Physical Properties of Hydrocarbons

Part 1—Methane-Ethane-Propane-Butane
Part 2—C_2 to C_4 Monoolefins
Part 3—C_2 to C_4 Alkynes
Part 4—C_2 to C_4 Diolefins

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FOR AN ENGINEER, whether he be designing a production unit, building a pilot plant, or starting a research project, the starting point is often the compilation of the physical properties of the chemicals used and produced in the process. Calculations of heat and material balances, distillation columns, heat exchangers, and pumps all involve a knowledge of the change with temperature and pressure of such properties as vapor pressure, heat of vaporization, heat capacity, density, viscosity, and surface tension.

For the engineer in a large company with extensive physical property data compilations and a well stocked library, this data finding is sometimes relatively easy, although often time consuming. But for the engineer in a small company or isolated company division, accessibility to this needed data can be not only very time consuming but also difficult. Even when available, data are often in tables or equations requiring calculations, plotting, and extrapolation to meet the conditions needed.

Faced with this problem many times in the past few years, the author finally decided to make a search of the literature for ready sources of physical data, and to compile in an easily accessible graph form, the physical properties of many of the more common chemicals. Where data are spotty, or of questionable reliability, estimation methods were used. Anyone attempting to search the literature for physical data immediately learns what is meant by the "literature explosion." Buried within the mass of chemical and engineering literature is a wealth of data, but it is scattered throughout dozens of journals over many years.

The purpose of this article is to first list some of the sources of data compilation and then to present in graph form the physical properties of some of the more common hydrocarbons.

Handbooks. First of all, there are a number of handbooks, familiar to all engineers, which are always the first place to look for data. These are the the following:

- Handbook of Physics and Chemistry.[1]
- Handbook of Chemistry.[2]
- Chemical Engineers Handbook.[3]
- International Critical Tables.[4]

Books. For more specific types of compounds, or books of less common usage, we can include the following:

- Physical Properties of Chemical Compounds, Vol. II[5]—This thorough compilation of a wide range of physical properties is an excellent starting place for data gathering. Volume II covers such straight chain hydrocarbons as the alkanes, alkenes, alkynes, and diolefins.
- Applied Hydrocarbon Thermodynamics[6]—A comprehensive book on hydrocarbon thermodynamics, including quite a bit of thermodynamic data.
- Data Book on Hydrocarbons[7]—For a petroleum engineer, this is the best physical properties book available. It includes extensive, easily accessible data on oils and the more important hydrocarbons.
- Physical Constants of Hydrocarbons, C_1 to C_{10}[8]—This book presents data mostly at the boiling point or 25° C.
- Selected Values of Properties of Hydrocarbons and Related Compounds[9]—This excellent compilation of data

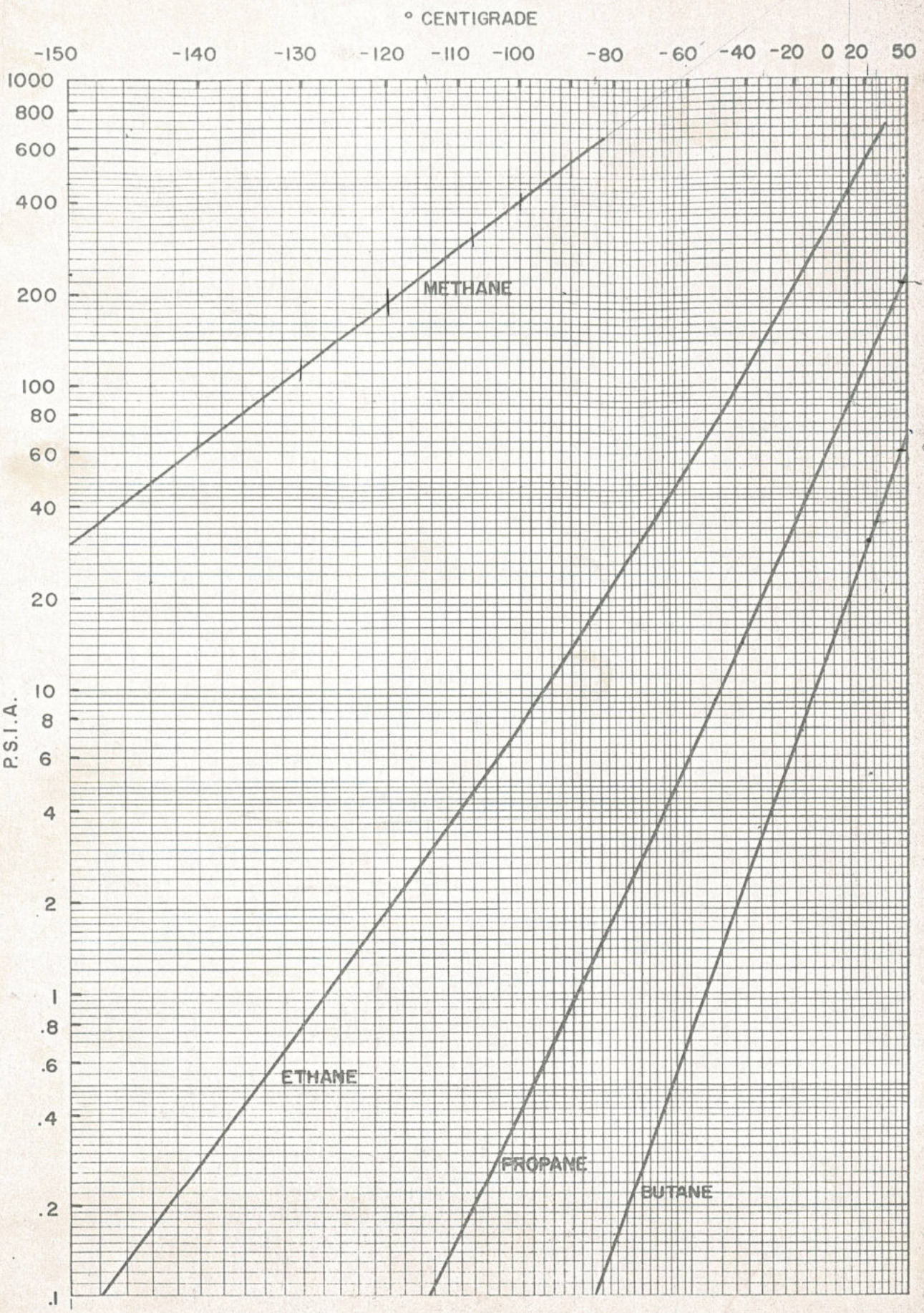

Fig. 1-1—Vapor pressure over a range of —150 to +50° C.

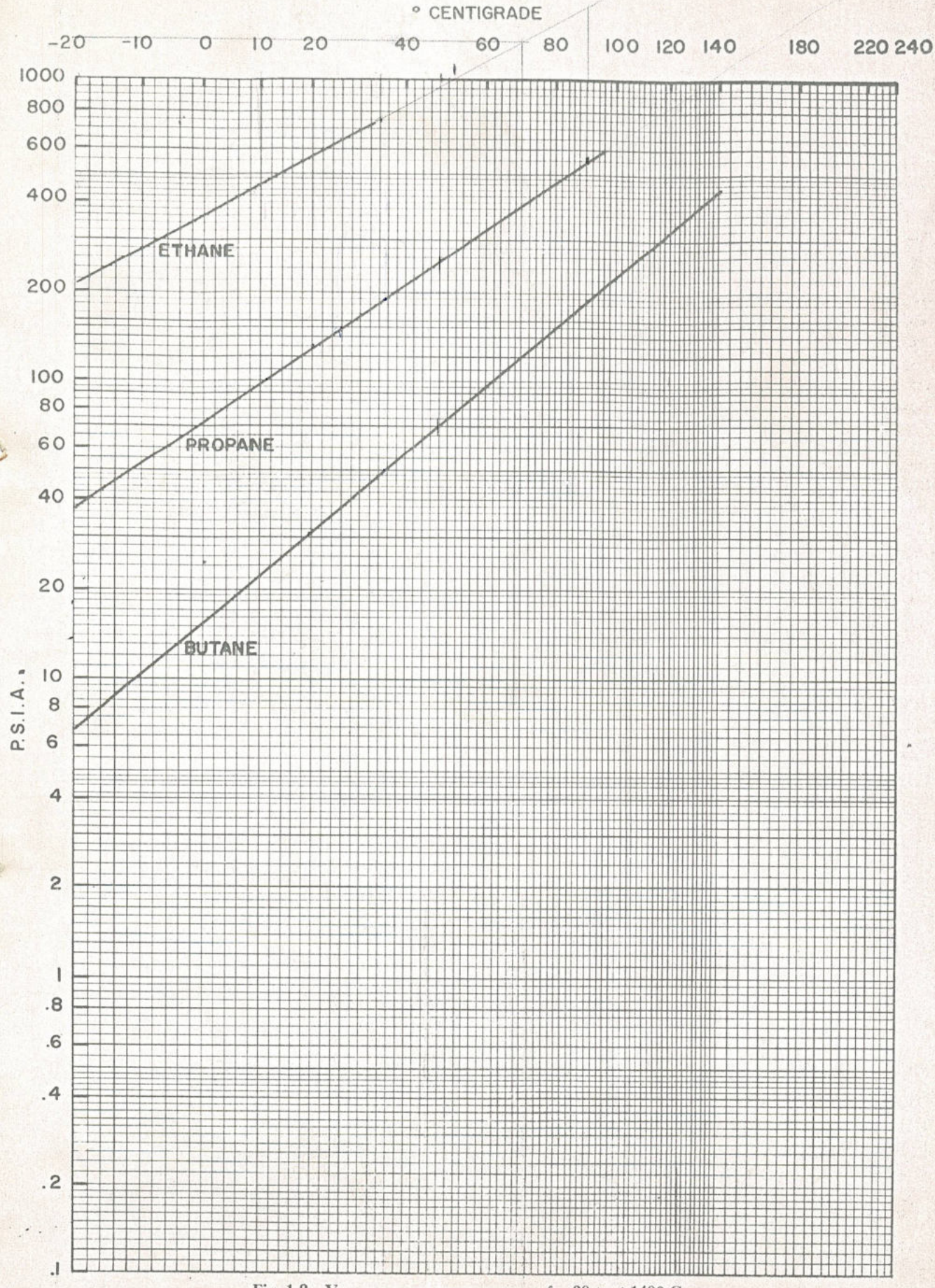

Fig. 1-2—Vapor pressure over a range of −20 to +140° C.

is the result of a continuing program of the API to provide one reliable source for hydrocarbon data. The high cost makes it a not-too-common library fixture, but for those who have access to a copy, it is the best, most reliable source of physical data over a wide temperature range. When the data are condensed into one book, it will be a must for most technical libraries.

• Thermodynamic Functions of Gases[10]—This is a European publication and if you can take such units as bars of pressure, it has a lot of good thermodynamic data.

• Bibliography on Hydrocarbons[11]—This book contains abstracts of over 1100 books and journal articles on hydrocarbons. As a starting point for a literature search on hydrocarbons, it is unexcelled. Chemical engineers could use a lot more such bibliographies.

Journal Articles. Finally, there are a number of excellent journal articles dealing with a specific physical property or group of compounds. These are listed under the specific physical property discussions. Several journals have been especially active in physical property data presentations. For many years *Industrial and Engineering Chemistry* was dominant in this area. The relatively new *AIChE Journal* has, in its short nine years, presented a number of excellent articles.

Of equal importance is the availability of several excellent articles on physical property estimation or correlation. In this series, reference will be made only to the method used.

Estimating Physical Properties. The following four references are recommended for information on estimating physical properties.

• The Properties of Gases and Liquids[12]—This is the most comprehensive single source of physical property estimation methods. The extensive tabulations which compare calculated data from various estimation methods against experimental data are an aid to selecting the best method for various compounds. A good set of references allows the reader to refer to original work for more details.

• Physical Property Estimation[13]—This series of articles is almost a must for the files of anyone who needs to estimate physical properties occasionally. Almost every conceivable physical property is covered.

• Estimating Vapor Pressures—A Comparison of Equations[14]—This is a very thorough and well written article on vapor pressure estimation.

• Reliable Latent Heats of Vaporization[15]—This three-part series covers estimation methods of heat of vaporization thoroughly.

Part 1 of this series will cover the straight chain paraffins methane, ethane, propane, and butane. The value of these four compounds as starting raw materials for the petrochemical industry can best be measured in terms of the billions of pounds consumed. There are few petrochemical plants that do not use methane somewhere in the process as a fuel, inert pad for tanks, or as a reaction diluent. The experimental data available on these compounds are quite extensive and most properties can be plotted over a wide temperature range with a minimum of extrapolation or property estimation.

Vapor Pressure. There is a wide variety of data available on vapor pressures. Although almost 20 years old, the compilation of Stull in 1947[16] remains the best single source of vapor pressures available for either hydrocarbons or nonhydrocarbons. The straight line rule on a Cox chart allows data at a few points to be extrapolated over a wide range with good accuracy. There are also a number of highly accurate estimation methods available where no data are known. Reliable experimental data over a wide temperature range are available for methane, ethane, propane, and butane. In addition to the aforementioned references, Hachmuch[17] and Nakanishi[18] have presented data on butane. The agreement from various sources is very good and this data can be considered highly reliable.

Thermal Properties. Under this heading come such properties as enthalpy, entropy, heat capacity, and heat of vaporization. The literature compilation by Kobe[19] is the outstanding work in this area, and is a must for any good library. He compiled all the literature sources up into the early 1950's and presented the results in tables. Daniel Stull also has been active in this area and his name is a good starting point for thermal data. Othmer has compiled and correlated some of the thermal properties and many physical properties in a series of articles appearing during the 1950's.[20,21,22] His approach has been a Cox chart-type graphical plot.

In this series the heat of vaporization and the liquid and vapor heat capacities are plotted over a wide temperature range. For methane, ethane, propane, and butane, the data have been experimentally determined and the data are available as nomographs or tables in several of the handbooks. Maxwell's book[7] is very good for these properties. However, liquid heat capacity data are very meager for butane and so the data were estimated by the method of Schiff (for hydrocarbons, liquid heat capacity is equal to 0.35 times the liquid density at that temperature). A calculation of 14 points for the four compounds, when compared to experimental data, gave a maximum error of 15 percent and an average error of 7 percent. In many cases, this is probably almost as good as the experimental data. Din[10] was the only source of liquid heat capacity for methane, ethane, and propane over a wide temperature range. Other single point sources did not agree too well.

Liquid Density. There is an abundance of good experimental data on the liquid density of all four compounds. The single best source for the first three is the work of Maass and Wright.[23] Francis[24] has developed a superb equation for the calculation of liquid density over a wide temperature range and evaluated the constants for about 50 hydrocarbons. The average error is about 0.1 percent, a rather phenomenal accuracy for such an easy calculation. These two sources, plus Din's[10] book provided all the density data plotted here. Pressure up to 1000 psi makes only a small difference on densities above 0.4

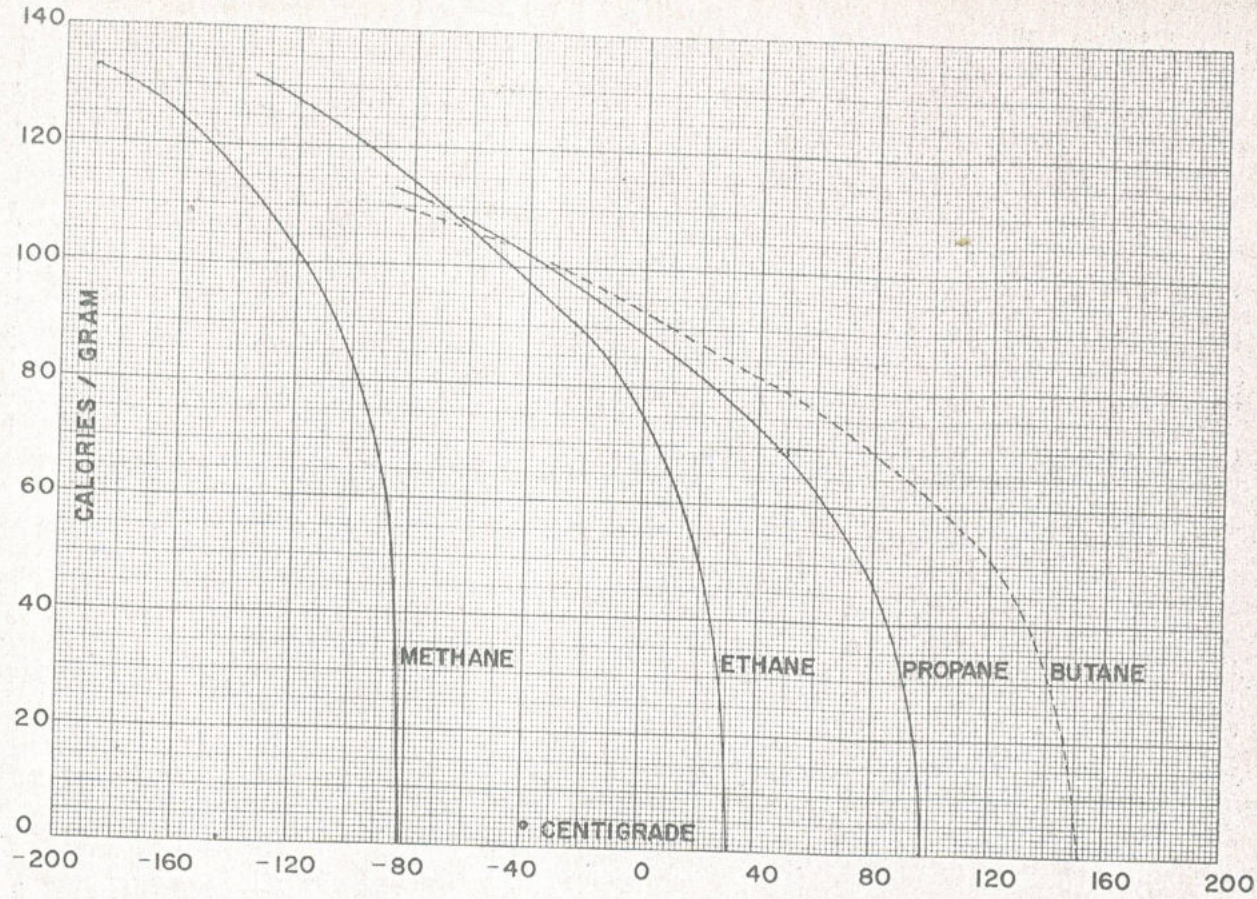

Fig. 1-3—Heat of vaporization over a range of −200 to +160° C.

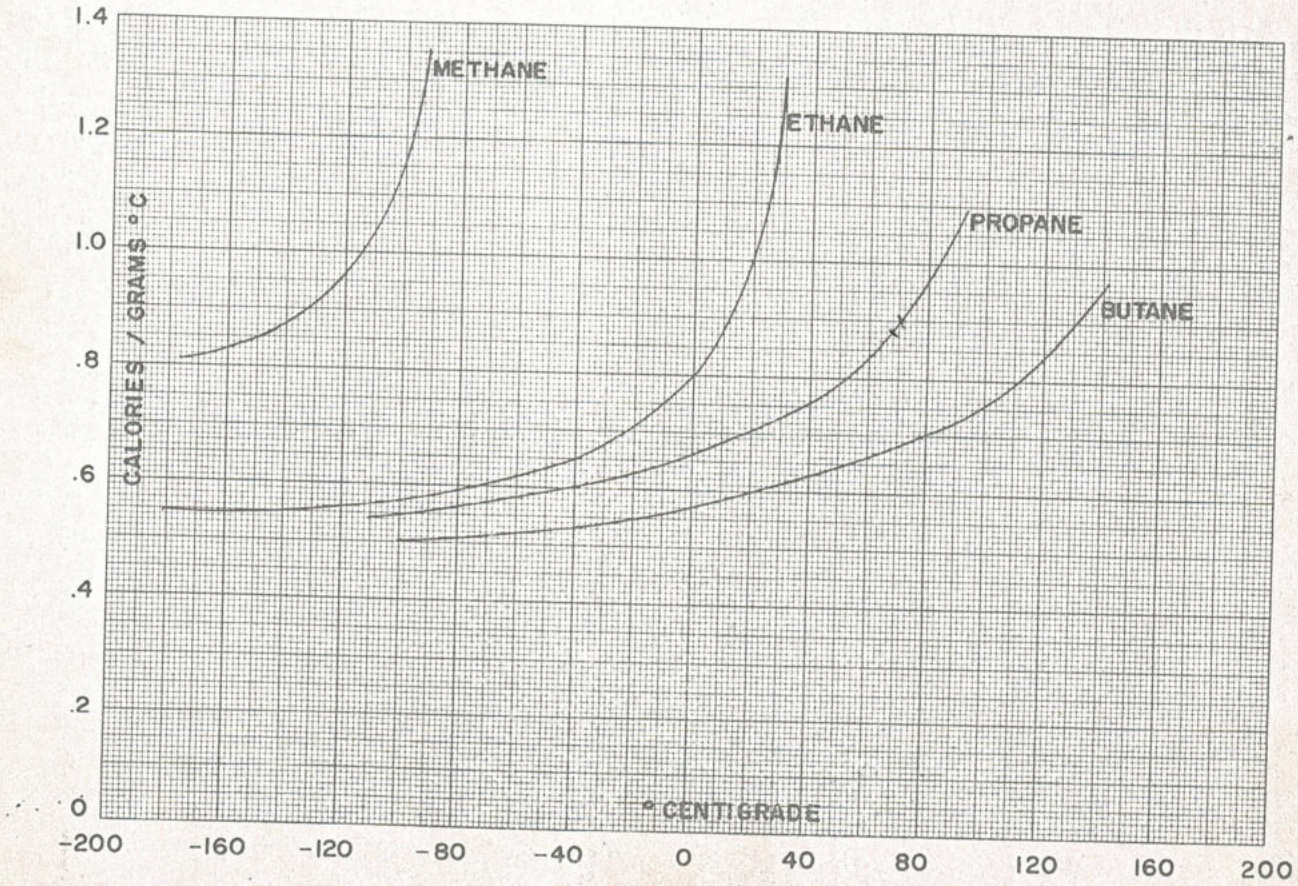

Fig. 1-4—Liquid heat capacity over a range of −200 to +140° C.

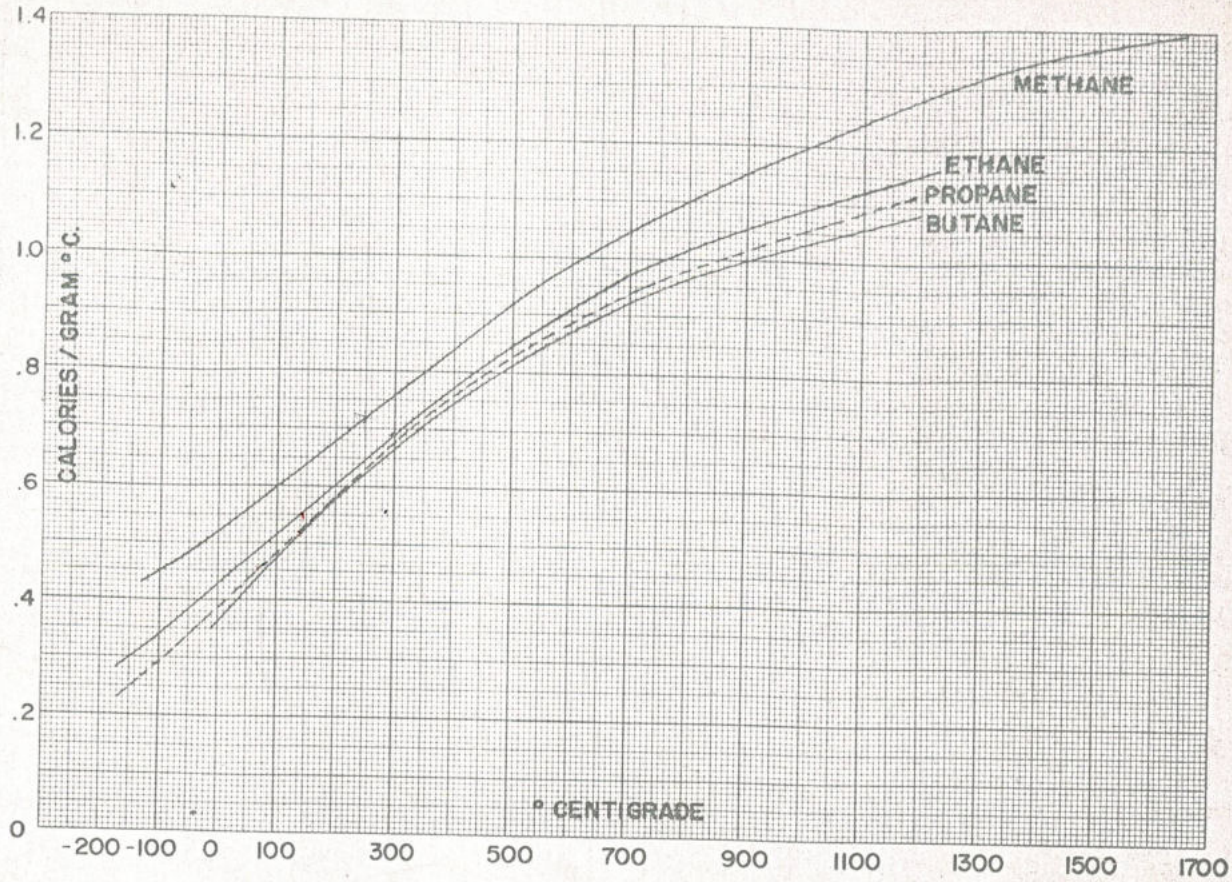

Fig. 1-5—Vapor heat capacity over a range of −200 to +1700° C.

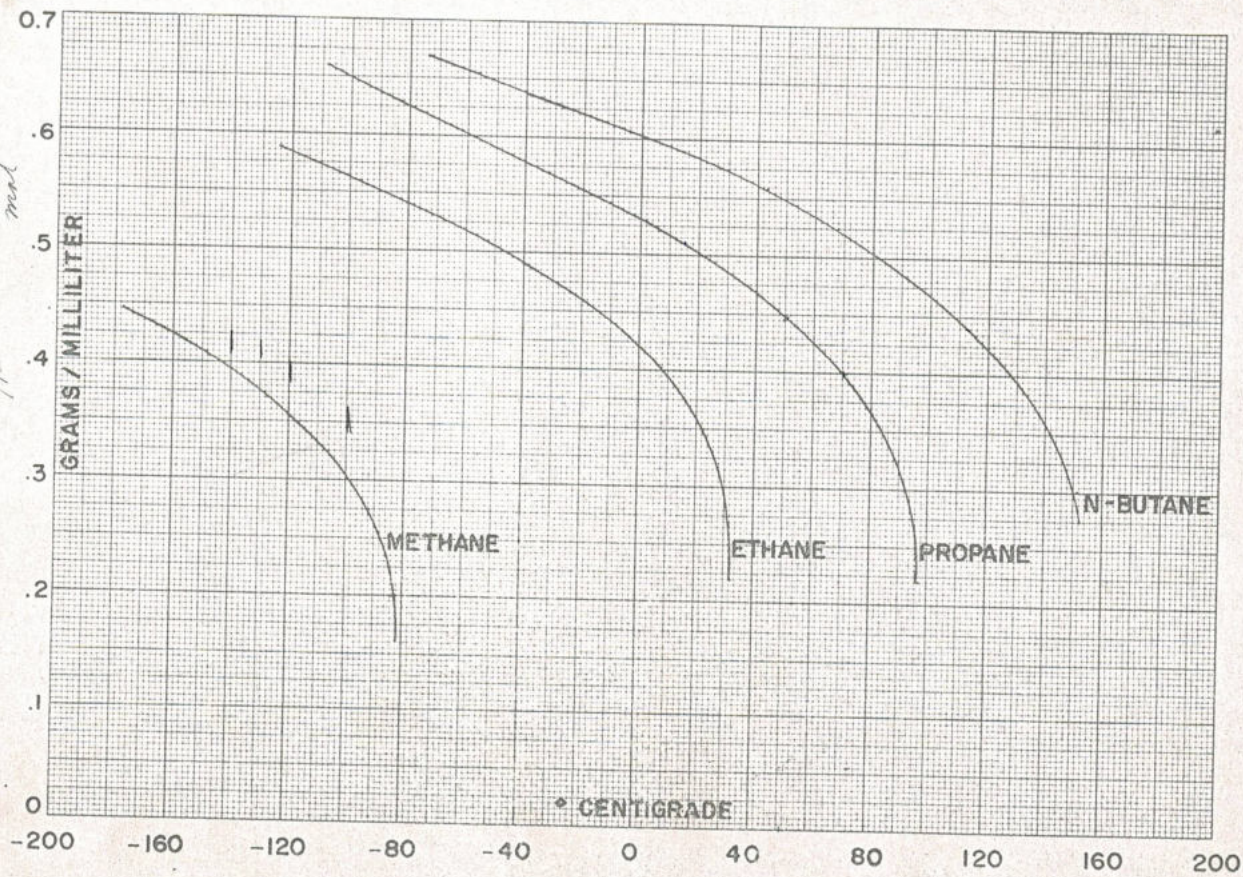

Fig. 1-6—Liquid density over a range of −200 to +160° C.

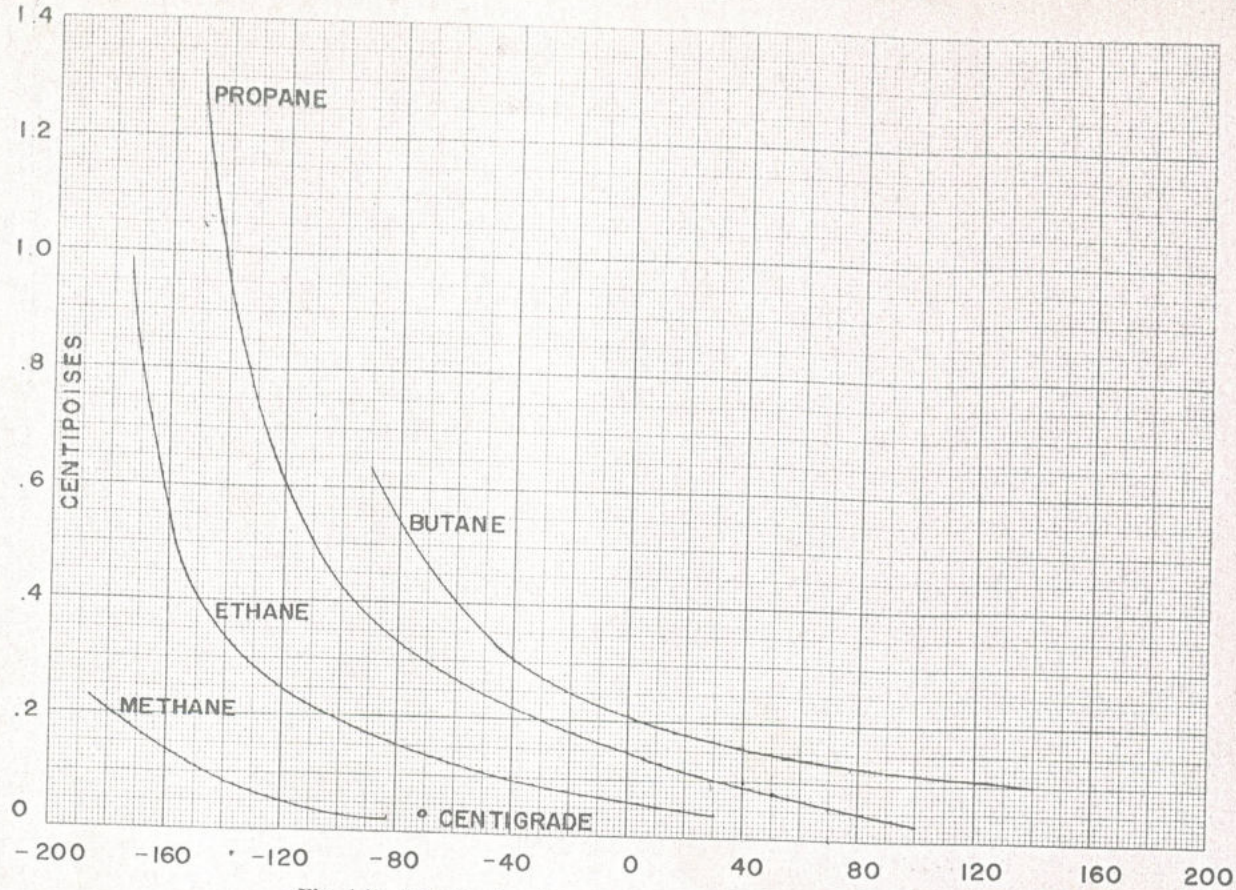

Fig. 1-7—Liquid viscosity over a range of −200 to +140° C.

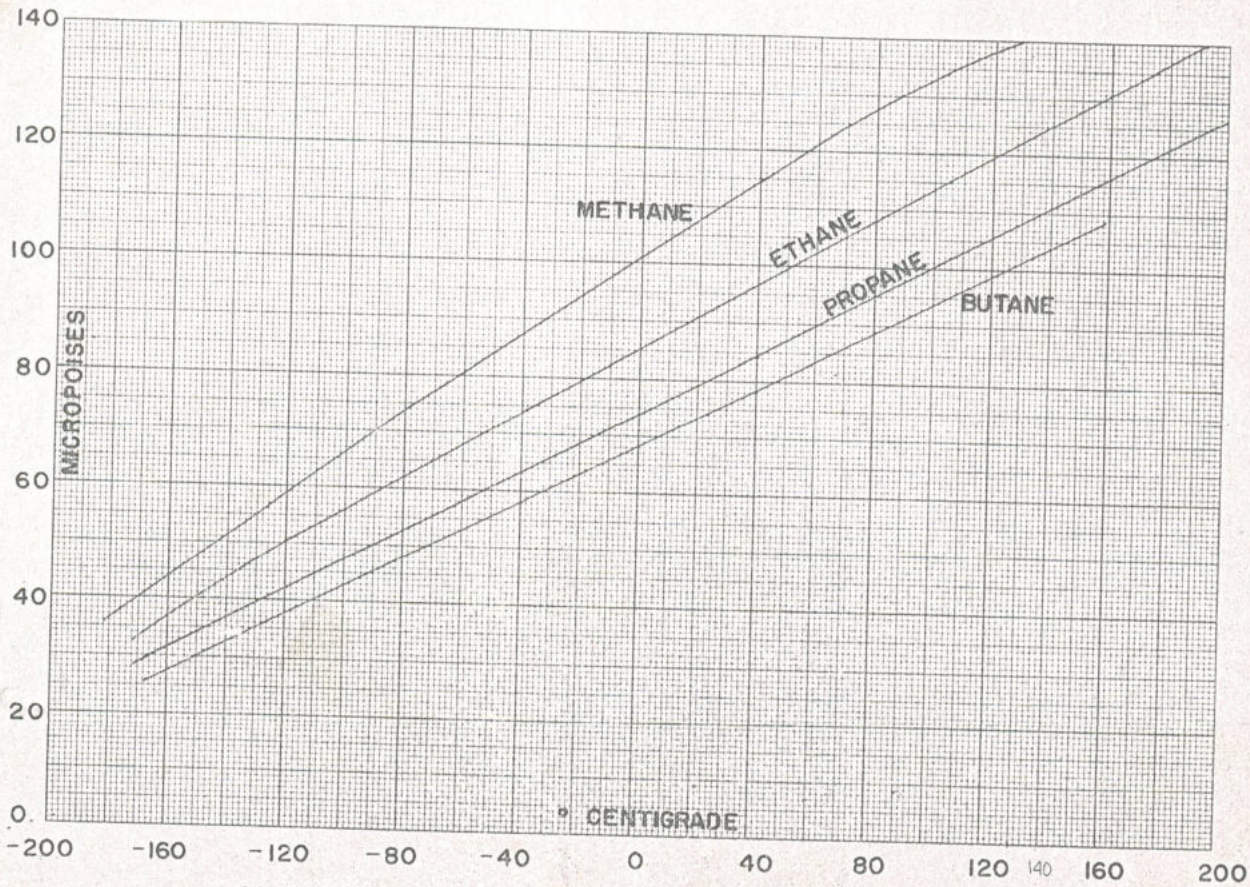

Fig. 1-8—Vapor viscosity @ 14.7 psia over a range of −200 to +200° C.

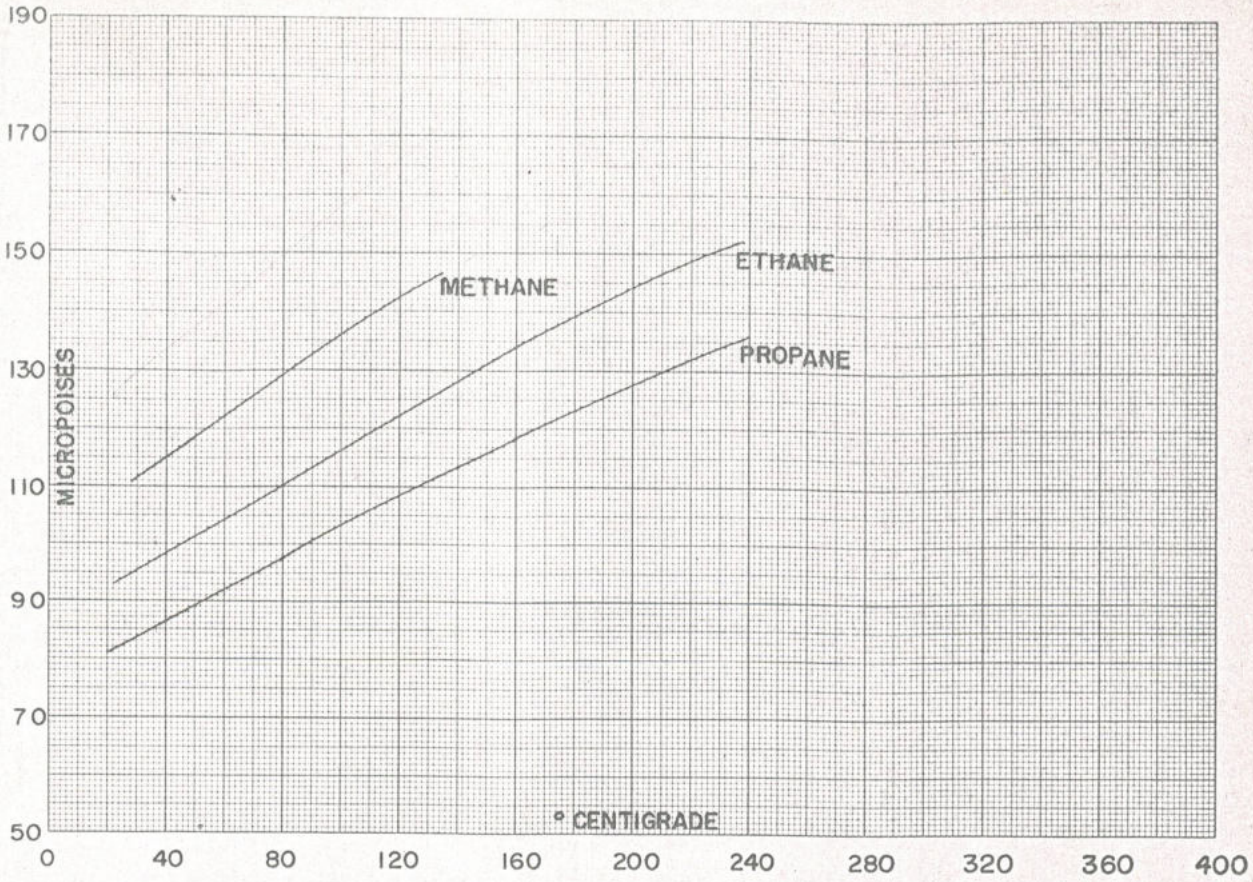

Fig. 1-9—Vapor viscosity @ 100 psia over a range of 0 to +240° C.

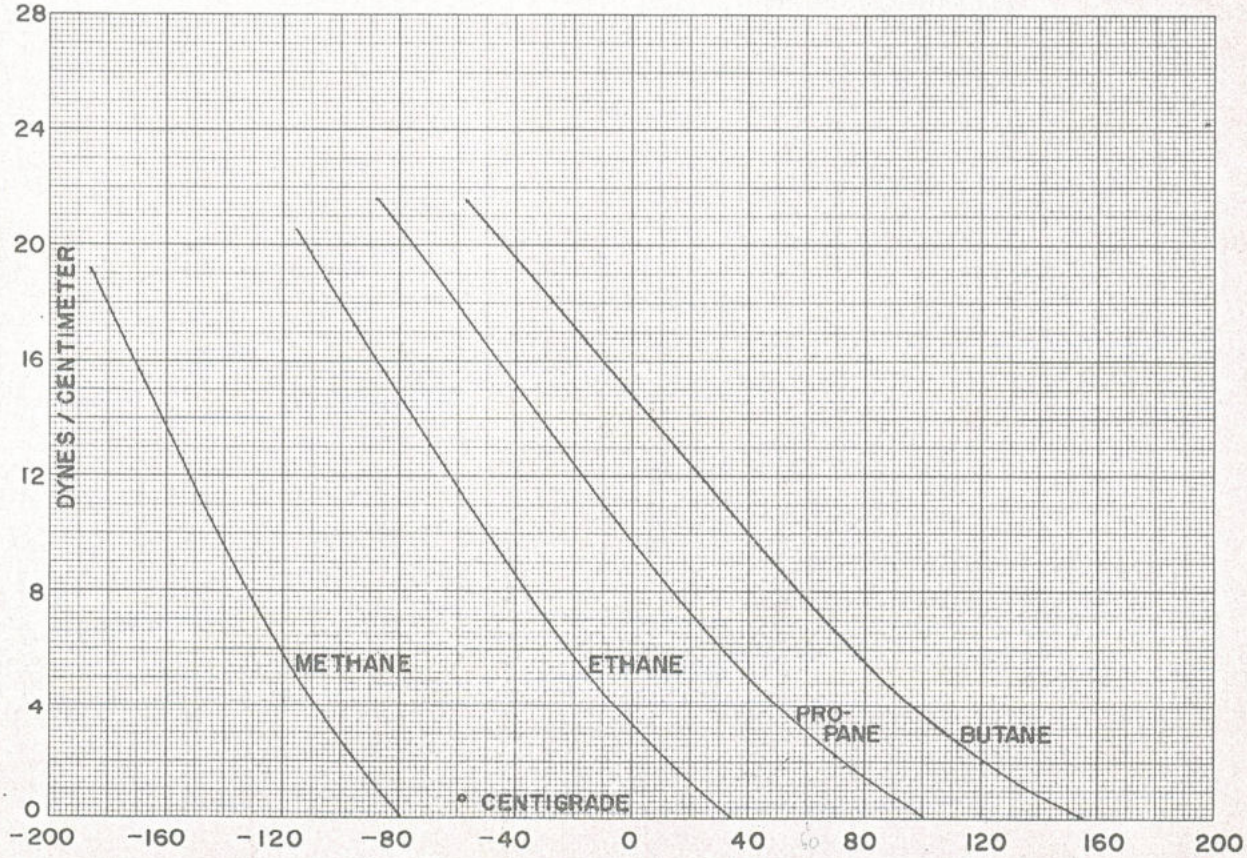

Fig. 1-10—Surface tension over a range of −200 to +160° C.

grams/cc. The increase is less than 10 percent and normally more like 1-2 percent.

Liquid and Vapor Viscosity. If there is any physical property that has benefitted from the efforts of the last five years it is vapor viscosity. The appearance of extensive experimental data, the refining of techniques for better accuracy, and great strides in estimation have all occurred in the last half decade. Tabulated data are available for all four compounds[25, 26] and experimental data at various temperatures and pressures are available for methane,[27] ethane,[27, 28] and propane.[27, 29] The author has plotted the vapor viscosity at atmospheric pressure and also at 100 psi to show the effect of pressure. The graph shows that viscosity increases only a few percent for this pressure change.

Unfortunately, liquid viscosity has not had the same rapid improvement as its vapor counterpart. Data generally are scarce and of questionable reliability. Estimation methods leave a lot to be desired, with typical errors ranging from almost nothing to over 100 percent, but generally averaging 10-30 percent. The data plotted here are from Project 44 data and the recent data of Swift.[30, 31]

For anyone interested in an in-depth study of the theoretical tools available for the calculation of gas and gas mixture viscosities, Hirschfelder[32] is an excellent reference. A fair amount of experimental data are also presented in this excellent review.

Surface Tension. Surface tension is a property that keeps popping up in a variety of chemical engineering correlations. Data are generally extremely meager for this property. Maass and Wright have presented experimental data for ethane and propane.[23] Dreisbach[5] tabulates it for a few temperature points, and Quayle[33] tabulates surface tension at 20° and 30° C for a large number of compounds in an article dealing with parachor. Since parachor is predominantly used in the petroleum industry and is a direct function of density, surface tension, and molecular weight, it is not included in this series but for anyone interested in this property, the article by Quayle is not only a probing analysis of the theories of parachor and its estimation but is also an extensive literature review of available data.

The meager surface tension data have been extrapolated by the method proposed by Othmer. A plot of the log of the critical temperature minus the actual temperature versus the log of the surface tension gives a straight line.

At this point it might be well to mention the units used for the various properties. With the exception of the vapor pressures which are plotted as pounds per square inch, all properties are presented in the metric system; namely, degrees Centigrade, calories/gram, dynes, etc. The author was initially determined to present all data in the engineering system but it becomes quickly evident that the chemists and physicists have a good reason for sticking with the metric system—the switch from one unit to another and the dimensional analyses are much easier, plus it is generally easier to switch from metric to engineering than vice versa. Many production plants now work in the Centigrade system and metric for density and viscosity. It is too bad we did not all grow up in the metric system.

METHANE—ETHANE—PROPANE—BUTANE
TABLE 1-1

Compound	Boiling Point °C	Freezing Point °C	Molecular Weight	Critical Properties °C tc	psi Pc	g/ml dc
Methane	—161.5	—182.5	16.042	— 82.1	673.1	0.162
Ethane	— 88.6	—183.3	30.068	32.3	709.8	.203
Propane	— 42.1	—187.7	44.094	96.8	617.4	.220
Butane	— 0.5	—138.3	58.12	152.0	550.7	.228

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Part 2 will appear in an early issue.

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