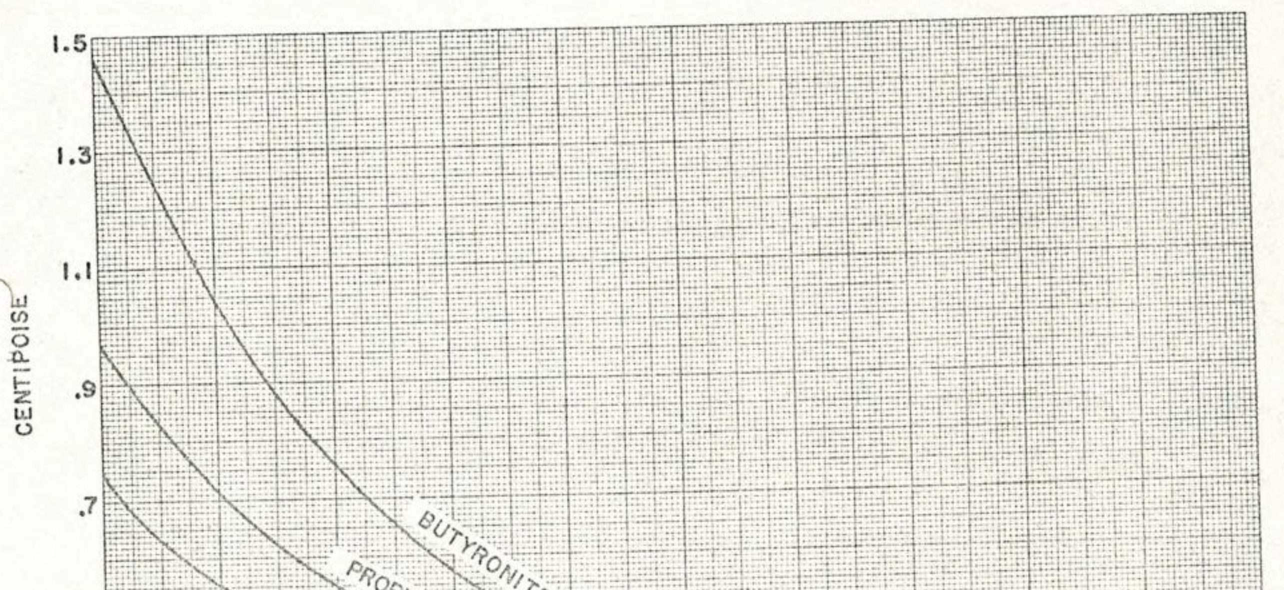

Fig. 36-7—Liquid viscosity of nitriles from −40° C to +160° C.

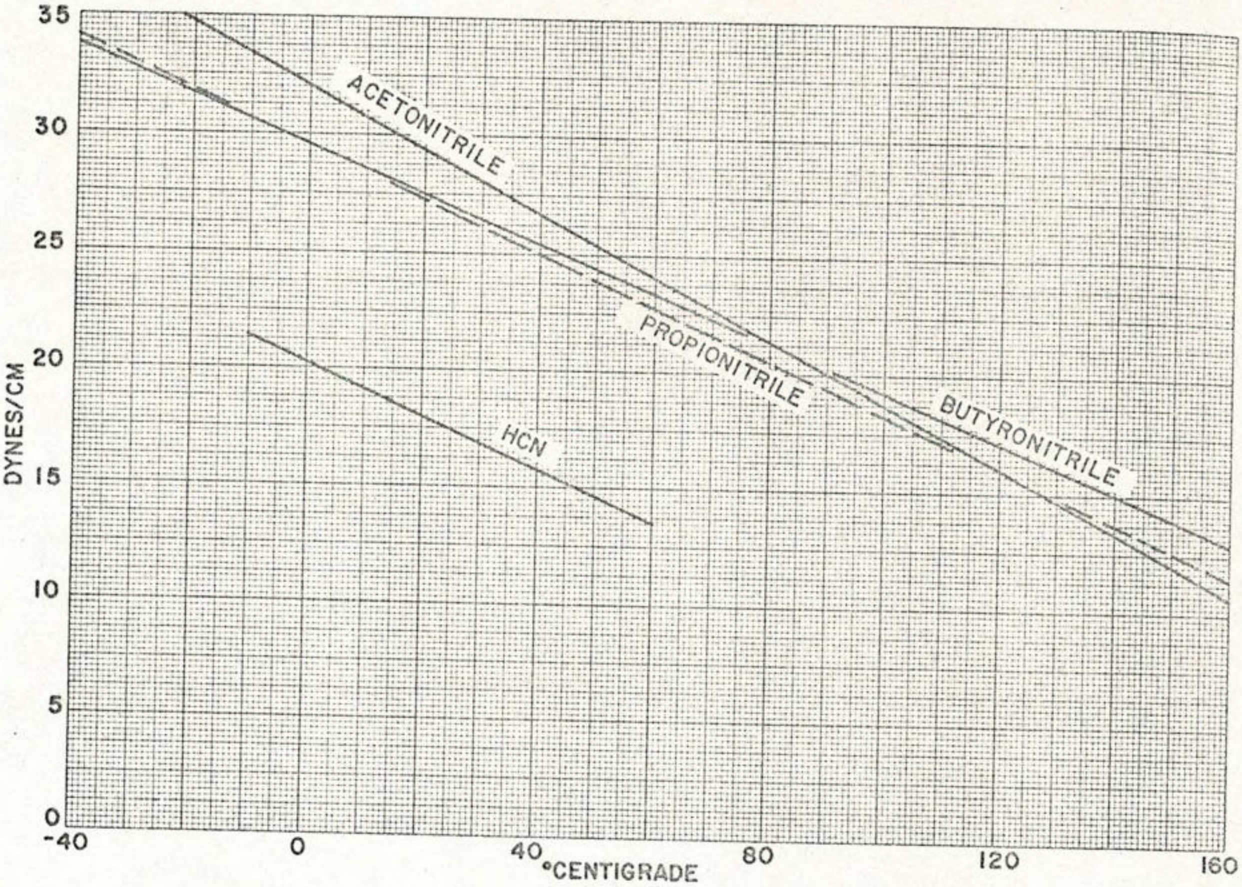

Fig. 36-8—Surface tension of nitriles from −40° C to +160° C.

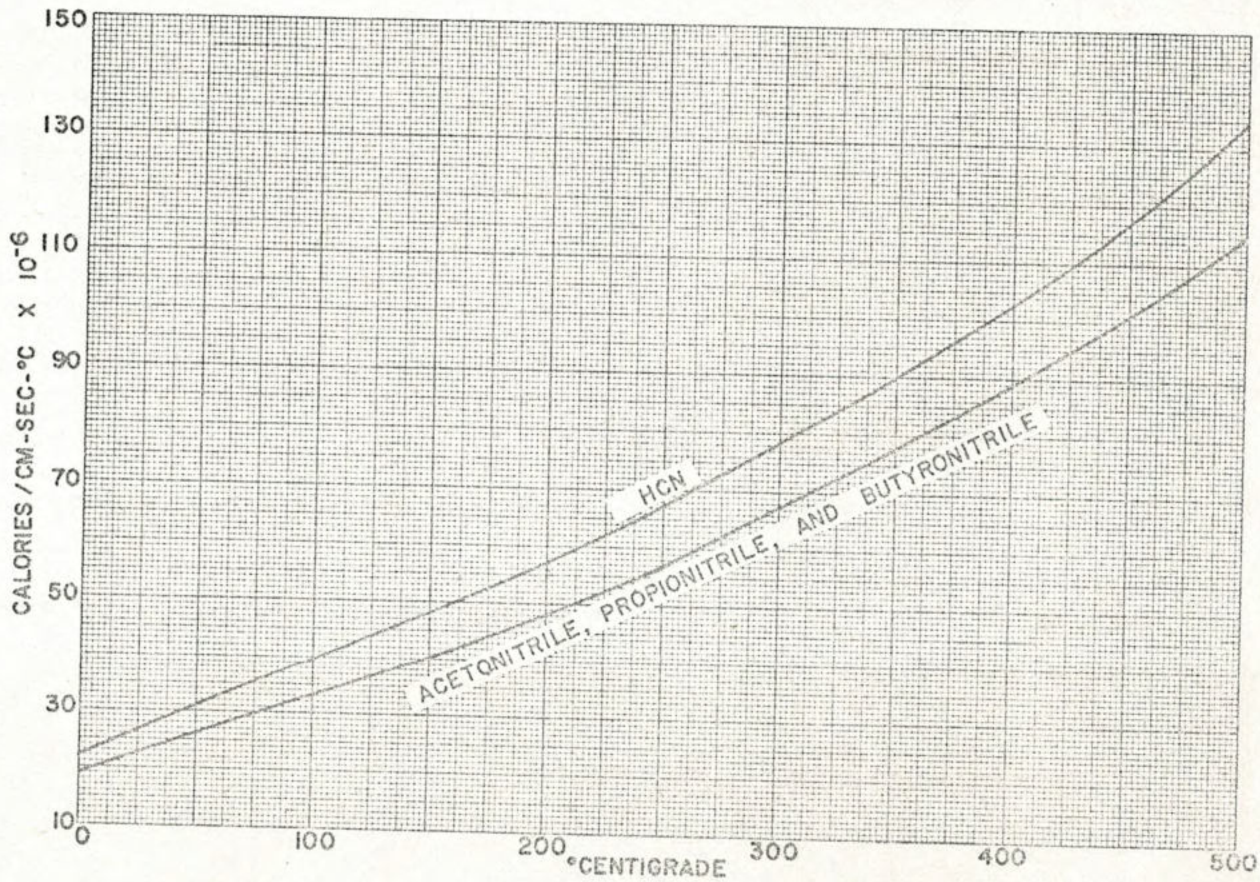

Fig. 36-9—Vapor thermal conductivity of nitriles from 0° C to 500° C.

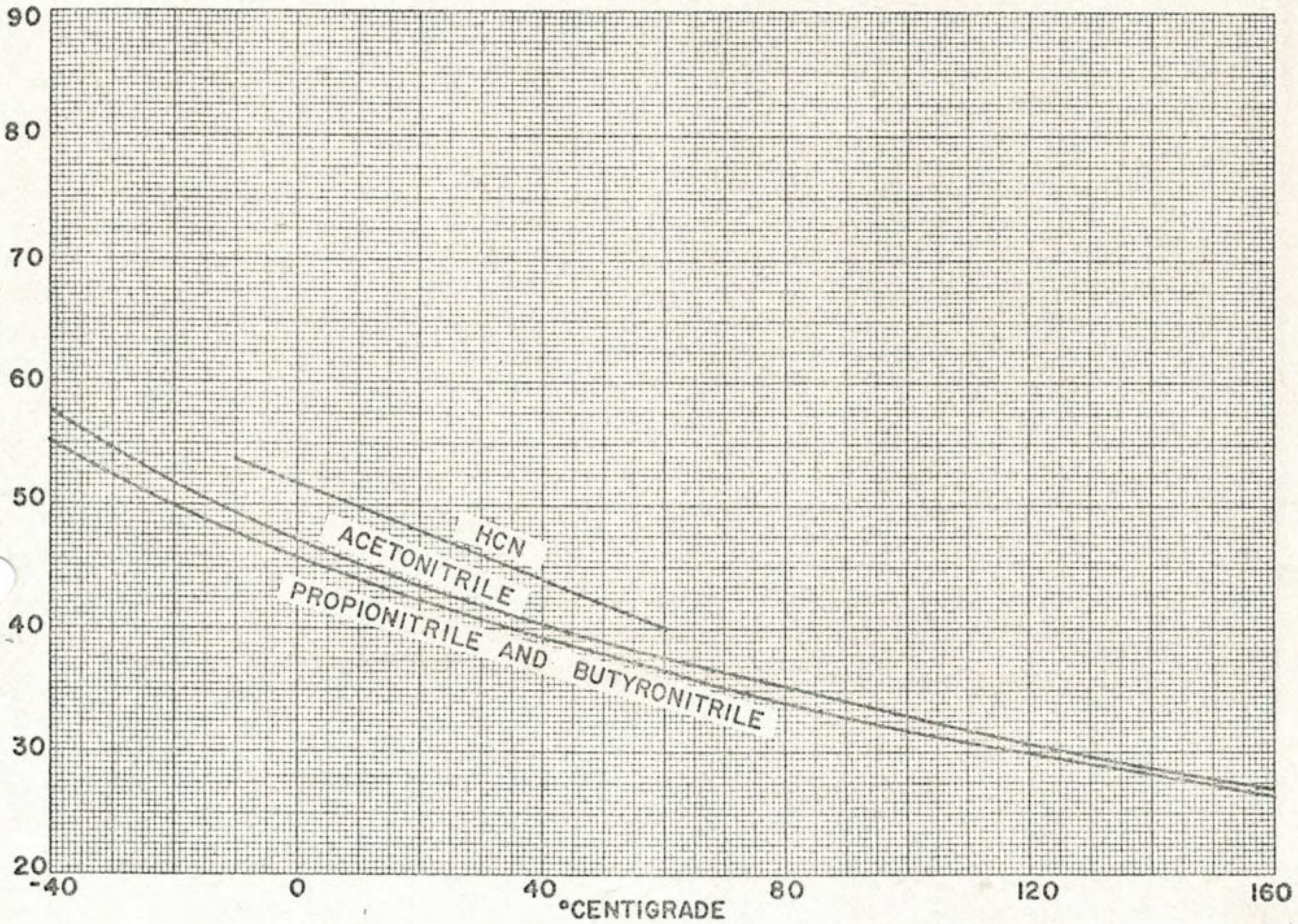

Fig. 36-10—Liquid thermal conductivity of nitriles from −40° C to +160° C.

critical point. Timmermans reports the density of butyronitrile from 0-100° C. The method of Lyderson and coworkers[3] was used to calculate the density of butyronitrile at other temperatures.

Viscosity. The vapor viscosities were estimated by the method of Bromley and Wilke.[11]

Liquid viscosity data are reported in the literature for HCN from −10° to +20° C,[1] for acetonitrile from 0 to 40° C,[2,5] for propionitrile from 0 to 80° C[1,2,12] and for butyronitrile at room temperature.[2] Thomas' method was used to calculate the viscosities at other temperatures.

The constant in the equation was calculated from experimental data. Comparison of estimated values with 16 experimental data points showed an average error of 1.6 percent.

Surface Tension. Extensive surface tension data are available for all four compounds.[1,5]

Thermal Conductivity. The vapor and liquid thermal conductivities were estimated.[13,14]

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