Physical Properties of Hydrocarbons

PART 27 — Ketones

From charts you can get these properties for ketones:

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

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MAJOR MARKETS as solvents and intermediates have made the ketones important commercial products for many years. Acetone dominates the group with sales of 1.3 billion pounds per year. While use as a solvent is still one of its major markets, the largest is as an intermediate in the production of methyl methacrylate, methylisobutyl ketone, and methylisobutyl carbinol. Acetone is largely produced by dehydrogenation of isopropyl alcohol, and so its price is closely tied to isopropyl alcohol. The commercialization of the cumene oxidation route to phenol, with acetone as a byproduct, could have a strong effect on acetone's future. If phenol usage continues to grow rapidly, excess acetone may become available. This should lead to aggressive development of new acetone outlets, including price cutting to make acetone competitive in some presently marginal markets.

Methylethyl ketone (MEK) and methylisobutyl ketone (MIBK) are used mainly as solvents, particularly for nitrocellulose. 300 million pounds/year of MEK is produced by dehydrogenation of sec-butyl alcohol. Mesityl oxide is the starting material for making the 200 million pounds/year of MIBK that is consumed. Diethyl ketone (DEK) is used in production of specialty chemicals and medicine. It is produced by distilling sugar with an excess of lime.

The physical properties of these compounds have been extensively studied, including the properties of aqueous acetone solutions.

Vapor Pressures and Critical Properties. Kobe and coworkers have measured the critical properties and vapor pressures of all four compounds.[1] Additional data are available from several other sources.[2,3] Only the critical density of MIBK has not been measured. This was estimated by the method proposed by Vowles, with a probable error of less than 1 percent.[4] Fig. 27-2 presents the boiling point of aqueous acetone solutions.[5]

Heat of Vaporization. Experimental data are available from 0-100° C for acetone[6,7,8] and MEK.[7,8,9] Only the heat of vaporization at the boiling point has been measured for DEK[6] and MIBK.[7] The data for all four compounds have been extended from −80° C to the critical point by the Kharbanda nomograph.[10] Comparison with five experimental data points gave an average error of 0.9 percent and a maximum error of 1.7 percent.

Heat Capacity. Kobe[11] and Nickerson[9] have determined the vapor heat capacities of acetone and MEK, respec-

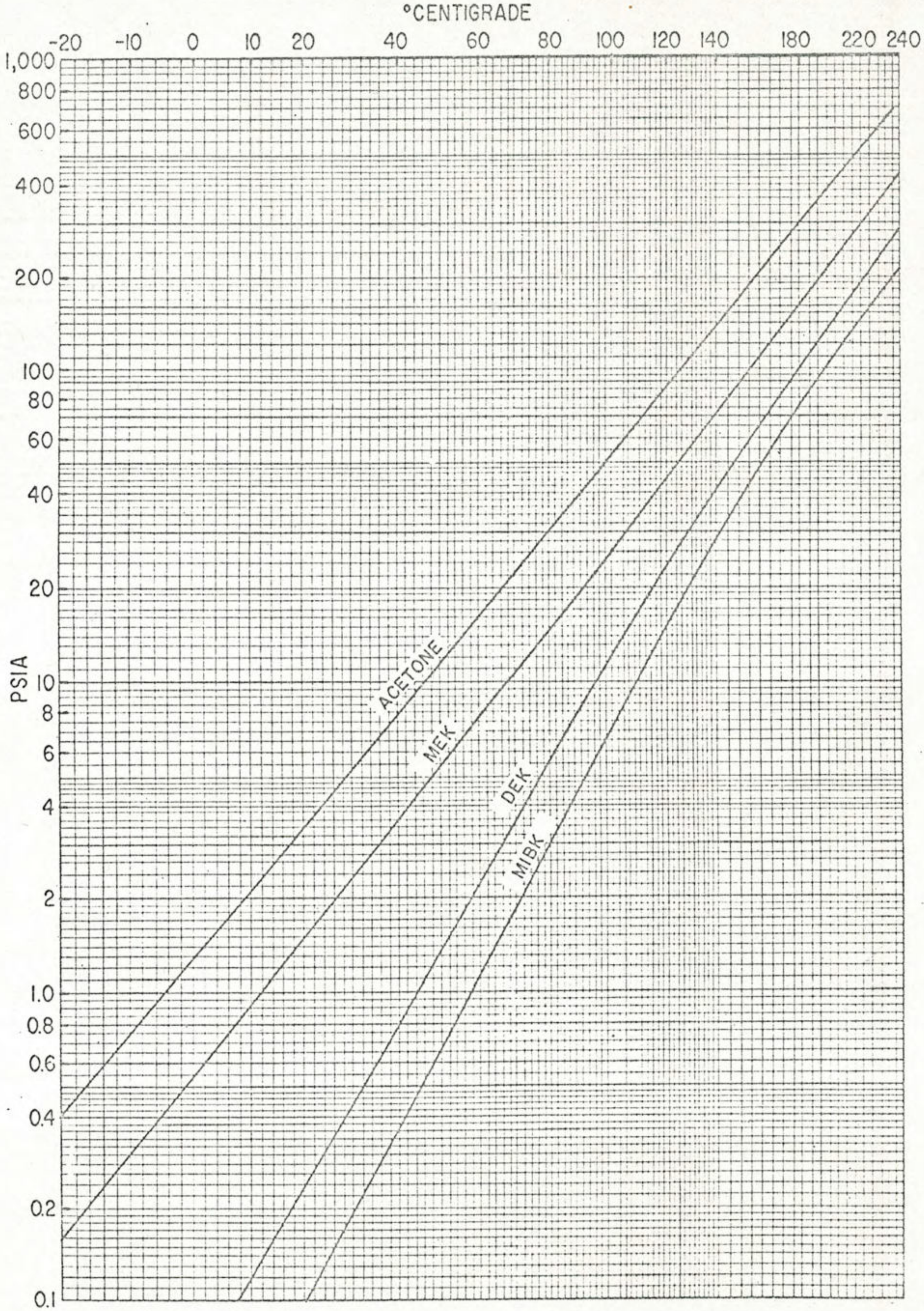

Fig. 27-1—Gives vapor pressure of ketones from −20° C to +240° C.

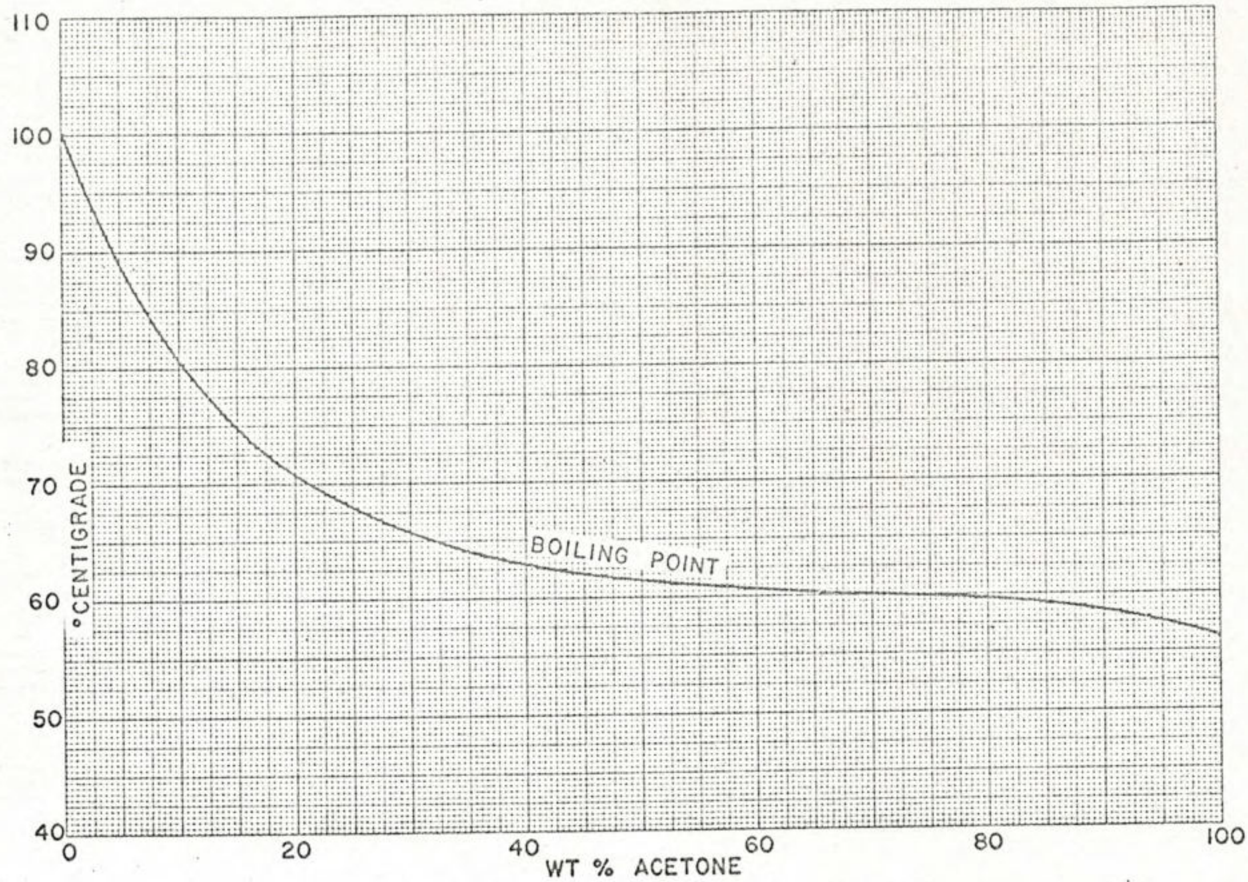

Fig. 27-2—Gives boiling points of aqueous acetone.

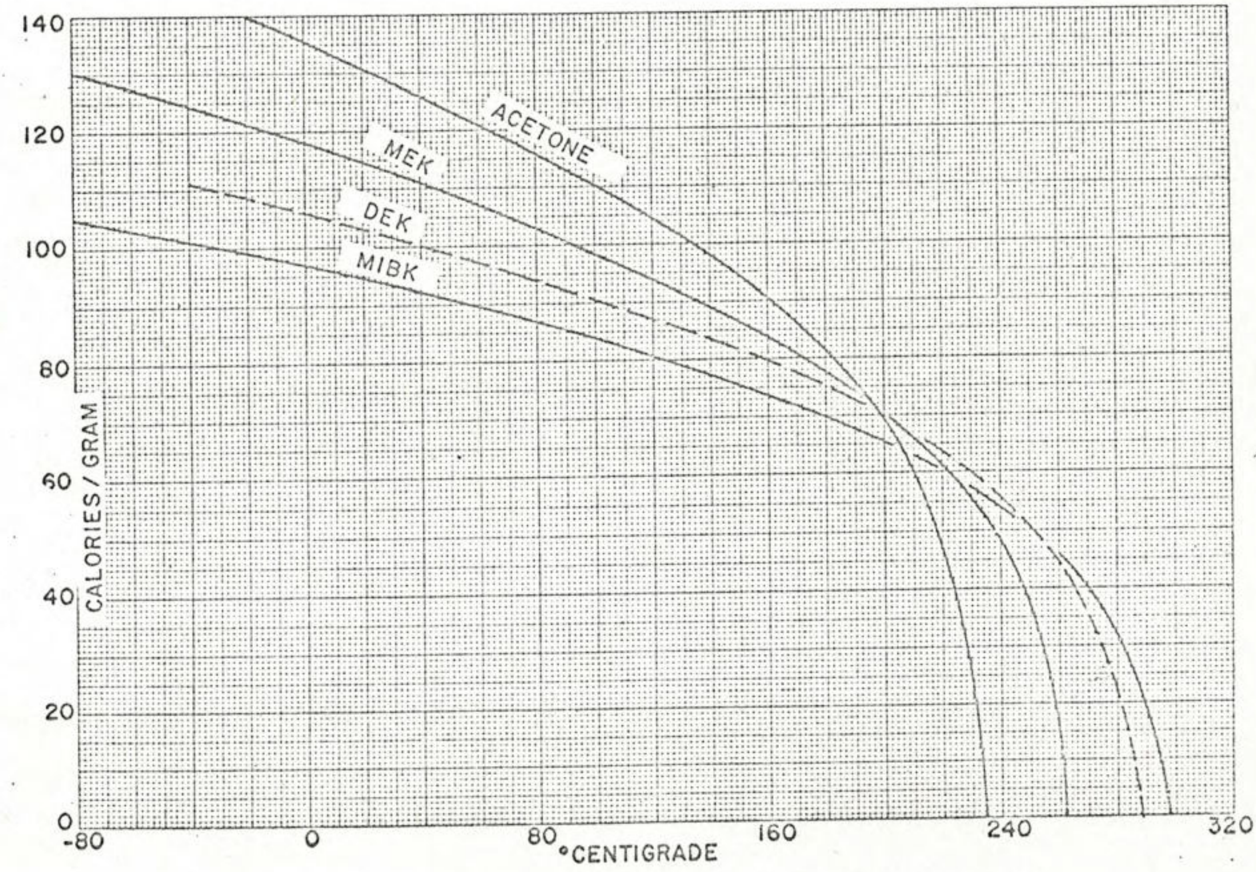

Fig. 27-3—Gives heat of vaporization of ketones from −80° C to +300° C.

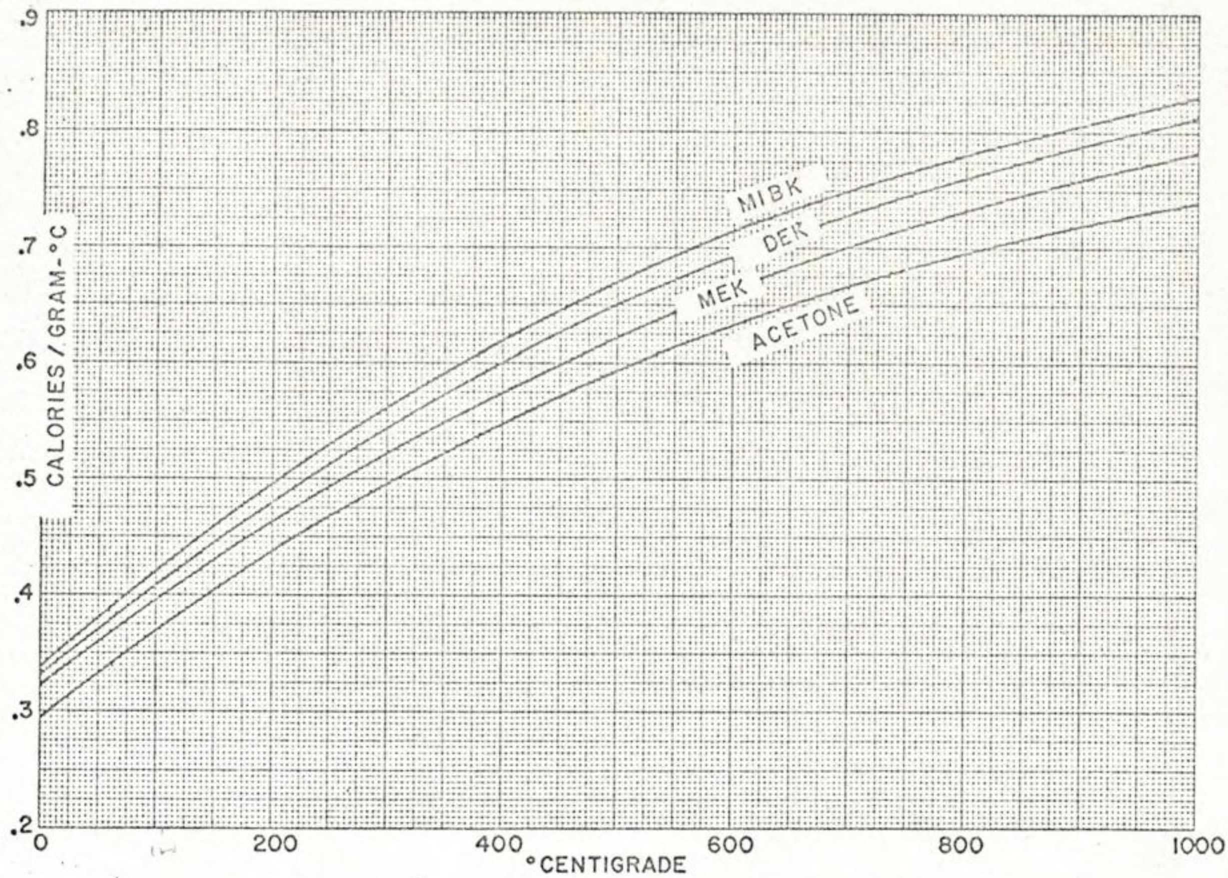

Fig. 27-4—Gives vapor heat capacity of ketones from 0° C to 1,000° C.

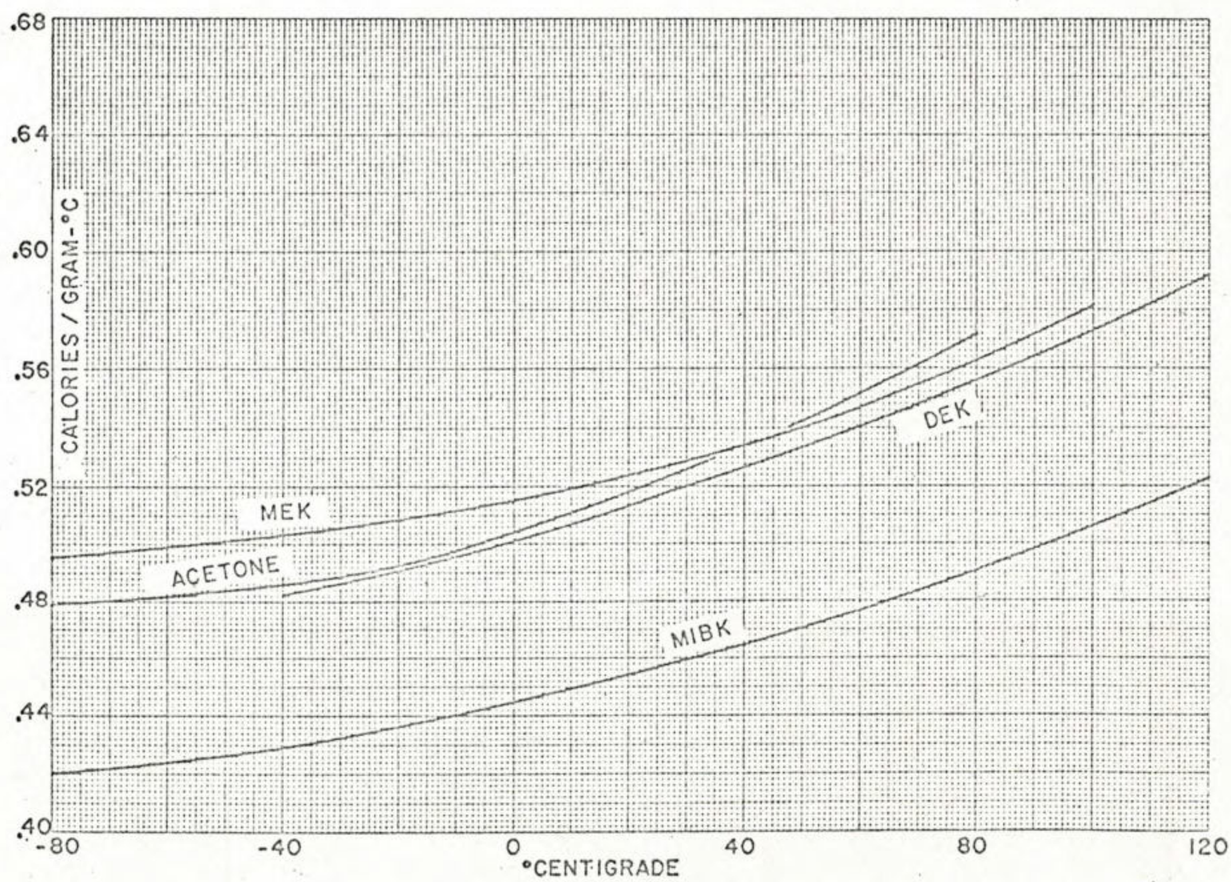

Fig. 27-5—Gives liquid heat capacity of ketones from −80° C to +120° C.

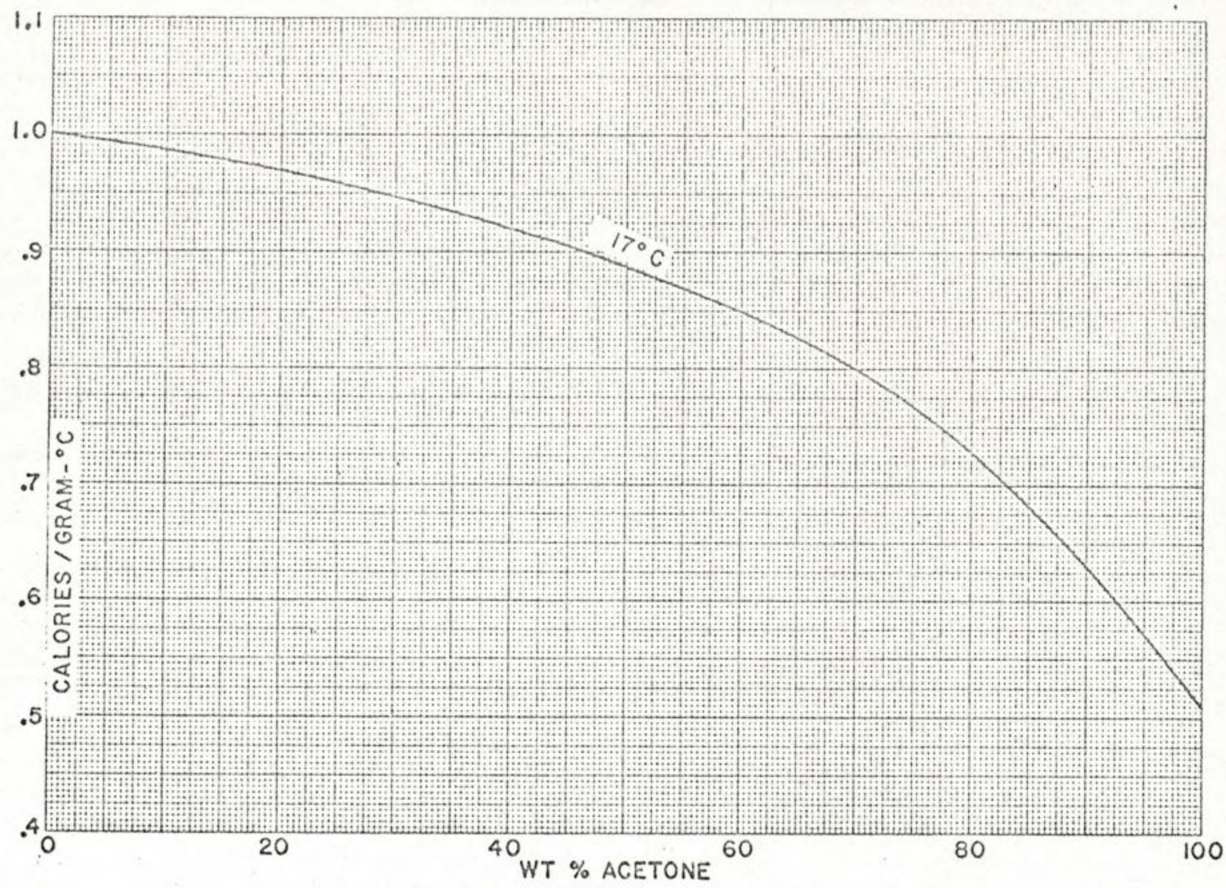

Fig. 27-6—Gives liquid heat capacity of aqueous acetone at 17° C.

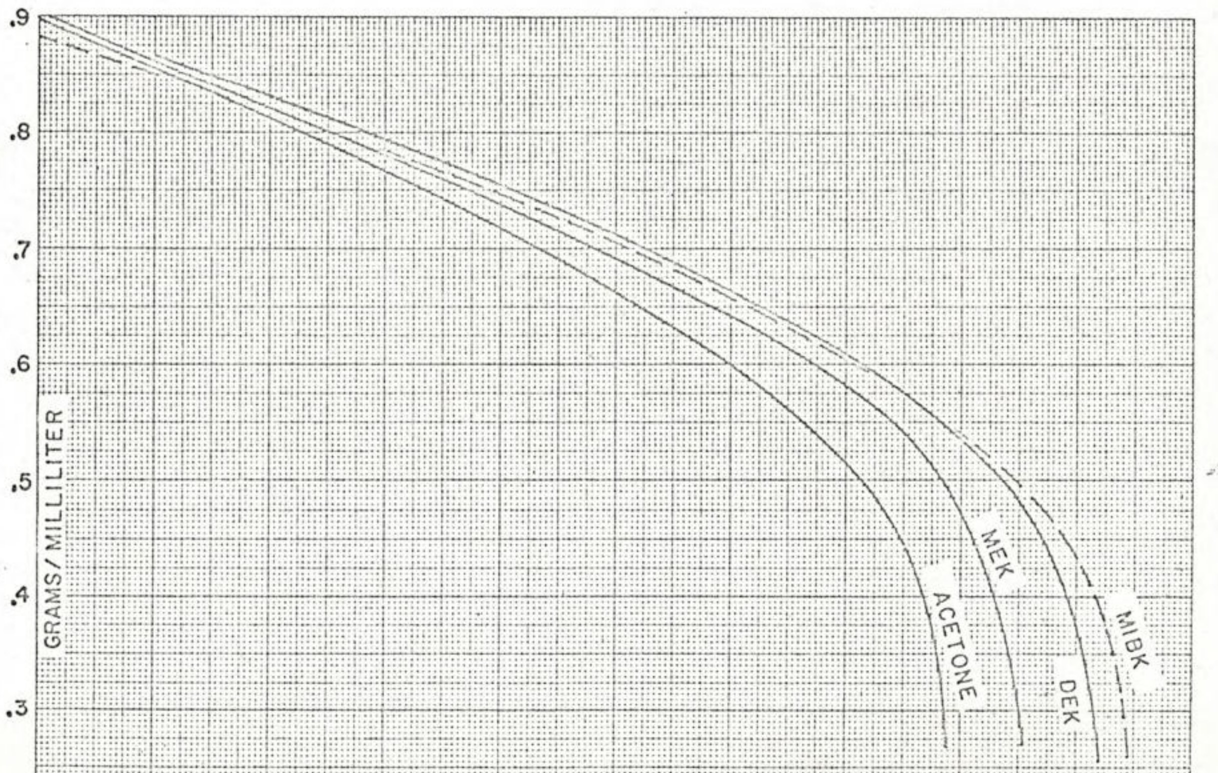

Fig. 27-7—Gives liquid density of ketones from −80° C to +300° C.

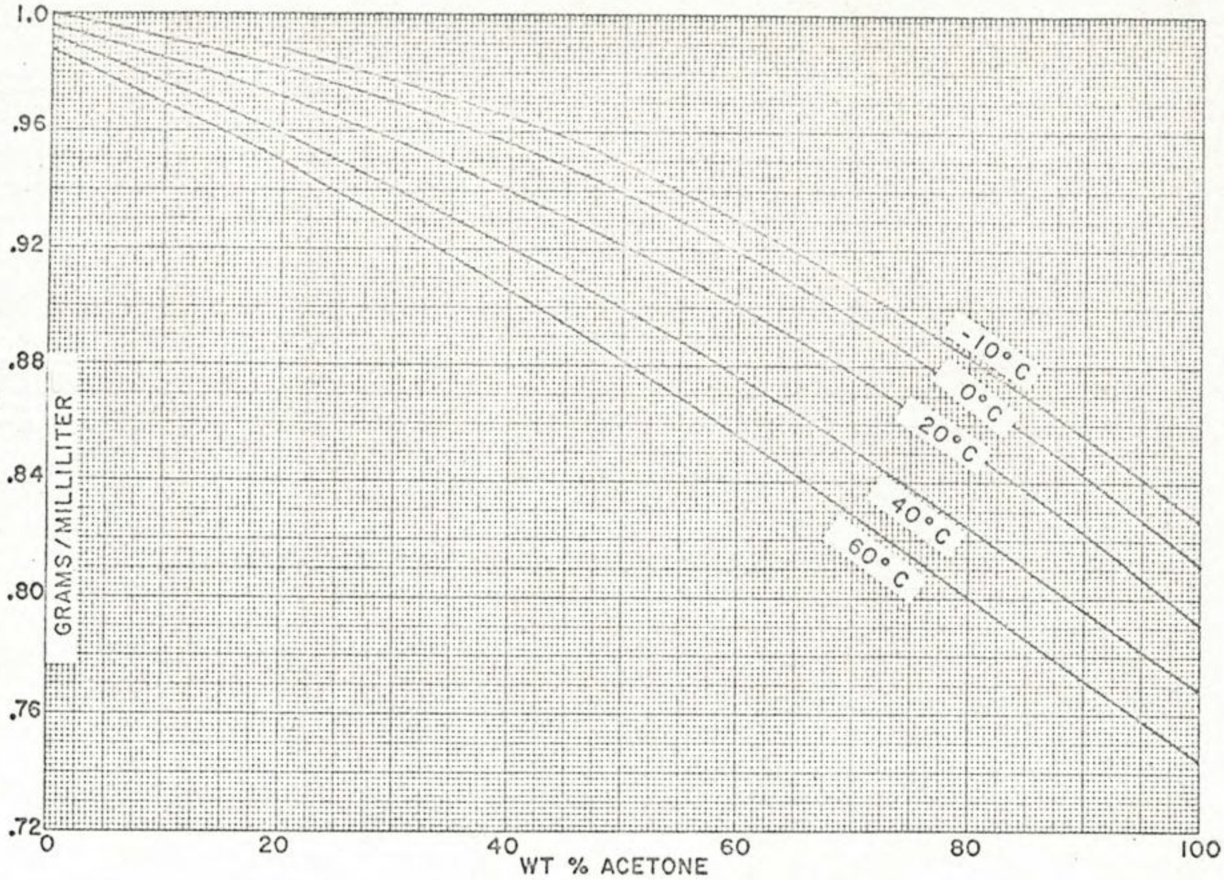

Fig. 27-8—Gives liquid density of aqueous acetone.

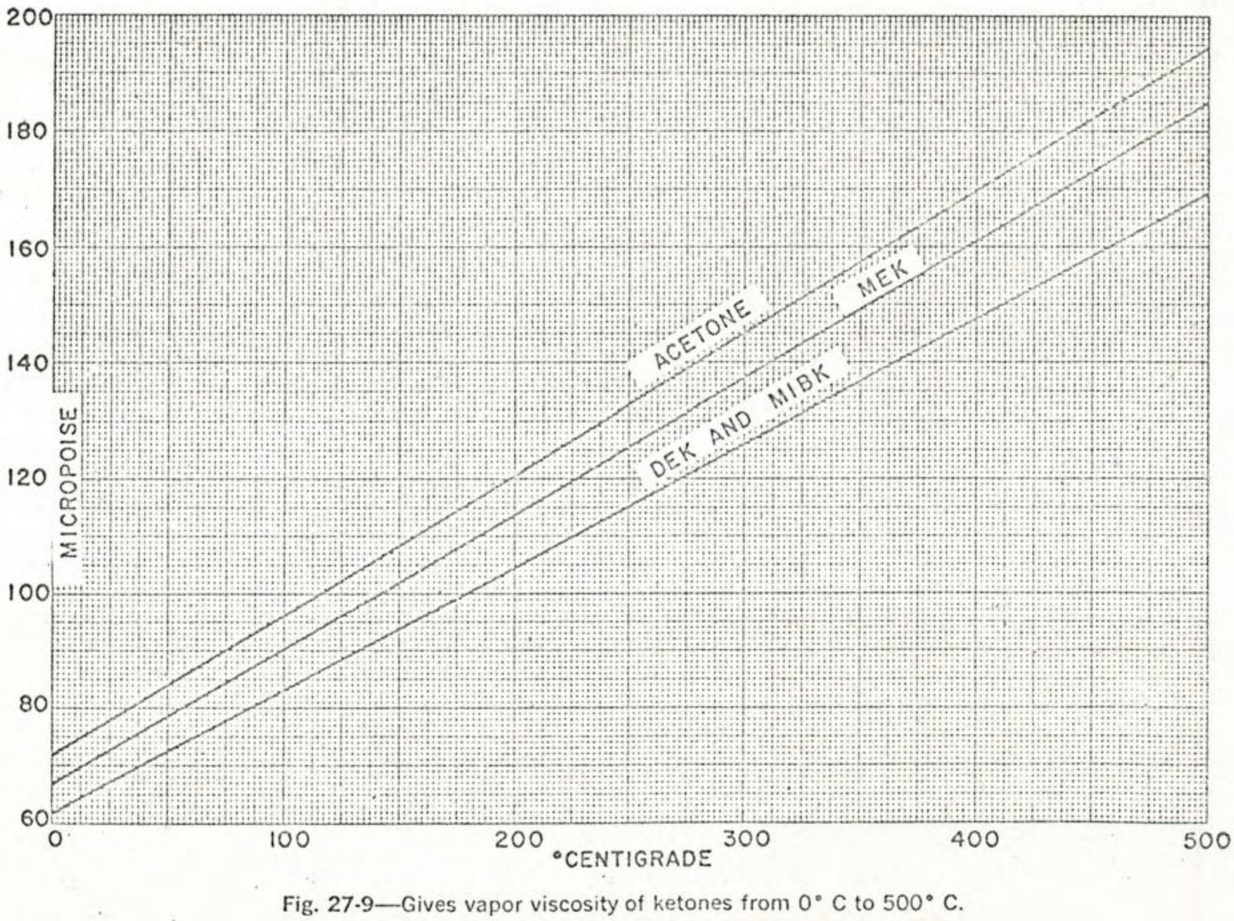

Fig. 27-9—Gives vapor viscosity of ketones from 0° C to 500° C.

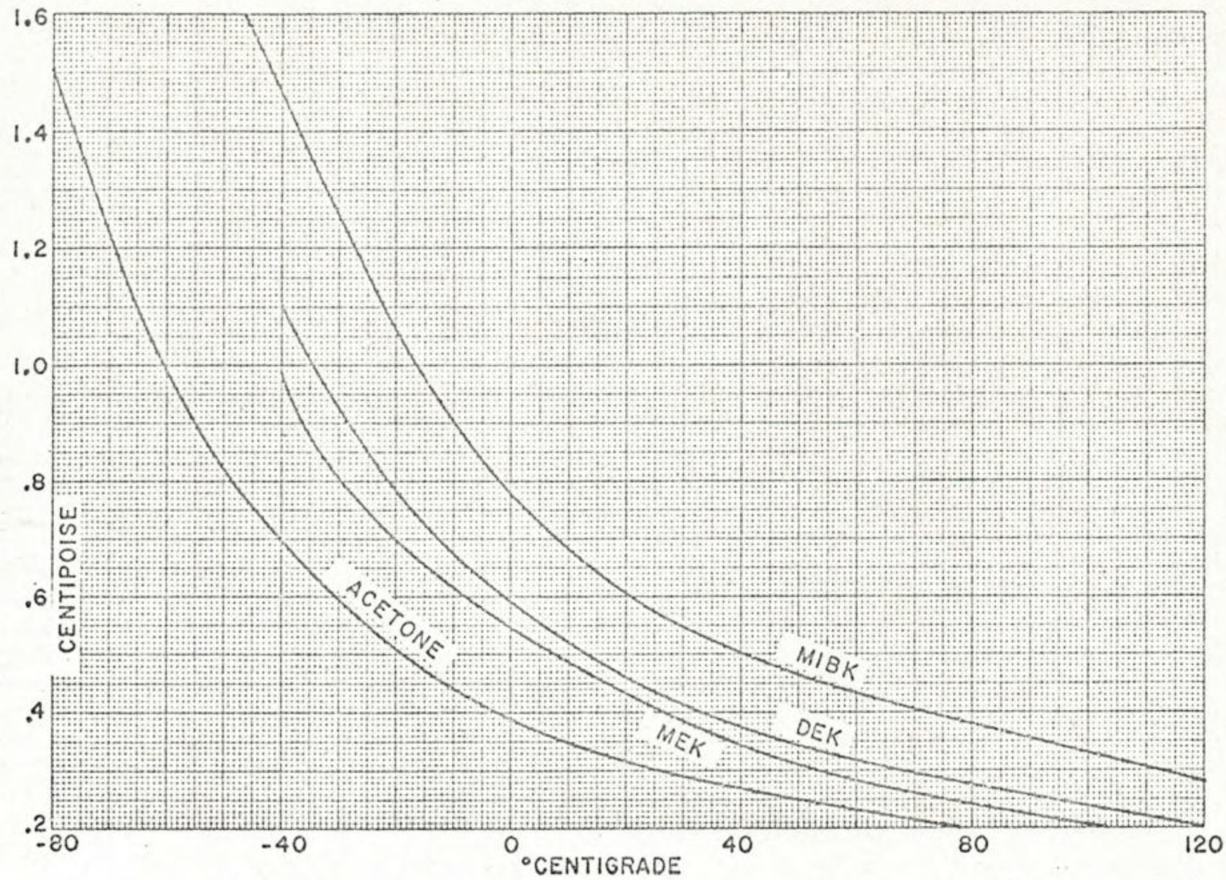

Fig. 27-10—Gives liquid viscosity of ketones from −80° C to +120° C.

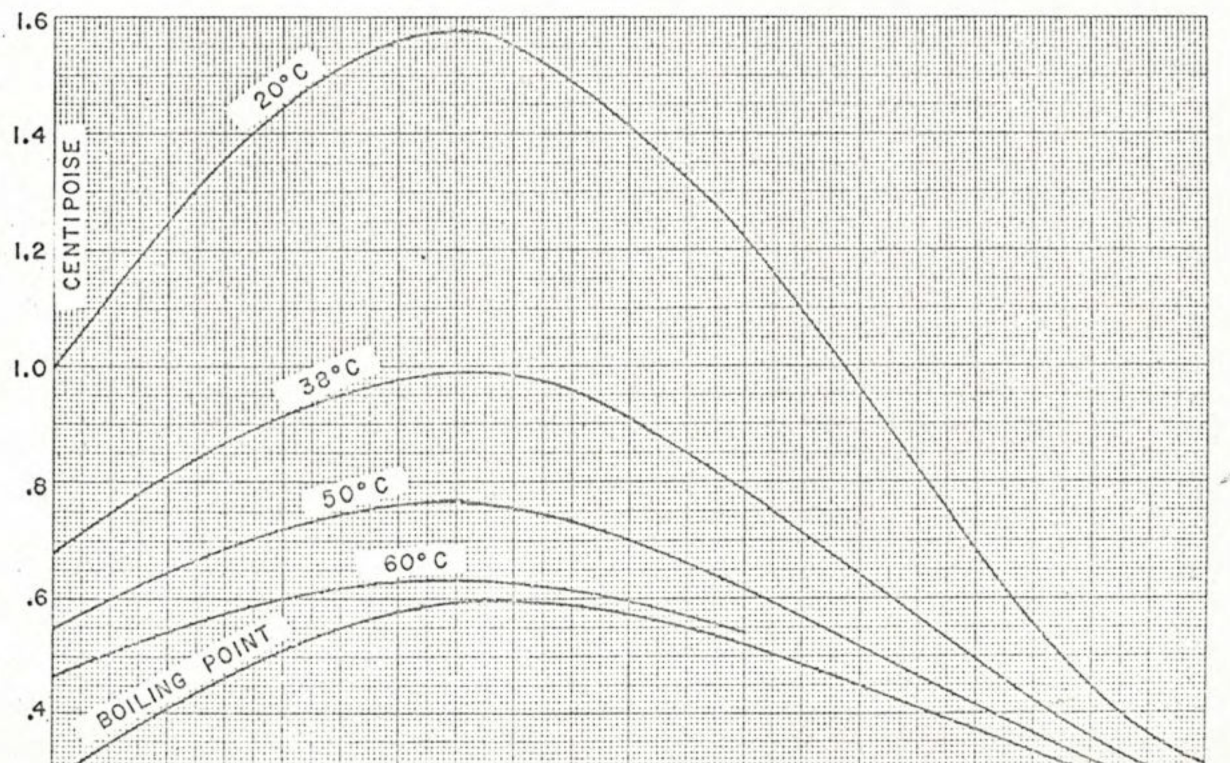

Fig. 27-11—Gives liquid viscosity of aqueous acetone.

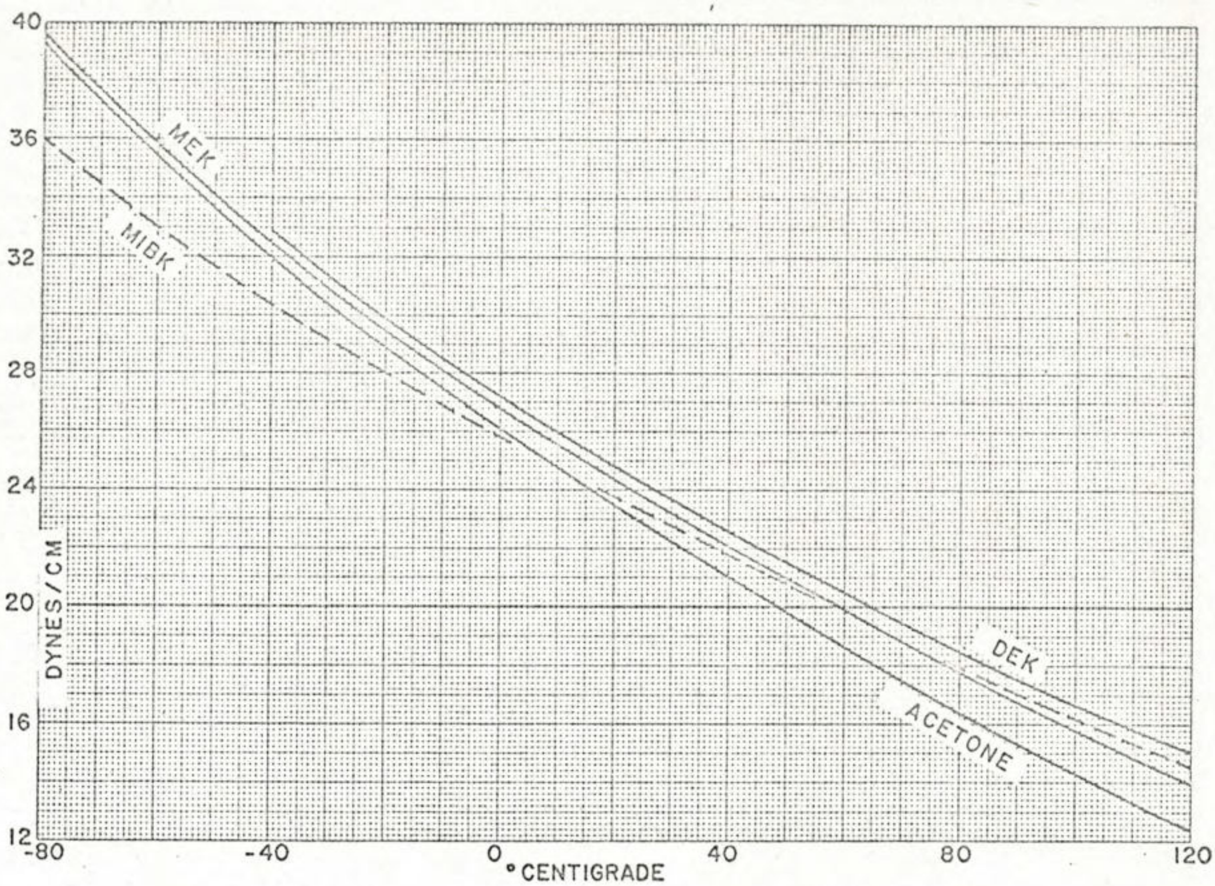

Fig. 27-12—Gives surface tension of ketones from —80° to +120° C.

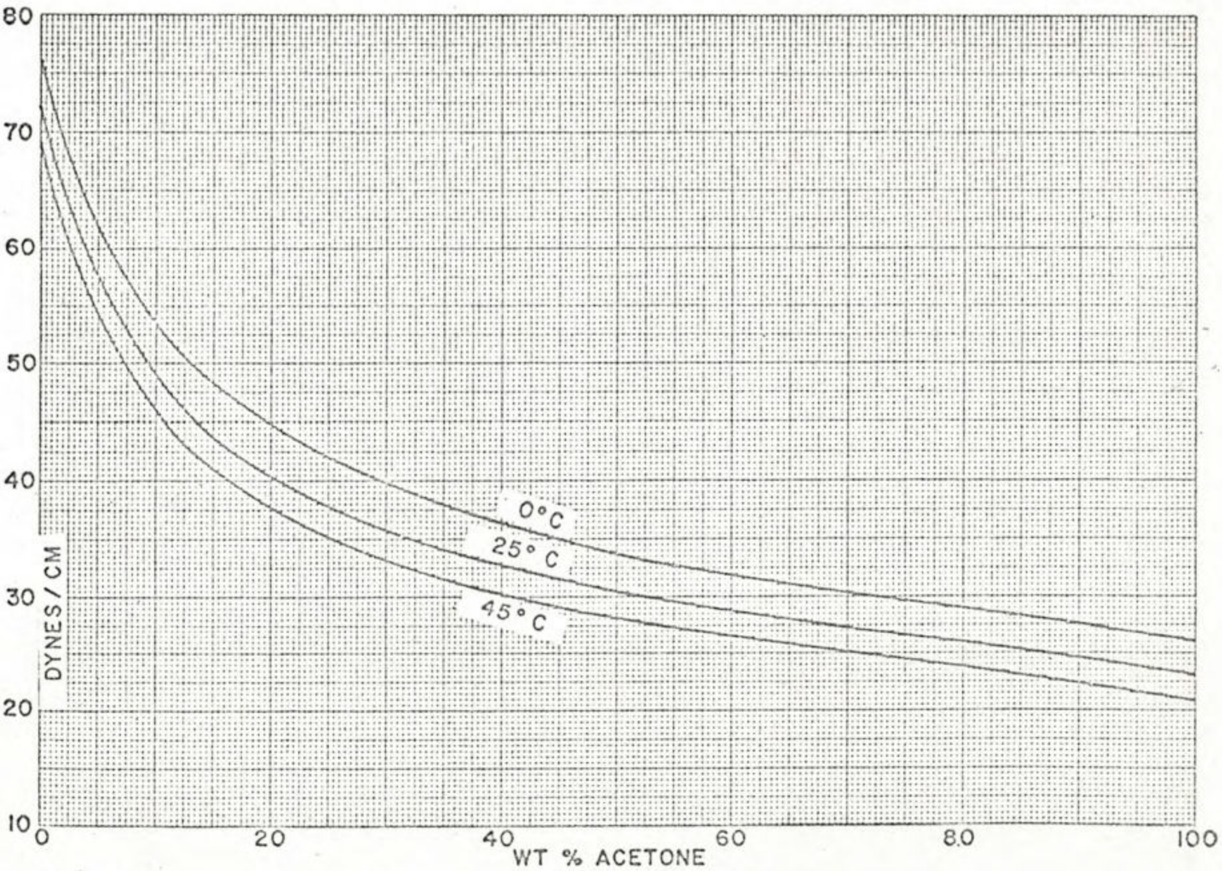

Fig. 27-13—Gives surface tension of aqueous acetone.

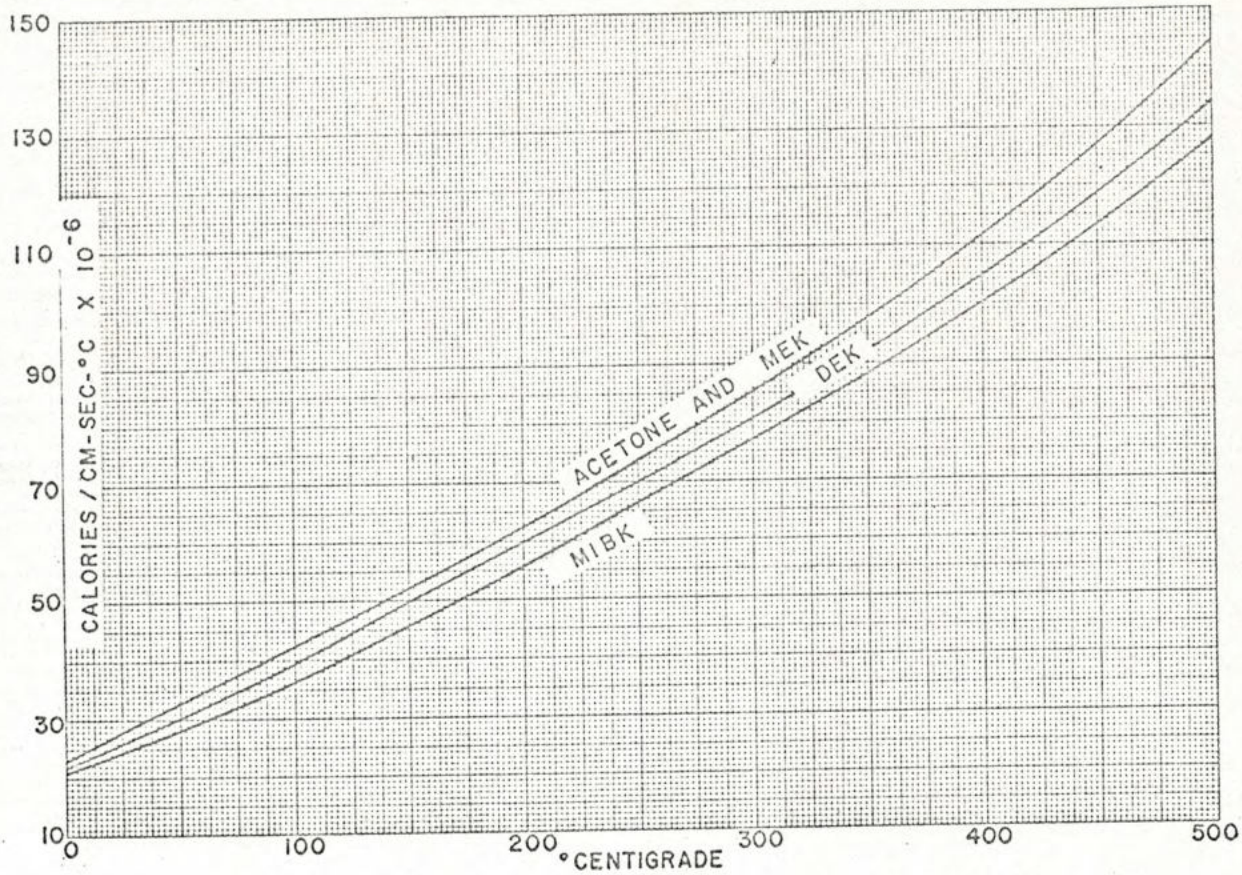

Fig. 27-14—Gives vapor thermal conductivity of ketones from 0° C to 500° C.

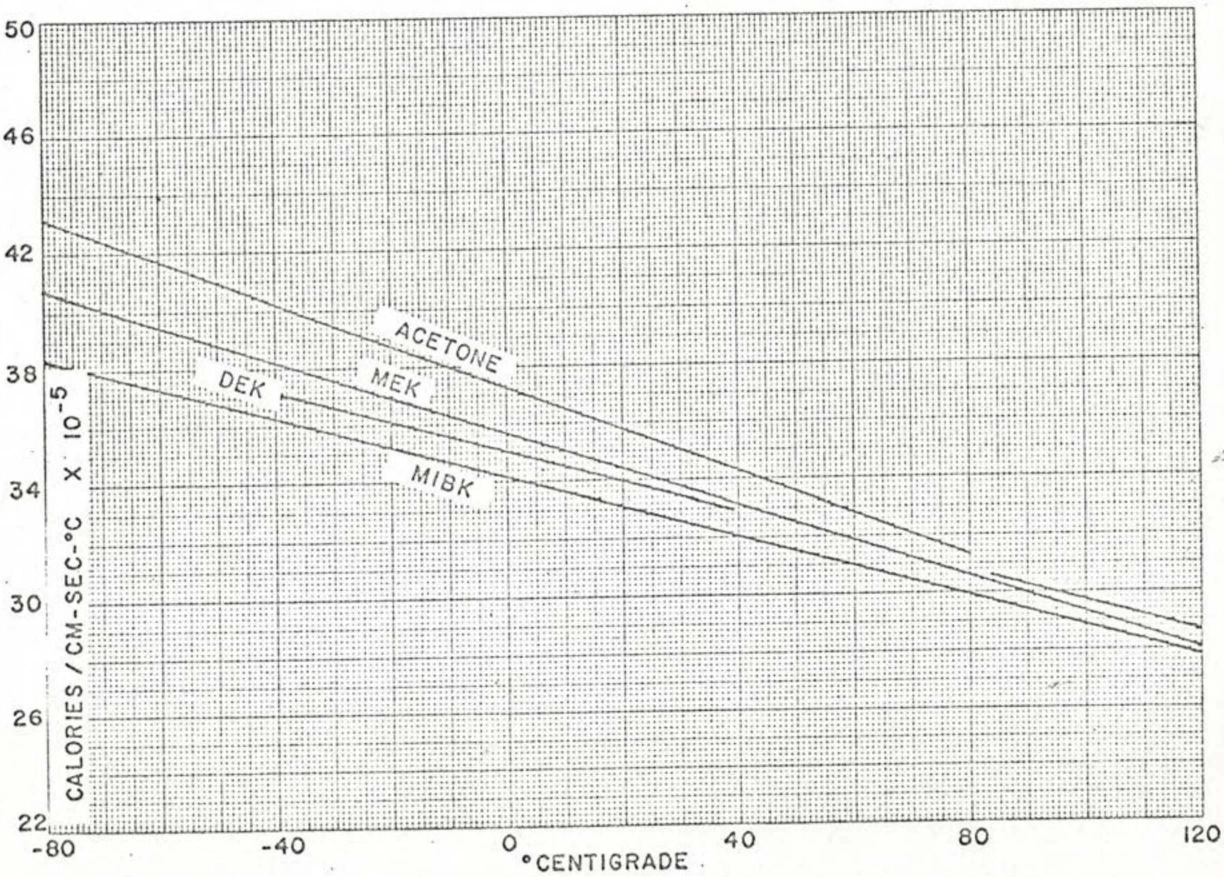

Fig. 27-15—Gives liquid thermal conductivity of ketones from −80° C to +120° C.

TABLE 27-1—Physical Properties of Ketones

	Common Name	Abbreviation	Boiling Point °C	Freezing Point °C	Molecular Weight	CRITICAL PROPERTIES		
						T_c °C	P_c PSIA	d_c g/ml
Acetone....................	....	......	56.2	−94.8	58.08	235	690	0.268
2-butanone....................	Methylethyl-ketone	MEK	79.6	−86.9	72.10	262.5	602	0.270
3-pentanone....................	Diethylketone	DEK	102.0	−39.9	86.13	287.8	542	0.256
4-methylpentanone-2............	Methyliso-butylketone	MIBK	116.2	−84	100.16	298.3	475	0.262*

* Estimated.

tively. The method of Rihani and Doraiswamy was used to calculate the vapor heat capacities of DEK and MIBK.[12] They used acetone data as their reference in calculating the constants for the ketone structure. Consequently, their estimation method agrees exactly with the acetone data. For MEK, the accuracy was almost as good, giving an average error of 0.5 percent for seven points. The estimated values for DEK and MIBK should be accurate within 1 percent at temperatures above the boiling point.

The liquid heat capacities of acetone[8,13] and MEK[14] have been measured from the melting point to + 50° C. The heat capacity only at 20° C has been determined for DEK and MIBK.[6] The equation, density times heat capacity equals a constant, has been used to extrapolate the data over the −80° C to + 120° C range. For nine experimental data points of acetone and MEK, this method yielded average and maximum errors of 2.0 percent and 4.8 percent respectively. Fig. 27-6 shows the change of the heat capacity with concentration for aqueous acetone solutions at 17° C.[7]

Liquid Density. The liquid density of acetone only has been experimentally determined up to the critical point.[6,7,8] The density has been measured from −80° C to + 30° C for MEK,[7,8,15] from 0 to 50° C for DEK;[8] and from 10 to 50° C for MIBK.[16] The densities of these three compounds have been estimated from −80° C to their critical temperature by the method proposed by Lydersen, Greenkorn, and Hougen.[4] When compared with 10 experimental values, the average error was 0.4 percent. The liquid densities of aqueous acetone solutions from − 10° C to + 60° C are presented in Fig. 27-8.[7]

Viscosity. The vapor viscosity of acetone has been measured from 0° C to 325° C.[4,6] The estimation method of Bromley and Wilke has been used to calculate the vapor viscosity of all four compounds over the 0-500° C range.[4] The average error for acetone was 2.5 percent.

The liquid viscosity has been measured for acetone from −80° C to + 54° C;[7,8,17] for MEK from 0 to 80° C;[6,8,17] for DEK from 0 to 100° C;[6,8,17] and for MIBK from 0 to 50° C.[7] These data have been extended over the −80° C to + 120° C range by plotting the logarithm of the viscosity against the reciprocal of the absolute temperature. This gives essentially a straight line. The error should be less than 5 percent.

Howard and McAllister have made extensive measurements on the effect of temperature and concentration on the viscosity of aqueous acetone solutions.[5] These data are shown in Fig. 27-11.

Surface Tension. The surface tensions of acetone[8,17,18] and MEK[6,17] have been measured from 0 to 80° C. Data on DEK are available from 0-50° C.[6,8] No literature values have been reported for MIBK. Sugden's method, which relates surface tension to molecular weight, density, and Parachor, has been used to calculate the surface tension of MIBK and to extend the data on the other three compounds.[19] The probable error is about 2 percent. Fig. 27-13 shows the effect of temperature on the surface tension of aqueous acetone solutions.[17]

Thermal Conductivity. The vapor thermal conductivities were estimated by the method of Owens and Thodos,[20] with a probable error of about 5 percent.

Jobst has measured the liquid thermal conductivities of acetone, MEK, and DEK.[21] Additional data are available for acetone,[6,22,23] but differences between experimenters are as much as 20 percent. The method of Robbins and Kingrea was used to calculate the thermal conductivity of MIBK.[24] However, the method gives a sharper change with temperature than the data of Jobst indicates, and so the method was revised somewhat to give results closer to the data of Jobst. The probable error is 5-10 percent.

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Indexing Terms: Acetone-9, Computations-4, Diethylketone-9, Heat-7, Liquid Phase-5, Methylethylketone-9, Methylisobutylketone-9, Physical Properties-7, Pressure-6, Properties/Characteristics-7, Temperature-6, Vapor Phase-5.

Part 28, "Ethers," will appear in an early issue.