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

R. W. Gallant

The Dow Chemical Co., Plaquemine, La.

AMONG THE ALKYNES, acetylene is the compound that has found wide industrial use. Of the almost one billion pounds per year presently being used to make petrochemicals, almost 60 percent goes into the two products—vinyl chloride and neoprene.

Methyl acetylene is one of these chemical compounds that has continually intrigued engineers as a potentially valuable basic raw material, but has never quite made the grade. The butynes fall in the same category. These compounds show up in refinery byproducts steams and as such, are a part of many calculations. Physical data are fairly good for acetylene and some experimental data are available for methyl acetylene but not much literature data are available on the butynes.

Vapor Pressure. Stull[16] presents extensive data for acetylene and methyl acetylene and the vapor pressure up to the boiling point for the butynes. Din also presents high pressure data on acetylene.[10] Hachmuth covers 1-butyne up to 15 psia and 2-butyne up to 30 psia. The data extrapolate quite well up to the critical point on a Cox chart.

Thermal Properties. Dreisbach[5] has presented data for the heat of vaporization of all four compounds from about

—50° up to +25° C. Din[10] presents data from —72 to +350° for acetylene. The experimental data were extrapolated over the temperature range by the method of Watson, which relates the change in heat of vaporization to the reduced temperature. This method gave errors of less than 2 percent in comparison with experimental data.

The vapor heat capacity data for acetylene and methyl acetylene is taken from the compilation by Kobe.[18] With almost no data reported for the butynes, it was necessary to determine the entire curve for these compounds by estimation methods. The method of Souders[34] was used here. Reid and Sherwood[12] report a maximum error of 10 percent and an average error of about 1 percent for 30 experimental points for alkenes and alkynes. As in the two previous parts, the method of Schiff was used to estimate the liquid heat capacities from the liquid densities.

Liquid Density. Maass and Wright[33] have determined experimentally the density of acetylene from —82° to —55° C, and the density of methyl acetylene from—55° to —12°. Din[10] covers acetylene from — 23° to +33° Dreisbach[5] presents the density in the 20 to 30° range for all four compounds. The experimental data have been extrapolated by the method of Othmer and are not very reliable for the butynes.

Liquid and Vapor Viscosity. There is very little viscosity data reported for the alkynes. Reid and Sherwood[12] present data for acetylene from 20 to 120° C, and Nakanishi[25] presents it for acetylene from —223° to 227°. Since there is no reliable experimental data for the methyl acetylene or butynes, the vapor viscosity has been calculated

TABLE 3-1—C_2 to C_4 Alkynes

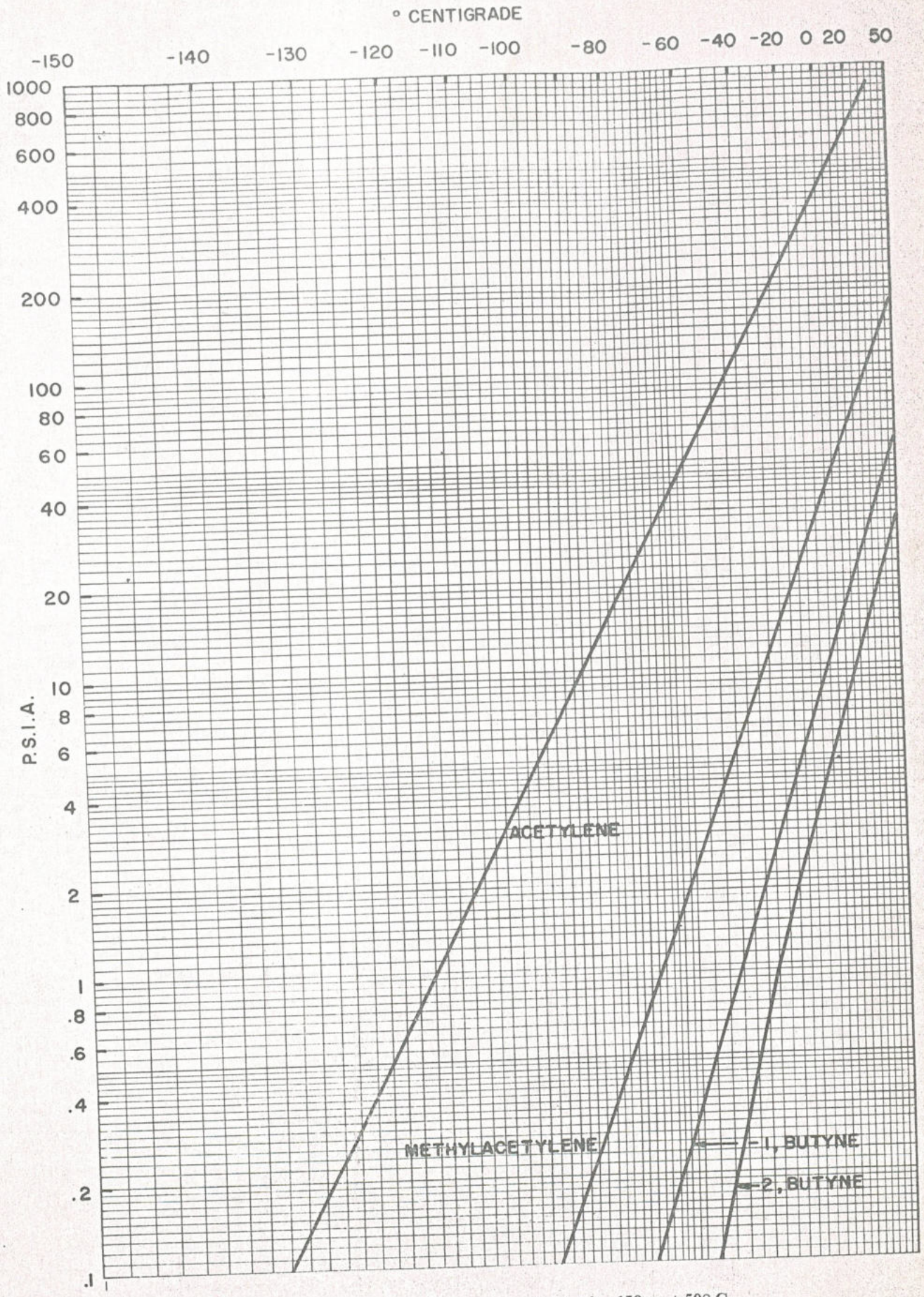| Compound	Boiling Point °C	Freezing Point °C	Molecular Weight	Critical Properties		
				°C tc	psi Pc	g/ml dc
Acetylene	—84.0	— 81	26.03	36	905	0.231
Methylacetylene	—23.3	—102.7	40.06	128	775	.229
1-Butyne	+ 8.7	—126	54.09	190	683	.245
2-Butyne	+27.2	— 32.3	54.09	213	738	.245

PHYSICAL PROPERTIES OF HYDROCARBONS . . .

Fig. 3-1—Gives vapor pressure over a range of —150 to +50° C.
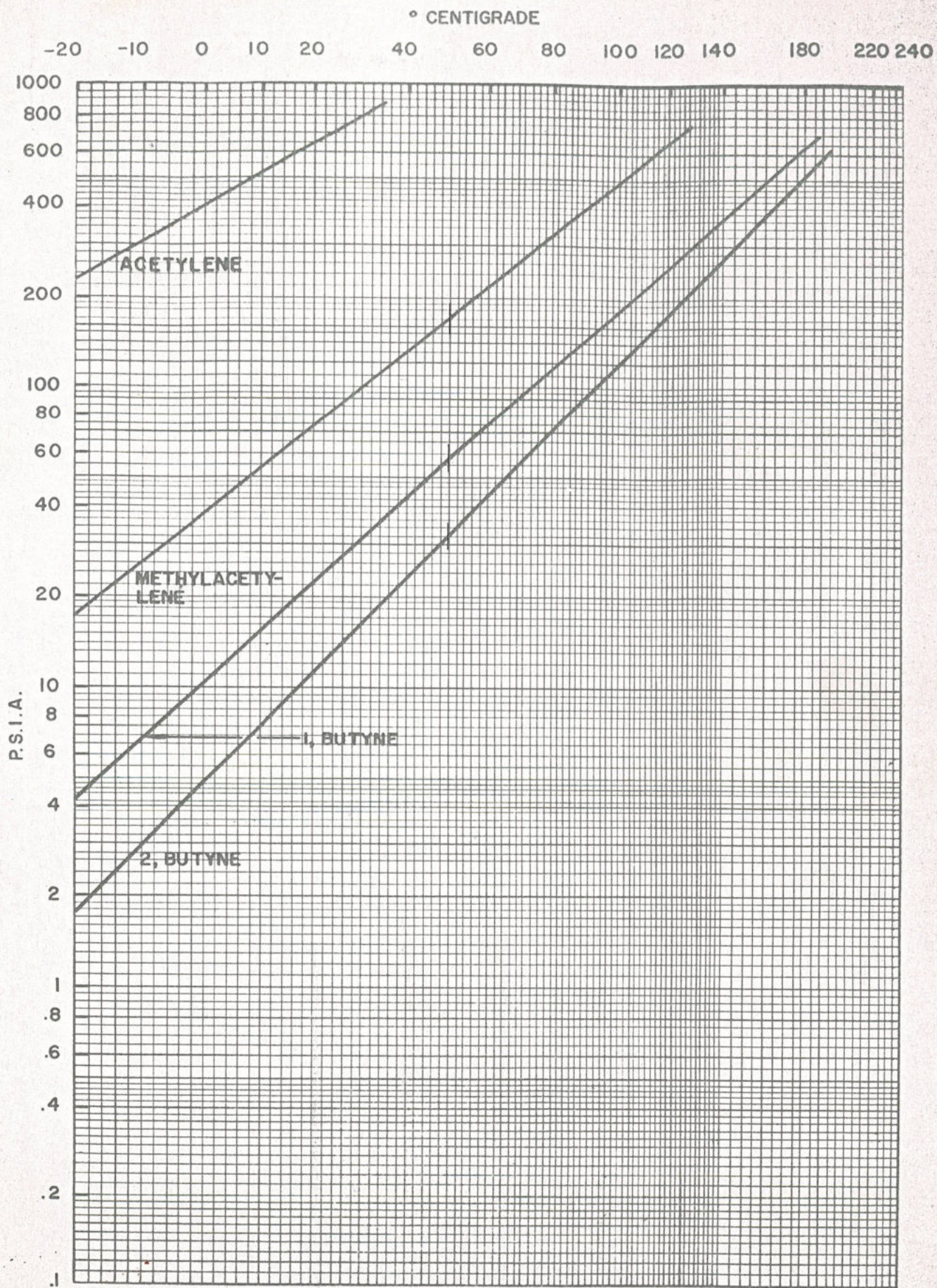
Fig. 3-2—Gives vapor pressure over a range of —20 to +213° C.
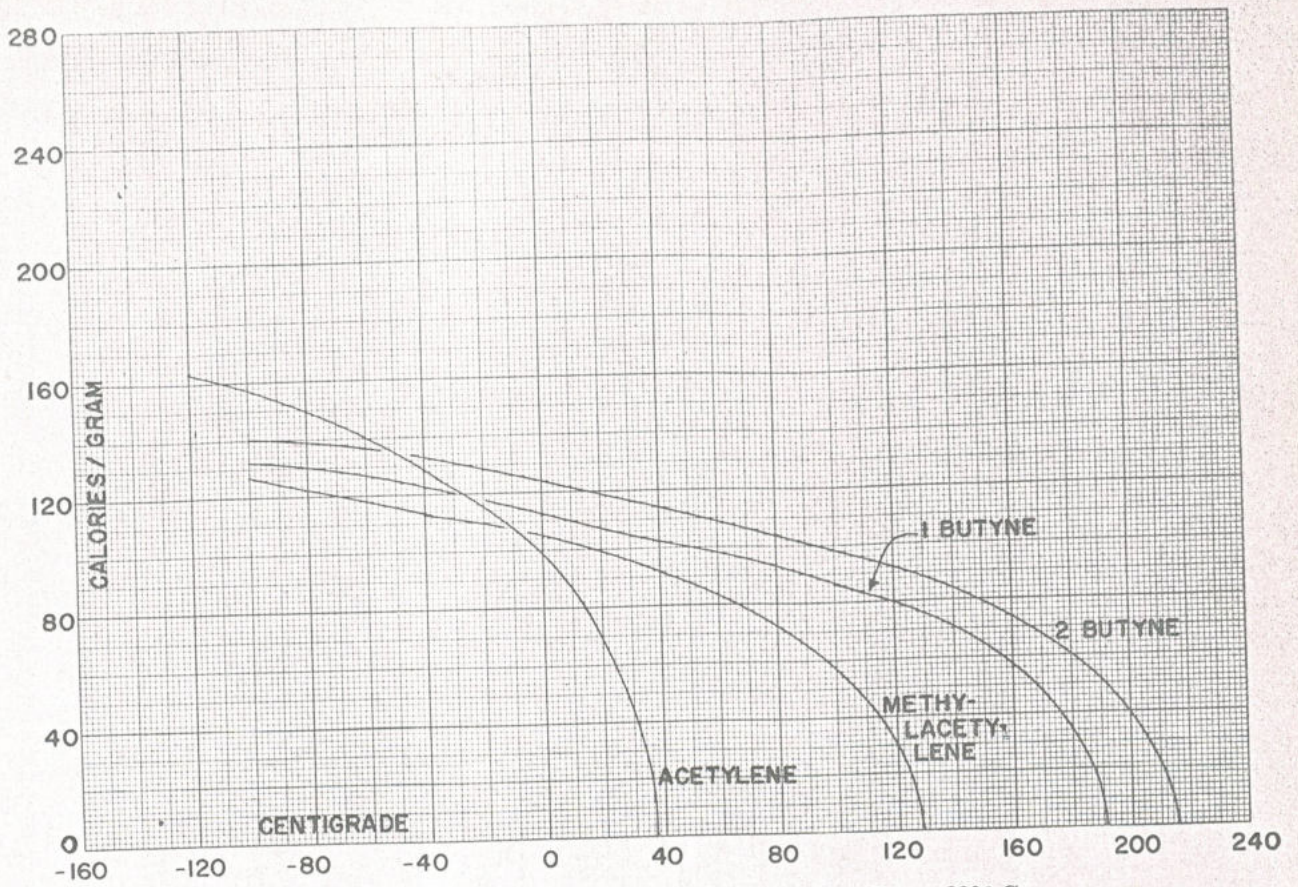
PHYSICAL PROPERTIES OF HYDROCARBONS . . .

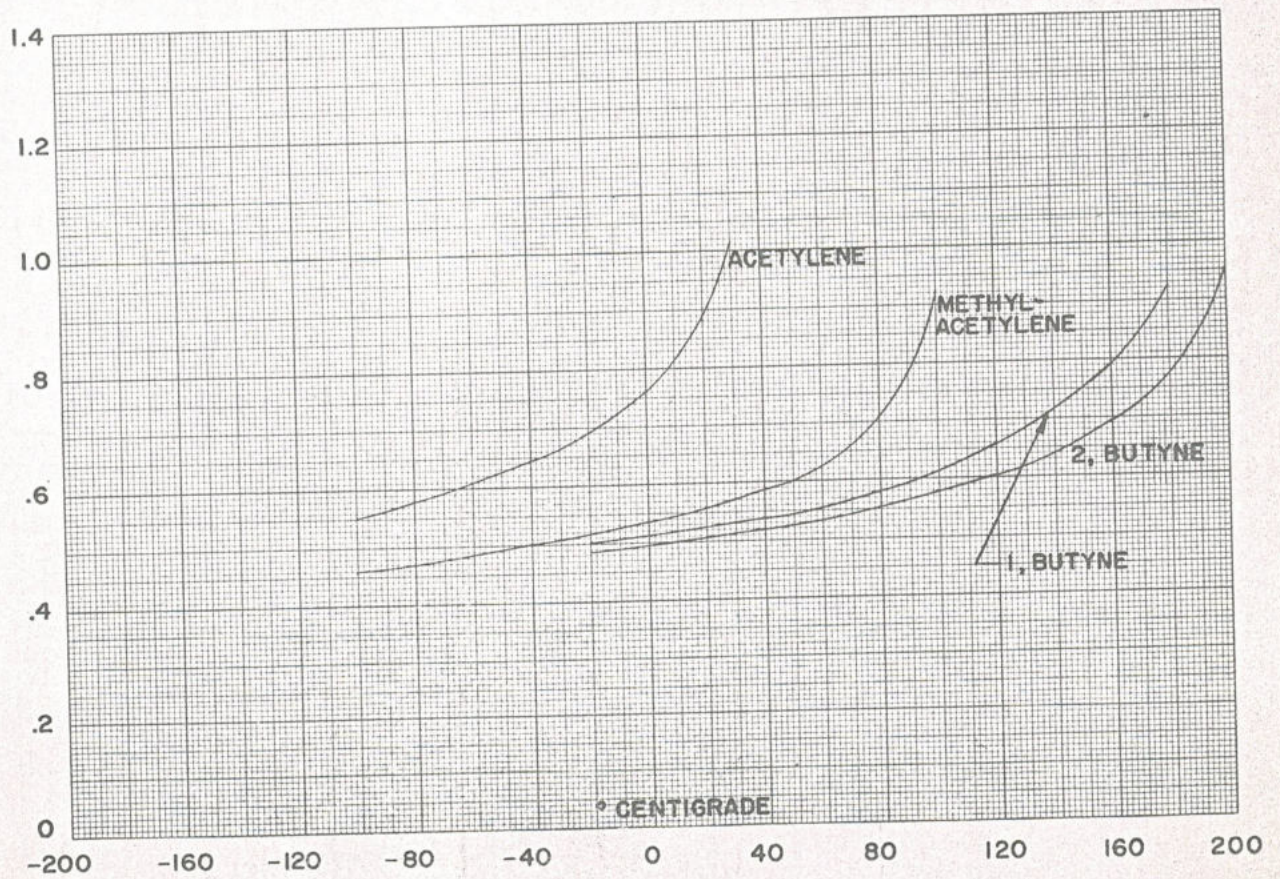Fig. 3-3—Gives heat of vaporization over a range of —120 to +220° C.

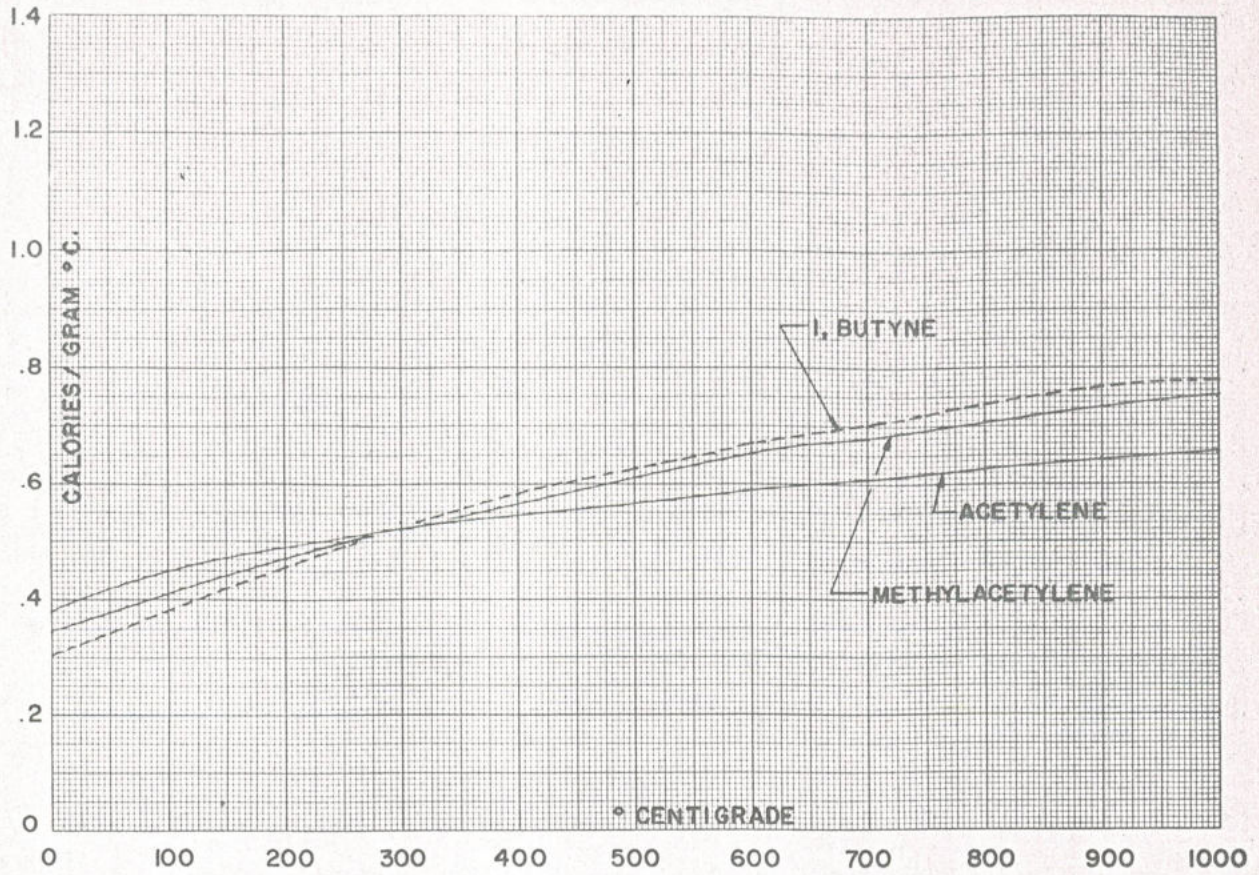
Fig. 3-4—Gives liquid heat capacity over a range of —100 to +200° C.

Fig. 3-5—Gives vapor heat capacity over a range of 0 to +1,000° C.

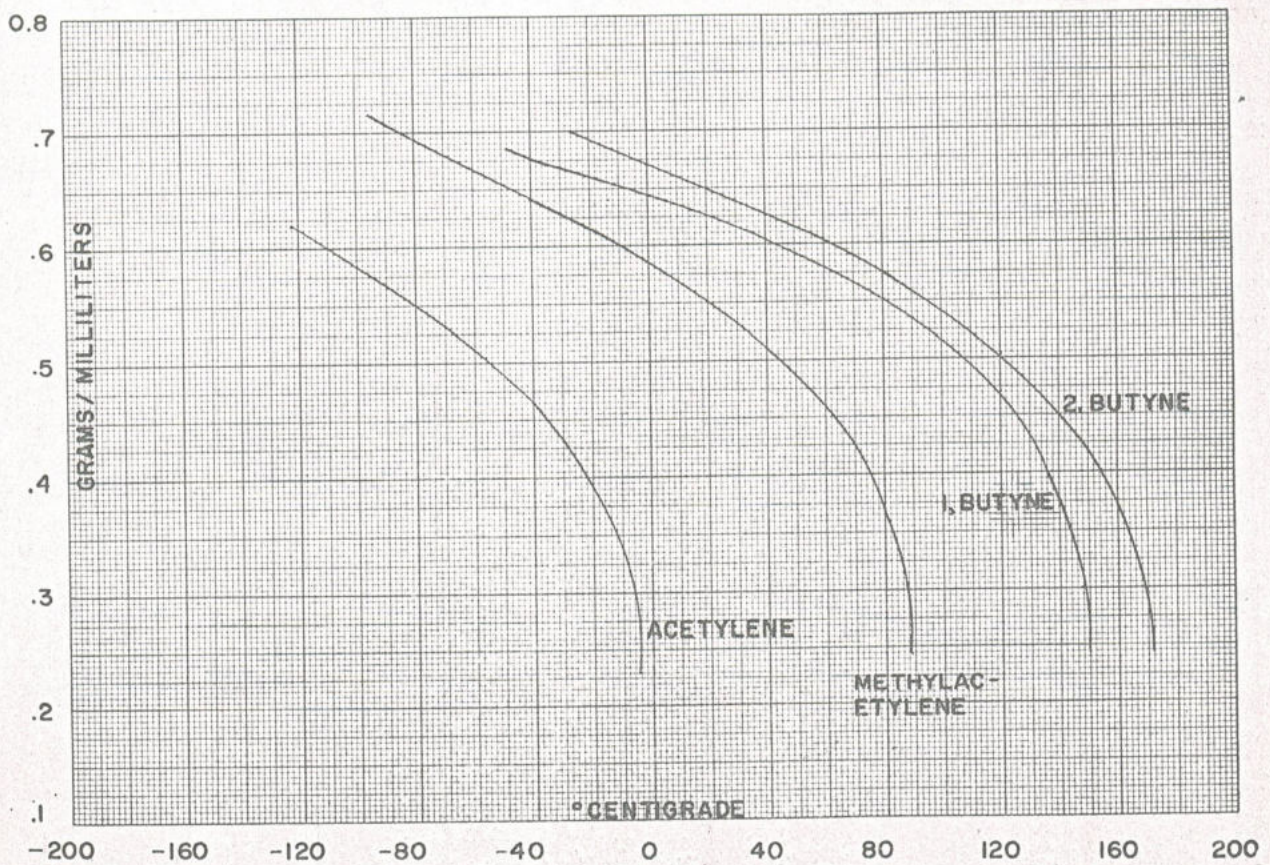Fig. 3-6—Gives liquid density over a range of —90 to +220° C.
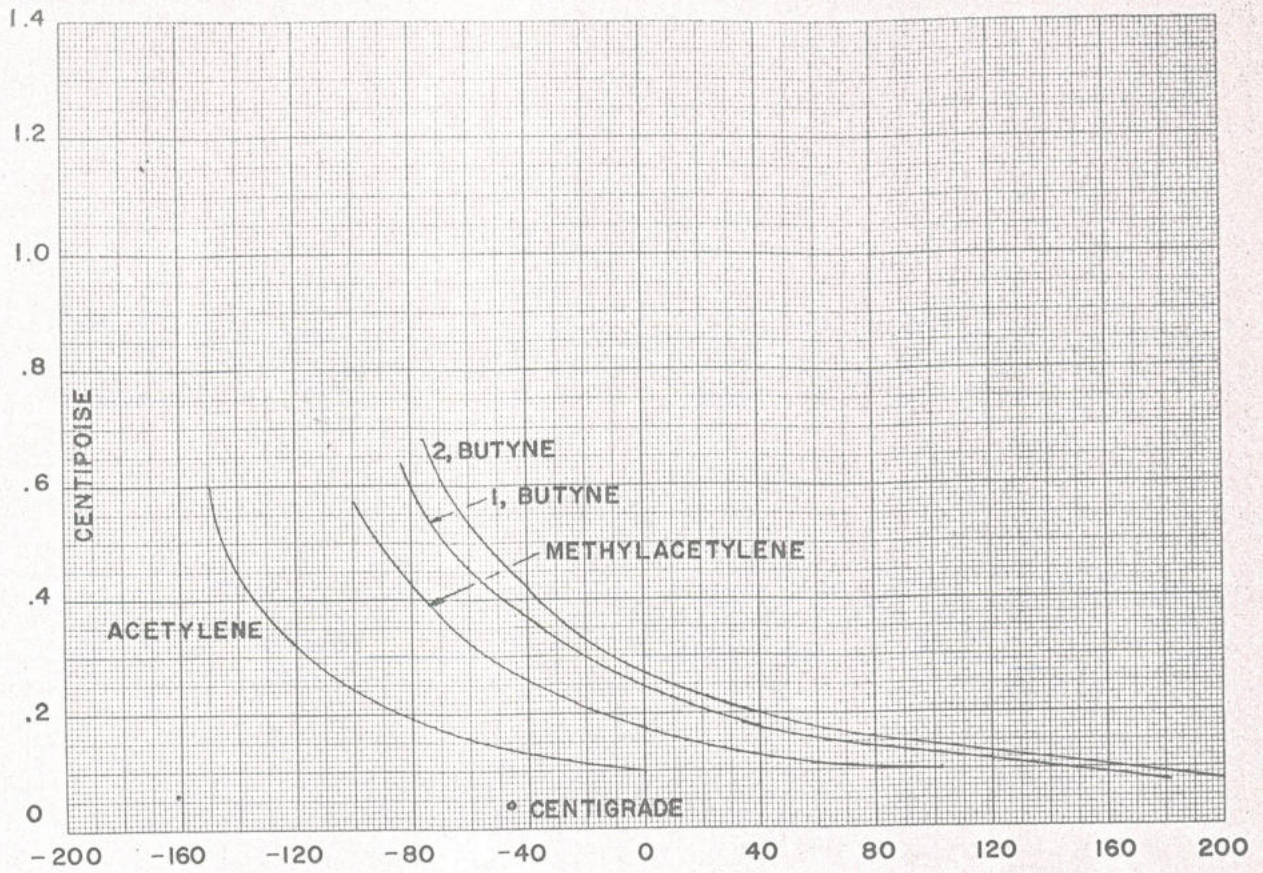
PHYSICAL PROPERTIES OF HYDROCARBONS . . .

Fig. 3-7—Gives liquid viscosity over a range of —150 to +200° C.
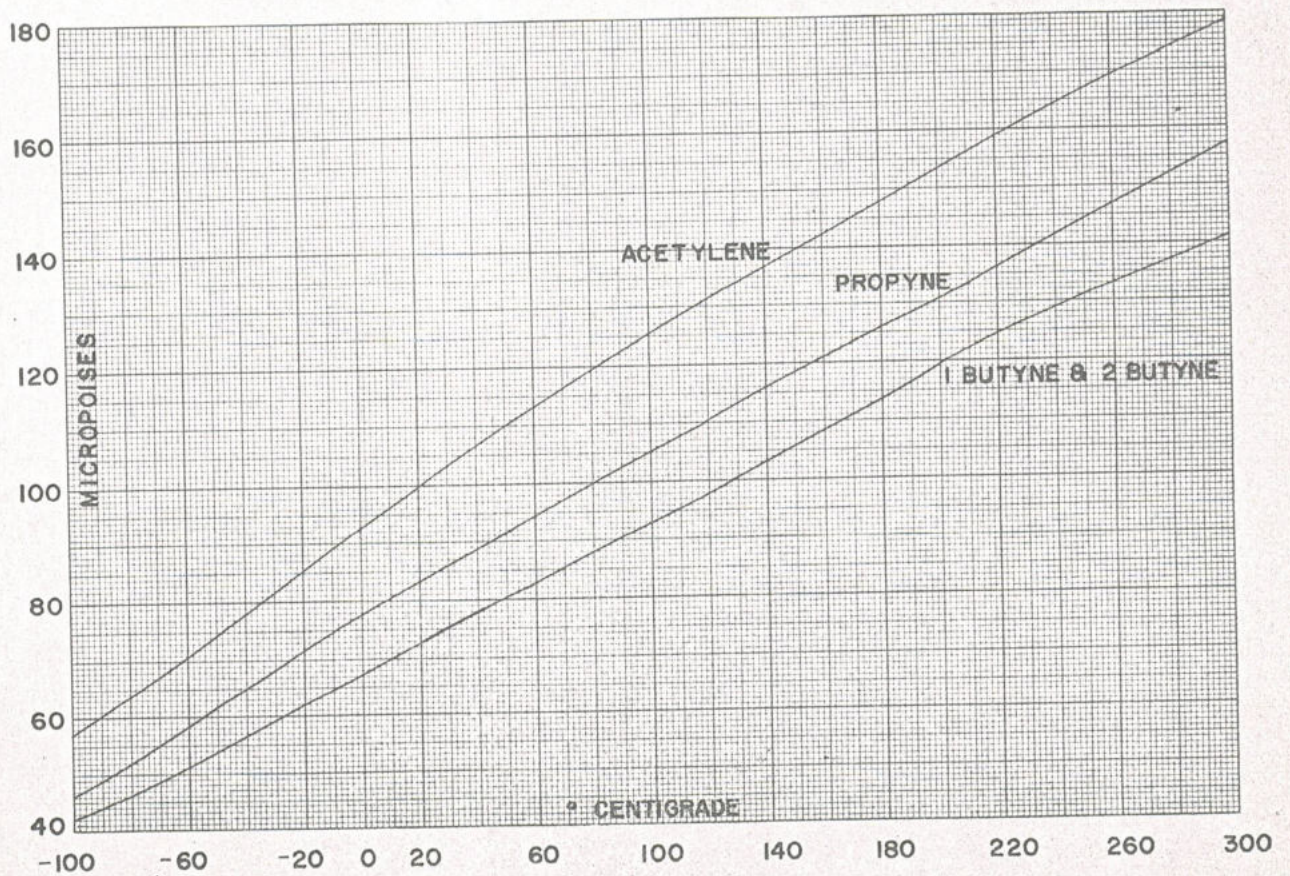

Fig. 3-8—Gives vapor viscosity over a range of —100 to +300° C.

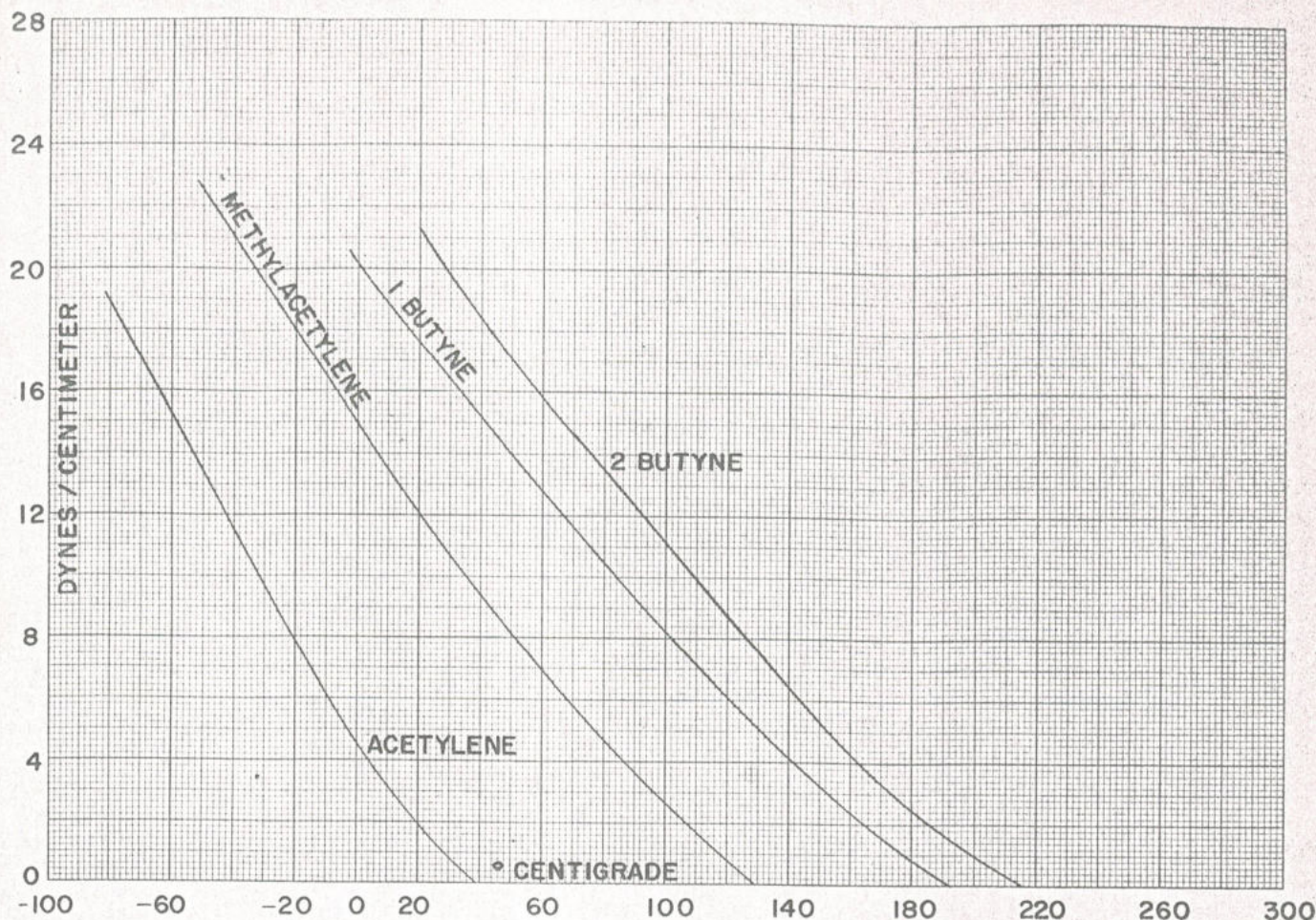Fig. 3-9—Gives surface tension over a range of —80 to +220° C.

by the estimation method of Thodos and Flynn.[34] The maximum error for four values calculated for acetylene was less than one percent when compared with experimental data. Since this method uses the critical pressure and temperature in the correlation, it is obvious that any error in the critical properties will greatly affect the results. The critical properties of methyl acetylene appear to be well established but there is some difference in the reported values for the butynes. The best apparent source was used for the butynes.

Liquid viscosity was calculated by the method of Thomas, as outlined by Reid and Sherwood in their book.

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.*

This relates the liquid viscosity to the liquid density, the reduced temperature, and a constant calculated from the structure of the compound. The error here can be quite large, sometimes in excess of 50 percent, but it is normally more like 15 percent, and generally the calculated results are higher than experimental values.

This method is rather tedious in its required calculations but is about as good a method as presently exists.

Surface Tension. Once again, the best source of experimental data is Maass and Wright,[23] who present low temperature data for acetylene and methyl acetylene. Quayles[34] gives the low temperature values for acetylene and Dreisbach[5] presents the surface tension values at 20, 30, and 40° C for the butynes. Available data were extrapolated by the method of Othmer and are not very reliable outside the low temperature ranges (up to —20° C) for acetylene and methyl acetylene.

LITERATURE CITED

[35] Souders, M.; *Industrial and Engineering Chemistry* 41, (5), pp. 1037-1048 (May 1949).

See Part 1 for other references.

To be continued. Parts 1 and 2 appeared in the July and August 1965 issues of HYDROCARBON PROCESSING & PETROLEUM REFINER.