

# The Viscosity of Hydrocarbon Gases at Normal Pressures

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RECENTLY developments by Hirschfelder, Curtiss, and Bird (9) have produced relationships capable of predicting transport properties of nonpolar gases at normal pressures. The relationships require the use of Lennard-Jones force constants,  $\epsilon/\kappa$  and  $\sigma$ , available only for a limited number of substances, and tabulated values of collision integrals (8). Furthermore, the available force constants are of questionable reliability unless sufficient viscosity and/or  $P$ - $V$ - $T$  data were used in their calculation. Therefore, properties more readily available and dependable are preferable to use in calculating Lennard-Jones force constants.

Several attempts in the past have been made to relate the viscosity of a gas to its critical properties. Kamerlingh Onnes (12) in 1894 deduced from kinetic theory that

$$\mu^* \left( \frac{T_c}{M^3 P_c^4} \right)^{1/6} = k \quad (1)$$

where  $k$  was assumed to be a universal constant. Licht and Stechert (15) using available viscosity data, established  $k$  to be  $3.5 \times 10^{-5}$  when the critical temperature is in degrees Kelvin, the critical pressure in atmospheres, and the viscosity in centipoises. Using Equation 1 and the Sutherland equation, they developed a relationship capable of determining viscosity at other temperatures (15). Bromley and Wilke (4) simplified the Hirschfelder, Curtiss, Bird equation for viscosity by relating the Lennard-Jones force constants to the critical temperature and critical volume of the substance. In all of these studies, the resulting viscosity relationship involved molecular weight, critical temperature, and critical pressure. In this study, an attempt has been made to determine the effect of these and other variables on the viscosity of hydrocarbon gases using a dimensional analysis approach.

## DIMENSIONAL ANALYSIS

Viscosity of a gas at normal pressures depends not only on molecular weight and temperature as predicted from kinetic theory, but also on the critical constants,  $T_c$ ,  $P_c$ , and  $v_c$ . Applying the Rayleigh method of dimensional analysis

$$\mu^* = \alpha T^a T_c^b M^c P_c^d v_c^e R^f \quad (2)$$

where  $R$  is the gas constant. Dimensions involved are mass, length, time, and temperature. Dimensional analysis produces the following values for the exponents:

$$\begin{aligned} a &= f - b & d &= \frac{1}{2} - f \\ b &= b & f &= f \\ c &= \frac{1}{2} & e &= -\frac{1}{6} - f \end{aligned}$$

Using these exponents and combining variables, Equation 2 becomes

$$\mu^* \frac{T_c^{1/6}}{M^{1/2} P_c^{2/3}} = \beta z_c^m T_R^n \quad (3)$$

where  $z_c = P_c v_c / RT_c$ . For convenience, the  $T_c^{1/6} / M^{1/2} P_c^{2/3}$  group is referred to in this study as  $\xi$ . This group is a characteristic constant for each substance. The task therefore becomes one of relating  $\mu^* \xi$  with both  $z_c$  and  $T_R$  in order to establish exponents  $m$  and  $n$  and constant  $\beta$ .

## TREATMENT OF EXPERIMENTAL VISCOSITY DATA

Viscosities at atmospheric pressure for 25 hydrocarbon gases were used to establish constant  $\beta$  and exponents  $m$

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and  $n$  of Equation 3. The gases considered include normal paraffins up to nonane, isoparaffins, olefins, acetylenes, naphthenes, and aromatics. They are listed in Table I along with their critical temperatures, critical pressures, critical compressibility factors, molecular weights, and calculated values of  $\xi$ . Sources of experimental viscosities used in this work are also listed.

For each temperature at which experimental viscosities are reported, the group  $\mu^* \xi$  was calculated and plotted vs.  $T_R$  on log-log coordinates for each hydrocarbon. These individual plots were found to coincide with one another, despite the fact that considerable differences exist among the  $z_c$  values of these hydrocarbons. The composite result of these comparisons is presented in Figure 1 for the 25 hydrocarbons investigated in this study. This behavior indicates that for the hydrocarbons, the product  $\mu^* \xi$  is independent of  $z_c$ , and therefore exponent  $m=0$  in Equation 3. This indicates that  $\mu^* \xi$  depends only on temperature as follows:

$$\mu^* \xi = \beta T_R^n \quad (4)$$

Equation 4 suggests a linear relationship between  $\mu^* \xi$  and  $T_R$  on log-log coordinates. While results presented in Figure 1 essentially confirm this behavior, a slight curvature exists throughout the entire temperature range. In order best to express the relationship between  $\mu^* \xi$  and  $T_R$ , this curvature should be taken into effect. Hence, the following relationship has been developed,

$$\mu^* \xi \times 10^3 = [0.291 T_R - 0.058]^{3/4} \quad (5)$$

and is applicable to hydrocarbon gases at normal pressures (0.2 to 5 atm.) over the temperature range,  $0.5 \leq T_R \leq 3.4$ . Since high temperature-viscosity data on hydrocarbon gases are limited to those of methane and ethylene, the validity of Equation 5 in the high temperature range cannot be checked with other hydrocarbons. Nevertheless, Equation 5 should be capable of producing dependable viscosities for other hydrocarbons at high temperatures.

## CONCLUSIONS AND RESULTS

A comparison between experimental viscosity values and those predicted by Equation 5 produces an average deviation of 2.75% for the entire 368 points upon which this study was based. When doubtful experimental viscosity data were eliminated, this deviation reduces to 2.18% for 302 points. Similar comparisons were also undertaken for the Bromley-Wilke and Licht-Stechert equations. The results of all these comparisons are as follows:

Equations	Considered Points	Av. Dev., %	Consistent Points	Av. Dev., %
Bromley-Wilke	122	4.15	84	2.87
Licht-Stechert	122	3.77	84	2.86
This investigation	368	2.75	302	2.18

For the Bromley-Wilke and Licht-Stechert equation, 122 experimental points were selected randomly to cover the entire temperature range of the data for each of the 25 hydrocarbons of this study. Under these conditions average deviations of 4.15 and 3.77%, respectively, were produced. When doubtful viscosity values included in these 122 points were eliminated, these deviations reduce for 84 points to 2.87 and 2.86%, respectively.

## NOMENCLATURE

$k$  = constant  
 $m, n$  = exponents, Equation 3

Table I. Basic Constants and Sources of Viscosity Data

	$M$	$T_c, ^\circ K.$	$P_c, \text{Atm.}$	$z_c$	$\xi$	References
<b>Normal paraffins</b>						
Methane	16.04	191.1	45.8	0.289	0.0464	(1, 2, 5, 10, 11, 18, 29, 30, 32, 33)
Ethane	30.07	305.5	48.2	0.285	0.0357	(1, 6, 10, 21, 23, 29)
Propane	44.09	370.0	42.0	0.277	0.0334	(1, 2, 5, 10, 21, 23, 27, 29, 33)
<i>n</i> -Butane	58.12	425.2	37.5	0.274	0.0321	(14, 20, 23, 33)
<i>n</i> -Pentane	72.15	469.8	33.3	0.269	0.0317	(3, 24)
<i>n</i> -Hexane	86.17	507.9	29.9	0.264	0.0315	(6, 24)
<i>n</i> -Heptane	100.2	540.2	27.0	0.260	0.0316	(16)
<i>n</i> -Octane	114.2	569.4	24.6	0.258	0.0318	(16)
<i>n</i> -Nonane	128.2	595.4	22.6	0.250	0.0320	(16)
<b>Isoparaffins</b>						
Isobutane	58.12	408.5	36.0	0.282	0.0327	(10, 20, 23)
Isopentane	72.15	461.0	32.9	0.268	0.0318	(3, 19)
2,2,3-Trimethylbutane	100.2	531.5	29.75	0.269	0.0296	(7)
<b>Olefins</b>						
Ethylene	28.05	282.4	50.0	0.267	0.0356	(5, 23, 25, 28, 31)
Propylene	42.08	365.1	45.4	0.280	0.0324	(1, 23, 26, 31)
1-Butene	56.10	419.6	39.7	0.276	0.0314	(23)
2-Butene	56.10	430	41.0	0.274	0.0308	(23, 26)
Isobutene	56.10	417.9	39.5	0.275	0.0315	(23)
Isoamylene	70.13	464.8	33.9	0.260	0.0317	(3, 23)
2-Pentene	70.13	475.0	36.0	0.268	0.0306	(3)
<b>Acetylenes</b>						
Ethyne	26.04	309.2	61.6	0.274	0.0326	(1, 13, 23, 32, 33)
Propyne	42.08	401.2	52.8	0.266	0.0297	(23)
<b>Naphthenes</b>						
Cyclohexane	84.16	553.2	40.0	0.272	0.0267	(6, 17, 24)
<b>Aromatics</b>						
Benzene	78.11	562.2	48.6	0.274	0.0244	(6, 17, 19, 22, 24)
Toluene	92.13	594.0	41.6	0.271	0.0251	(17)
Trimethylbenzene	120.19	641.2	33	0.282	0.0260	(7)

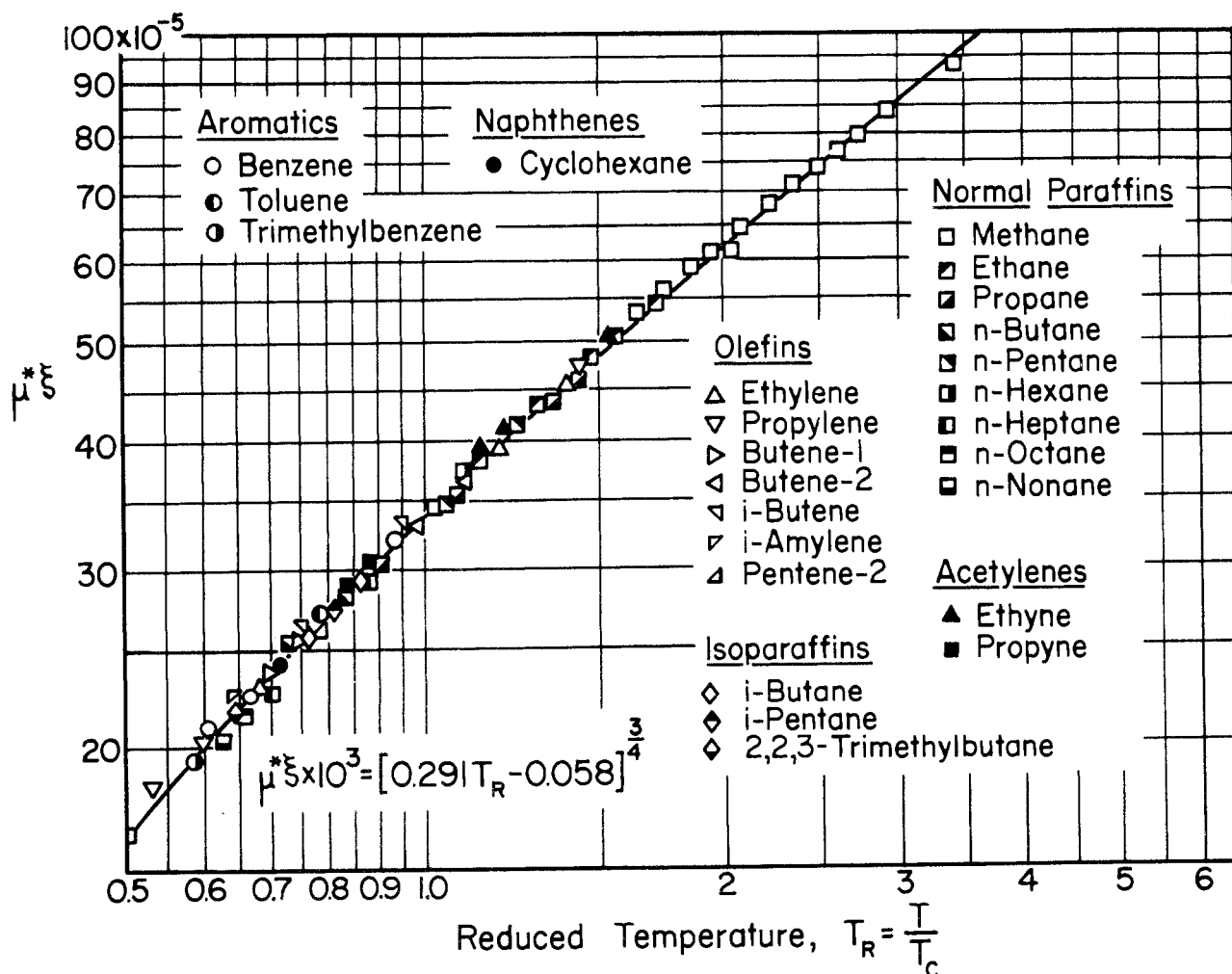


Figure 1. Relationships of  $\mu^*\xi$  and  $T_R$  for hydrogen gases at normal pressures

$M$  = molecular weight  
 $P_c$  = critical pressure, atm.  
 $R$  = gas constant  
 $T$  = temperature, ° K.  
 $T_c$  = critical temperature, ° K.  
 $T_R$  = reduced temperature,  $T/T_c$   
 $v_c$  = critical volume, cc./gram-mole  
 $z_c$  = critical compressibility factor,  $P_c v_c / RT_c$

#### Greek

$\alpha$  = constant, Equation 2  
 $\beta$  = constant, Equation 3  
 $\epsilon$  = maximum energy of attraction for Lennard-Jones potential, ergs  
 $\kappa$  = Boltzmann constant,  $1.3805 \times 10^{-16}$  ergs/° K.  
 $\mu^*$  = viscosity at normal pressures (0.2 to 5 atm.), centipoises  
 $\mu_c^*$  = viscosity at normal pressures and critical temperature, centipoises  
 $\xi$  =  $T_c^{1/6} / M^{1/2} P_c^{2/3}$   
 $\sigma$  = collision diameter for Lennard-Jones potential, A.

#### LITERATURE CITED

- (1) Adzumi, Hiroshi, *Bull. Chem. Soc. Japan* **12**, 199 (1937).
- (2) Bicher, L.B., Jr., Katz, D.L., *Ind. Eng. Chem.* **35**, 754 (1943).
- (3) Bleakney, W.M., *J. Appl. Phys.* **3**, 123 (1932).
- (4) Bromley, L.A., Wilke, C.R., *Ind. Eng. Chem.* **43**, 1641 (1951).
- (5) Comings, E.W., Mayland, B.J., Egly, R.S., *Univ. Illinois Eng. Expt. Sta. Bull.* No. 354, 7-68 (1944).
- (6) Craven, P.M., Lambert, J.D., *Proc. Roy. Soc. (London)* **A205**, 439 (1951).
- (7) Everhart, W.A., Mack, E., *J. Am. Chem. Soc.* **55**, 4894 (1933).
- (8) Hirschfelder, J.O., Bird, R.B., Spotz, E.L., *Chem. Revs.* **44**, 205 (1949).
- (9) Hirschfelder, J.O., Curtiss, C.F., Bird, R.B., "Molecular Theory of Gases and Liquids," Wiley, New York, 1954.
- (10) Ishida, Yoshio, *Phys. Rev.* **21**, 550 (1923).
- (11) Johnson, H.L., McCloskey, K.E., *J. Phys. Chem.* **44**, 1038 (1939).
- (12) Kamerlingh Onnes, H., *Communs. Phys. Lab. Univ. Leiden* No. 12 (1894).
- (13) Kiyama, Ryo, Makita, Tadashi, *Rev. Phys. Chem. Japan* **22**, 49 (1952).
- (14) Kuenen, J.P., Visser, S.W., *Verslag. Gewone Vergader Afdeel. Natuurk. Ned. Akad. Wetenschap.* **22**, 336 (1913).
- (15) Licht, W., Stechert, D.G., *J. Phys. Chem.* **48**, 23 (1944).
- (16) Melaven, R.M., Mack, E., *J. Am. Chem. Soc.* **54**, 892 (1932).
- (17) Nasini, A.G., *Proc. Roy. Soc. (London)* **A123**, 692 (1929).
- (18) Rankine, A.O., Smith, C.J., *Phil. Mag.* **42**, 615 (1921).
- (19) Rappenecker, K., *Z. physik. Chem.* **72**, 695 (1910).
- (20) Sage, B.H., Yale, W.D., Lacey, W.N., *Ind. Eng. Chem.* **31**, 223 (1939).
- (21) Smith, A.S., Brown, G.G., *Ibid.*, **35**, 705 (1943).
- (22) Suhrmann Rudolph, *Z. Physik.* **14**, 56 (1923).
- (23) Titani, T., *Bull. Chem. Soc. Japan* **5**, 98 (1930).
- (24) *Ibid.*, 7-8, 255 (1933).
- (25) Trautz, M., Baumann, P.B., *Ann. Physik.* [5], **2**, 733 (1929).
- (26) Trautz, M., Hussein, I., *Ibid.*, **20**, 121 (1934).
- (27) Trautz, M., Kurz, F., *Ibid.*, **9**, 981 (1931).
- (28) Trautz, M., Melster, A., *Ibid.*, [5], **7**, 409 (1930).
- (29) Trautz, M., Sorg, K.G., *Ibid.*, **10**, 81 (1931).
- (30) Trautz, M., Zink, R., *Ibid.*, [5], **7**, 427 (1930).
- (31) Van Cleave, A.B., Maass, O., *Can. J. Research* **13B**, 140 (1935).
- (32) Vogel, H., *Ann. Physik.* **43**, 1258 (1914).
- (33) Wobser, R., Müller, F., *Kolloid-Beih.* **52**, 165 (1941).

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## Heat Transfer Characteristics of Fluorochemical Inert Liquid FC-75

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**I**NERT FLUORO-CHEMICAL LIQUIDS, particularly 3M's FC-75, are excellent heat transfer media for cooling electronic components. Chemically, FC-75 (3M) is a fully fluorinated product composed of a mixture of compounds containing eight carbons, principally perfluoroethers (see Table I for typical properties). The unique heat transfer properties of this material have been recognized, but factual data have been lacking.

In this work, variables affecting heat transfer to FC-75 were determined. Comparisons were also made with other commercial dielectric coolants in a forced convection system on the basis of heat transfer properties, not considering other advantages such as high electric strength, non-flammability, thermal stability, low temperature fluidity, chemical inertness, and capability of allowing equipment miniaturization.

The heat transfer properties of inert fluorochemicals have been of interest in the past few years. In 1954, Olyphant and Brice (6) recognized that for natural convection liquid cooling, FC-75 had only a modest heat transfer advantage over transformer oil. However, boiling FC-75 transferred ten times as much heat as transformer oil when the oil was under natural convection at the same temperature. This advantage was limited to a factor of 1.5 when applied to experimental transformers, because of steep temperature gradients induced in parts of the cell winding not exposed to the coolant.

Kilham and others (4, 5) at Raytheon found that inert fluorochemical liquids were the most effective coolants for

miniaturized transformers which operate around 375° F. Cooling, accomplished in these studies by boiling without forced circulation, was 1.5 to 3 times more effective than natural convection using either transformer oil or silicone oil.

Etter at RCA (2) studied forced circulation cooling for a high-power transmitting tube. FC-75 was selected as coolant on the basis of heat transfer coefficients calculated by the Dittus-Boelter equation. This calculation indicated a twofold advantage over the next best liquids, transformer and silicone oil. Experimentally, RCA utilized boiling of FC-75 with forced circulation of liquid at 3.5 feet per second over a heated wire. The maximum heat flux obtained was 350 watts per square inch (171,000 B.t.u./hr./sq. ft.)

Fairbanks (3) of Raytheon calculated relative heat transfer rates using various liquids and conditions of heat transfer at 185° F. His analysis showed FC-75 to be 20% more effective than commercial silicate ester for natural convection, 80% more effective for forced convection in turbulent flow, but 10% less effective for forced convection in laminar flow. However, he did not compare boiling heat transfer for FC-75 with nonboiling heat transfer for other commercial materials.

From these investigations, it was apparent that the principal advantage of FC-75 as a heat transfer fluid was its ability to transfer heat by boiling. This advantage can be obtained by natural circulation pool boiling, as in Raytheon's transformer, or by forced circulation local boiling as with RCA's transmitting tube.