the intermolecular-force term may be considered to be independent of temperature, and a function of density only (at least for the temperature ranges studied). Therefore, Eq. 6 can be rewritten

$$\mu = G_f(\rho) + G_m(T) \qquad \qquad (8)$$

Jossi, Stiel and Thodos[18] developed a generalized viscosity equation based on this concept.

EXPERIMENTAL RESULTS

In the initial viscosity study at Institute of Gas Technology, Carr[7] utilized a high-pressure Rankine-type capillary viscometer to obtain relatively extensive data on methane and light natural gases. When attempts were made to obtain data on heavier hydrocarbons, this particular viscometer would not give reproducible results, even though Baron, Roof and Wells[3] utilized a similar instrument to obtain good data on nitrogen, methane, ethane and propane. A completely different type of viscometer was developed,[11] which has proved to be very flexible in operation, to yield data of high reproducibility and give over-all run times short enough that data fields of significant detail can be obtained in relatively short times. Data have been obtained for ethane,[12] propane[29] and n-butane[10]; and the critical point region of each material was investigated in great detail separately.[28] Work on binary mixtures is in progress.

STATE EQUATION FOR VISCOSITY

The proposed equation is based in part on the theoretical considerations reviewed and in part on observed behavior. At low densities the equation reduces to Eq. 2, Sutherland's equation for temperature dependence of gas viscosity. At high densities the equation approaches Eq. 3, which is fairly accurate for light hydrocarbon liquids. The equation also represents observed behavior in the region between that for dilute gas and that for liquid; there has been no satisfactory theoretical equation for this region.

To insure that the equation will represent the temperature dependence of liquid viscosity for high densities, it is necessary to transform Eq. 3 into the corresponding density function, since G_f is a function of density only. It is assumed that, for small temperature changes at constant pressure, the linear equation for thermal expansion of a liquid is sufficiently accurate:[23]

$$\rho_o/\rho_t = 1 + a(T - T_o) \qquad \qquad (9)$$

or, by expansion,

$$\rho_t/\rho_o \cong 1 - a(T - T_o) \qquad \qquad (9a)$$

When Eq. 9 is solved for T, and this expression is substituted into Eq. 3,

$$\mu = A e^{B/T_o + (1 - \rho_t/\rho_o)/a} \qquad \qquad (10)$$

or, by expansion,

$$\mu \cong A e^{B(1 - 1/aT_o + \rho_t/aT_o\rho_o)/T_o} \qquad \qquad (10a)$$

If $K = A e^{B(1 - 1/aT_o)/T_o}$ and $b = B/aT_o^2\rho_o$,

$$\mu = K e^{b\rho} \qquad \qquad (11)$$

Eq. 11 might be expected to represent the dependence of the liquid viscosity on density only approximately, at best. If it should be valid, however, a semilog plot of $\mu - \mu_{g,a}$ vs density should result in almost straight lines for each material at high densities. Fig. 4 shows this plot for the four hydrocarbons, for density in grams per cubic centimeter. The curves appear to be parallel straight lines at high densities. Thus, it is worthwhile to try to represent the residual viscosity, $\mu - \mu_{g,a}$, by an equation of the form of Eq. 11 for densities greater than about 0.23 gm/cc.

At low densities the residual viscosity is always less than that represented by Eq. 11, and it decreases to zero at very low densities. A general equation can therefore be written.

$$\mu - \mu_{g,a} - A e^{b\rho} = g(\rho) \qquad \qquad (12)$$

where $g(\rho) \to 0$ as $\rho \to 0.21$ gm/cc, and

$$g(\rho) \to -A \text{ as } \rho \to 0.$$

A form which satisfies these conditions and also represents the curvature of the data is

$$\mu - \mu_{g,a} = A (e^{b\rho} - e^{-C\rho^k}) \qquad \qquad (13)$$

By examination of the high density values for ethane, propane and n-butane, it was determined that $b = 7.237$ cc/gm accurately represented the data when individual values of A were used for each component. Similarly, from the low density values it was determined that $k = 2.0$ and $C = 45.9$ (cc/gm)^2 accurately represented these data. The value of A for methane was evaluated from data of Carr[7] and Comings[9] by use of the b, k and C previously determined, and represented the 100 data points with a standard deviation of only 1.03 per cent.
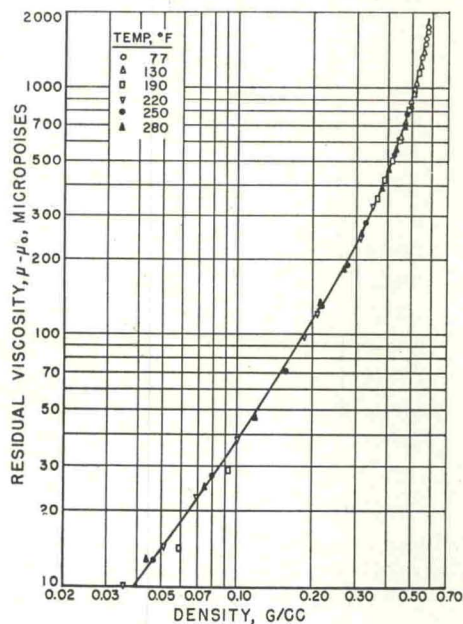
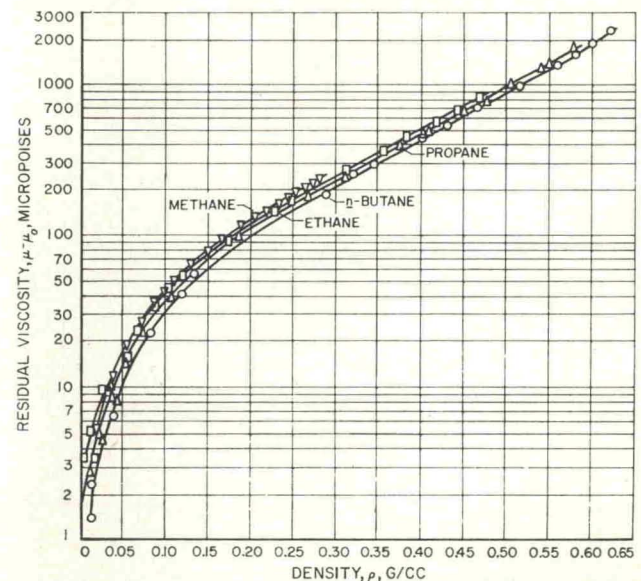FIG. 3—RESIDUAL VISCOSITY VS DENSITY FOR PROPANE.

FIG. 4—SIMILARITY OF RESIDUAL VISCOSITY DEPENDENCE ON MASS DENSITY FOR FOUR HYDROCARBONS.

The values of the individual A's were plotted vs molecular weight (Fig. 5) and found to yield essentially a straight line. Therefore, the general equation was rewritten as

$$A = A_o - a\,(M), \qquad \qquad (14)$$

and all of the data for the four hydrocarbons were treated simultaneously by computer to obtain

$$\mu - \mu_{g,a} = A(e^{7 \cdot 237\rho} - {}^{-45 \cdot 9\rho^2}) \qquad \qquad (15)$$

where $A = 32.80 - 0.1637\,(M)$, and

$$\mu_{g,a} = BT^{3/2}/(T+S).$$

Values of B and S for the four hydrocarbons are given in Table 1. A summary of observed and predicted viscosity values is given in Table 2.

This equation predicts the available data on methane, ethane, propane and n-butane from the dilute gas to densities up to 2.4 times the critical density with a standard deviation of 1.6 per cent for 288 points. The difference between the predicted and observed viscosity was always less than 4.4 per cent except for densities within 10 per cent of the critical density. For the same data, the results obtained with the equation of Jossi, Stiel and Thodos[18] are considerably less accurate, as shown in Table 3.

EQUATION REPRESENTED GRAPHICALLY

The graph in Fig. 6 was prepared to facilitate use of Eq. 15. The $\mu - \mu_{g,a}$ co-ordinate was modified from a logarithmic scale so that a straight line results. This line represents the equation evaluated for a fluid of zero molecular weight. To convert the value obtained from the graph to that for the real gas at some given density, the graphical value is multiplied by a correction factor (X).

$$(X) = \frac{A_o - a\,(M)}{A_o} = 1 - 0.00499\,(M), \qquad (16)$$

which is also plotted in Fig. 6. To obtain the value of $\mu - \mu_{g,a}$ for the real gas at a given density, the $(\mu - \mu_{g,a})^*$ from the plot is multiplied by (X) for the corresponding molecular weight.

$$\mu - \mu_{g,a} = (\mu - \mu_{g,a})^* (X) \qquad \qquad (17)$$

APPLICATION TO MIXTURES

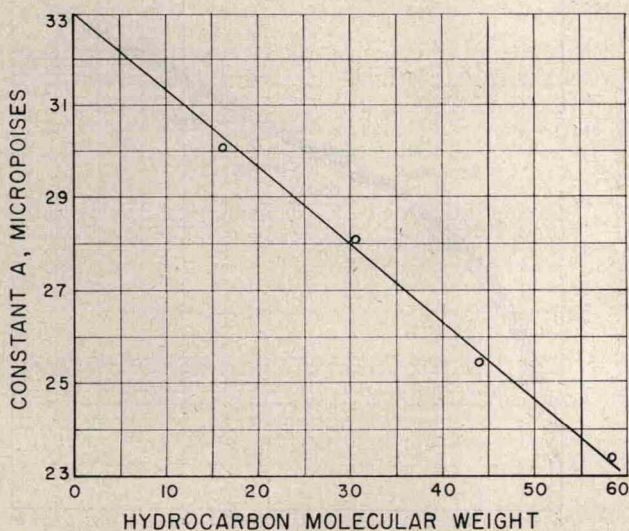It is possible that the form of this equation may also be applicable to mixtures. The composition dependent para-

FIG. 5—APPARENT LINEAR RELATIONSHIP BETWEEN THE MOLECULAR WEIGHT AND CALCULATED CONSTANT "A" IN EQUATION.

Y axis: CONSTANT A, MICROPOISES; X axis: HYDROCARBON MOLECULAR WEIGHT

TABLE 1—SUTHERLAND-EQUATION CONSTANTS FOR THE ATMOSPHERIC-PRESSURE VISCOSITY OF LIGHT HYDROCARBONS

Component	Sutherland Constants*		Data Ref.
	B	S	
Methane	7.390	295.2	(34)
Ethane	7.461	466.2	(34)
Propane	6.805	502.4	(34)
n-Butane	6.861	600.0	(26, 32, 33)

*For temperatures in °R, calculates viscosity in micropoises.

TABLE 2—SUMMARY OF EXPERIMENTAL VALUES AND THOSE PREDICTED BY THE VISCOSITY EQUATION

Component	No. of Points, n	Std. Dev.* σ, (per cent)	Max. Dev. (per cent)
Methane	100	1.01	2.65
Ethane	47	1.61	3.52
Propane	88	1.79	4.30
n-Butane	53	2.42	7.92

$$^*\sigma = 100 \left(\frac{\frac{\Sigma}{n}\,(\Delta n)^2}{n-1} \right)^{1/2} \text{ and } \Delta = \frac{\mu_{calc} - \mu}{\mu}$$

meter A is a linear function of molecular weight for pure components, and its behavior for mixtures should be examined. It is anticipated that $\mu_{g,a}$ might be replaced by the atmospheric-pressure viscosity of the mixture, $\mu_{m,a}$, which Carr[7] showed could be represented by

$$\mu_{m,a} = \frac{\displaystyle\sum_i x_i \sqrt{M_i}\,\mu_{g,a,i}}{\displaystyle\sum_i x_i \sqrt{M_i}} \qquad \qquad (18)$$

However, Eq. 15 has not been tested for mixtures due to the lack of data on a given mixture of known accuracy for wide-enough ranges of temperature and pressure.

NOMENCLATURE

A = constant

A_o = constant

a = constant

B = constant

b = constant

C = constant

$f(\ )$ = function of variables in $(\ )$

$G_f(\ )$ = intermolecular-force contribution to viscosity

$G_m(\ )$ = momentum-transfer contribution to viscosity

$G_o(T)$ = atmospheric-pressure viscosity as function of T

$g(\ )$ = function of variables in $(\ )$

K = constant

k = constant

M = molecular weight

p = pressure

S = Sutherland constant

T = temperature, absolute

T_r = reduced temperature

X = multiplying factor for graphical solution

x_i = mole fraction of the ith component

ρ = density

ρ_o = density at base temperature, T_o

ρ_t = density at temperature T

σ = molecular diameter

μ = viscosity

$\mu_{g,a}$ = atmospheric-pressure gas viscosity

μ_r = reduced viscosity