Therefore, utilizing a straight-line equation of the form $y = mx + b$, a general equation was evaluated.

The equation for the viscosities of benzene–methyl ethyl ketone mixtures in the liquid phase for temperature in the range –32.4° to 26.0° C. is as follows:

$$\mu = e^{\left(\frac{848.2}{T} - 3.7516\right)} + e^{(-0.0216T + 4.914)}(0.0300 + 0.1850\ V_B + 0.8620\ V_B^2 - 0.1000\ V_B^3) \quad (8)$$

or

$$\mu = e^{\left(\frac{1526.7}{T'} - 3.7516\right)} + e^{(-0.0120T' + 4.914)}(0.0300 + 0.1850\ V_B + 0.8620\ V_B^2 - 0.1000\ V_B^3) \quad (8a)$$

where μ is the viscosity of the mixture.

A comparison of observed viscosities with those calculated by the empirical equation is presented in Table IV. The root mean square deviation of viscosities obtained by Equation 8 from the observed data was 1.20% for the total of 52 points of data.

NOMENCLATURE

m = volume fraction
M = mole fraction
T = absolute temperature, °K.
T' = absolute temperature, °R.
V_B = volume fraction of benzene at 25° C. or mole fraction of benzene
X_B = corrected volume fraction of benzene at 25° C. or corrected mole fraction of benzene
η = viscosity, centipoises

Subscripts

i, *w*, and *m*, define system

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Viscosity of Nitrogen, Methane, Ethane, and Propane at Elevated Temperature and Pressure

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Numerous determinations of the viscosity of fluids at either elevated temperature or elevated pressure are reported in the literature. However, measurements at both elevated temperature and pressure are scarce and have occasionally been made by techniques that cannot be considered quantitative. In this investigation quantitative measurements were made on the coefficient of viscosity of nitrogen and the three lowest paraffins over a range of conditions significant for theories of dense gases and of practical importance in the petroleum industry. The nitrogen data provide a comparison with what is considered the most reliable information on the viscosity of a compressed gas at elevated temperature.

EXPERIMENTAL

Principle of Viscometer. Rankine (*18*) devised a clever transpiration viscometer for handling small volumes of gases. A pellet of mercury descending in one leg of a closed loop of glass tubing exerts a piston-like action which forces the gas through a capillary comprising the other leg of the loop. The volume rate of gas transpired through the capillary of length, L, and radius, r, is obtained from the time, t, for the descent of the pellet between two marks on the fall tube, the volume, v, between marks being known by previous calibration. The pressure differential across the capillary is approximately the mass of the pellet, m, divided by the mean cross-sectional area, A, of the fall tube. At high pressures the density, ρ, of the gas becomes an appreciable fraction of that of the mercury, ρ_m, and a buoyancy factor for the pellet must be included. The maximum correction was 4.0% for propane and less for the other fluids. Numerical values for the density of these four fluids are available in a recent compilation (*21*). Also, a small experimentally determined term, α, which corrects for the unbalance of surface forces existing between the leading and trailing surfaces of the descending pellet must be subtracted. The instrument is symmetrical and can be inverted for repeated timing in either direction of pellet fall.

The equation for the determination of viscosity by this instrument is given by

$$\eta = \frac{\left[\left(\frac{\rho_m - \rho}{\rho_m}\right) m - \alpha\right] \pi g t}{8va \int_0^L dl/r^4} \quad (1)$$

Questions of the importance of the capillary end effects and of the varying velocity of the mercury pellet caused by the compressibility of the fluid have been discussed in detail (*7*).

Description of Viscometer. The Rankine viscometer cannot be used in its most simple form for viscosity measurements at elevated pressure. For sample pressures above several atmospheres, the glass instrument must be installed within a thermostated pressure vessel with a pressure balance maintained between the inside and the outside of the glass. Provision for charging sample gases at high pressure and elevated temperature is necessary, and a means of sensing and timing the descent of the pellet is required.

The glass viscometer with several dimensions indicated is shown schematically in Figure 1. The loop at the lower end has been enlarged so gas can bypass the mercury pellet when it is within this enlargement during pressuring and depressuring operations. This instrument differs from earlier high-pressure Rankine viscometers (*4,7*) in several respects. It has two side arms, one at either end of the capillary tubing. When connected to appropriate metal parts, they provide a sample inlet and a sample outlet. A single connection is not used because plans call for using this viscometer in the examination of mixtures exhibiting retrograde condensation, in which case the samples are charged to the viscometer at an elevated pressure by displacing a miscible nonretrograde prepressuring gas. A major benefit from two connections is the ease and thoroughness of cleaning. By proper manipulation, cleaning solutions and rinse water can be flowed through the whole glass system.

Two pairs of tungsten electrodes are sealed into the wall of the fall tube. A timer operating from a 60-c.p.s. tuning fork, calibrated for frequency against radio station WWV, is automatically started and stopped as the mercury pellet contacts the upper and the lower pair of electrodes, respectively. The number of cycles is recorded on an electronic pulse counter. The integral $\int_0^L dl/r^4$ for the capillary was determined by the method of Fischer (*9*) by measuring the variation in length l of a short pellet of mercury as it occupies many positions along the capillary. Uncertainties in other physical dimensions are all small compared to that of this integral. Two independent determinations of this integral on the capillary used in this viscometer differed by 0.6%. A second viscometer, with a smaller and more irregular bore, gave results about 0.5% higher than those reported here.

Of the proposed methods (*7*) for obtaining α, the interface correction for the descending pellet, the one used here is the determination of descent time of the pellet at each of four angular positions ω from the horizontal; nominally, 90°, 60°, 45°, and 30°. Actual angles are measured to the nearest 5 minutes of arc. Linear plots of $\sin \omega$ *vs.* $1/t$ are obtained. The intercept at $1/t = 0$, determined by a least-squares method, permits calculation of α for the given gas at that temperature and pressure. The individually determined value of α is used for each pressure in each run rather than a value obtained from smoothed plots of α *vs.* pressure (*4,7*). The numerical value of this correction term ranges between 6 and 10% of the term $m(\rho_m - \rho)/\rho_m$.

For each determination of viscosity in these experiments the Reynolds number for flow of the gas in the capillary is calculated. Whenever the value of this dimensionless number is much in excess of 2000, the plot of $\sin \omega$ *vs.* $1/t$ is no longer linear and the value of viscosity calculated is too great to be consistent with the other data. Hence, the pellet size is chosen to keep the value of the Reynolds number well under 2000, and only infrequently has it exceeded 1000. (The values of Reynolds number reported by Comings, Mayland, and Egly appear to be one half the correct value.)

The temperature of the viscometer is controlled by rapid circulation of oil from a large reservoir through a shell surrounding the pressure vessel. A Thermotrol regulator, with a resistance thermometer as sensing element, controls the temperature of the oil reservoir. Iron-constantan thermocouples, calibrated against a certified platinum thermometer, are placed inside the pressure vessel to measure temperatures at one end and at the mid-point of the glass viscometer. These temperatures are made to agree within 0.1° F. by heating the ends with small electric heaters. Temperature fluctuations observed during a complete determination at one temperature and pressure did not exceed ±0.05° F. Pressure is determined through a flexible bellows carrying an electrical contact and serving as a null-point detector. The Crosby fluid-pressure balance is sensitive to 1 p.s.i. and has been calibrated against a certified deadweight gage.

The criticisms that the mercury pellet cannot be used when even traces of propane or heavier hydrocarbons are present in the gas (*8*) or that use of electrical contacts is impractical (*4*), are not valid if three conditions are met:

1. The walls of the fall tube must be essentially undeformed near the electrodes, and the latter must not interfere with the pellet movement. In this instrument the electrodes protrude into the fall tube only a few thousandths of an inch to preclude serious deformation of the nose of the descending pellet.
2. All parts of the glass system contacted by mercury must be most scrupulously cleaned—for example, by the sequence of chromic acid, distilled water, dilute potassium hydroxide, and distilled-water steam.
3. The gas must not be in contact with rubber in the system. In this instrument the gas contacts only metal, glass, and teflon.

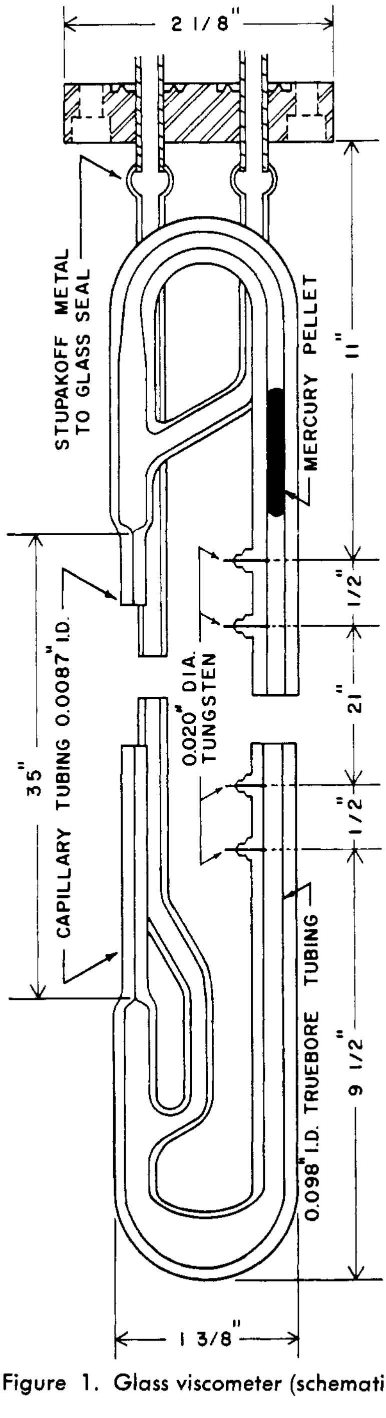

Figure 1. Glass viscometer (schematic)

Design of Electrical Contacts. A method was devised for inserting tungsten wires into thick-walled tubing with minimal deformation of the inner walls. This technique has made the use of mercury pellets practical in this equipment (Figure 2) and may be useful in other applications.

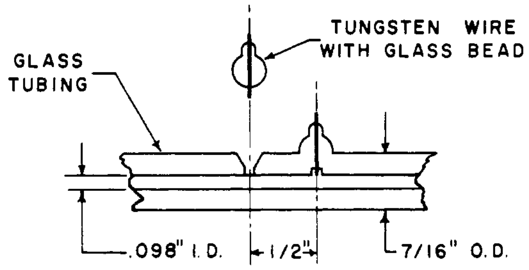

Figure 2. Method of sealing in tungsten contacts

Holes of about 0.020 inch in diameter are drilled through the glass with copper wire and a fine abrasive. The wire is held in the chuck of a sensitive drill press for this operation. The holes are then countersunk with a 1/8-inch tungsten carbide glass drill. Beaded tungsten electrodes 0.020 inch in diameter are then sealed into the countersink with a minimum distortion of the inner wall. During the sealing of the tungsten into the glass, an almost invisible film may condense on some of the cool inner surface of the glass tubing. This film changes the surface properties of the glass and causes the mercury pellet to subdivide as it passes over the area. Furthermore, the electrodes then have a heavy oxide coating which may prevent electrical contact with the mercury or at least offer a high resistance. The coatings are removed from the glass and the tips of the electrodes by buffing the inner surface of the tube with a pipe cleaner impregnated with a slurry of cerium oxide and water. After the tube containing the electrodes is sealed into the completed glass apparatus, any residual high-resistance coatings can be removed from the tungsten electrodes by electrolysis while the viscometer contains a dilute potassium hydroxide solution.

Precision. After a few passes to ensure equilibrium in the system, the reproducibility in timing successive descents of the pellet in a given direction in an experiment is about 1 part in 2000, occasionally being as good as 1 in 10,000 for several successive passes.

Internal consistency of the data indicates that the precision is better than 1%. Included in the results are some figures which, though not significant, are useful in estimating the rate of change of viscosity with temperature or pressure.

Materials. All gases were products of the Matheson Co. The nitrogen, prepurified grade of 99.9 mole % minimum purity, was passed at 1000 p.s.i. through silica gel and Ascarite columns and a dry ice trap before use. Methane, 99% minimum purity, was passed through a potassium hydroxide pellet column and a dry ice trap at 1000 p.s.i. The minimum purity of ethane was specified as 95%. Mass-spectrometric analysis at this laboratory indicated the following composition: ethane, 97.1; ethylene, 2.0; propylene, 0.9 mole %. The ethane was passed through a potassium hydroxide pellet column at 700 p.s.i. as was the propane at 200 p.s.i. The latter was of 99% minimum purity.

Experimental Results. Two or more separate runs—i.e., separate charges of a given gas, with cleaning of the viscometer between runs—were made on each of the four gases at the four isotherms. The data were plotted to permit interpolation to selected even pressures for each isotherm. These results are designated as η_{exp} in Table I.

COMPARISONS WITH PUBLISHED DATA

Comparing the numerical values of the coefficient of viscosity in Table I with published values is possible over only limited ranges of pressure and temperature.

Nitrogen. On nitrogen, Michels and Gibson (*16*) made absolute measurements to about 14,500 p.s.i. at 77°, 122°, and 167° F. by a transpiration method. These data appear to be the only reliable absolute determinations available over this range. The work of Boyd (*3*) covered the range from 86° to 158° F. and from 1000 to 2800 p.s.i.; however, the precision of the data was poor, the uncertainty being as much as 10% at the higher pressures. Lazarre and Vodar (*14*) made relative measurements at 77°, 122°, and 167° F. at pressures to 44,000 p.s.i. Their equipment was calibrated on benzene, ether, and nitrogen at atmospheric pressure.

Methods other than transpiration have also been used on nitrogen. Makita (*15*) used a rolling-ball viscometer to measure the viscosity up to 11,000 p.s.i. at several temperatures in the range 79° to 392° F. Viscosity *vs.* temperature plots of Makita's data show erratic behavior below 4000 p.s.i., but smooth curves are obtained at higher pressures. Iwasaki (*12*) reported the viscosity of nitrogen at 77°, 212°, and 302°F. to about 2800 p.s.i., as determined on an oscillating-disk viscometer.

An extrapolation by 3° F. of the authors' results permits comparison with those of Michels and Gibson, Lazarre and Vodar, and Makita, as shown in Figure 3. At low pressures the present results are lower than those of Michels and Gibson, whereas they are greater at pressures above about 1900 p.s.i. Of Lazarre and Vodar's two observed values, the one at lower pressure falls between the other observations, while the higher pressure point is close to that of Michels and Gibson. Makita's results generally agree with the latter at each of the three temperatures at which comparison is possible.

The authors' data, when compared to those of Michels and Gibson extrapolated from 167° to 175° F., are again lower at lower pressures, crossing over at about 1600 p.s.i. and continuing above the others. The curves are practically parallel above 3000 p.s.i., with a difference of 5 to 6 micropoises. Similarly, at 275° F. and 8000 p.s.i., the present results are greater than Makita's by nearly 6.5%.

Methane. The viscosity of methane has been determined in both the rolling-ball viscometer and the Rankine viscometer.

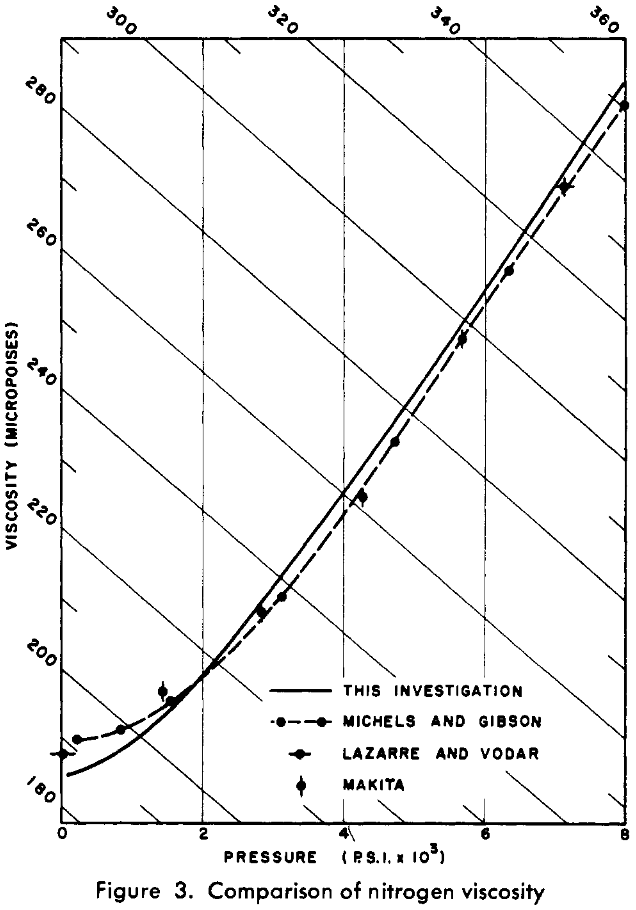

Figure 3. Comparison of nitrogen viscosity

Some of the data taken with the rolling-ball instrument (*2,22*) were under turbulent conditions, and, as a consequence, yield numerical values much higher than those obtained by the Rankine method (*4,7*). As shown in Figure 4, the authors' results are neither consistently higher nor lower than those obtained by earlier workers using the Rankine method.

Ethane. The viscosity of ethane has been measured using a rolling-ball viscometer (*23*) to 5000 p.s.i. up to 392° F. At 100 p.s.i. the results agree with those in Table I, but at higher pressures the results are as much as 20% lower.

Propane. Data on propane in portions of the region of interest have been obtained by rolling-ball (*2,20,23*), modified Rankine (*7*), and falling-needle (*25*) viscometers. The higher results of two of these investigations (*20,23*) are explained (*7*) as being due to turbulence. When the data of Bicher and Katz (*2*) are presented on plots of viscosity *vs.* temperature, each isobar in the range 1000 to 5000 p.s.i. has a pronounced upward curvature. Interpolations of the data by van Wijk and others (*25*), show a less pronounced upward curvature (6000 to 8000 p.s.i.). The data reported herein show a slight downward curvature (1000 to 8000 p.s.i.). Compared to these results, those of Bicher and Katz are 5 to 7% higher at 125° F., essentially identical at 155° to 160° F., lower by as much as 6% at 200° F., and again greater at 275° F. at the higher isobars. The data of van Wijk and others, at 125° F. are higher than the present results by less than 1%, are between 2.1 and 4.3% lower at 200° F., and again become equal at 260° to 280° F., depending on pressure.

The data of Comings, Mayling, and Egly (*7*) on propane cover only the range of 65 to 615 p.s.i. at 220° F. and smaller pressure ranges at lower temperatures. At the few points at which comparison can be made, the present results are higher by about 1 micropoise.

Table I. Coefficient of Viscosity

(Micropoises)

Pressure, P.S.I.	125° F.		175° F.		225° F.		275° F.	
	$\eta_{exp.}$	D, %[a]	$\eta_{exp.}$	D, %[a]	$\eta_{exp.}$	D, %[a]	$\eta_{exp.}$	D, %[a]
				Nitrogen[b]				
100	185.9	+ 0.86	200.1	+ 1.60	213.1	+ 1.69	223.8	+ 1.25
500	190.3	- 0.16	204.2	+ 0.44	216.9	+ 0.46	227.9	- 0.18
1000	198.0	- 1.67	210.5	- 0.81	222.5	- 0.72	233.0	- 1.37
2000	216.5	- 3.65	226.6	- 2.74	236.5	- 2.41	246.4	- 3.33
3000	238.1	- 4.41	245.4	- 3.50	253.2	- 3.32	261.5	- 4.24
4000	260.9	- 4.33	265.8	- 3.57	271.4	- 3.46	277.8	- 4.43
5000	283.5	- 3.52	286.2	- 3.04	289.3	- 2.87	294.7	- 4.11
6000	307.2	- 3.16	306.5	- 1.86	308.2	- 2.30	312.5	- 3.62
7000	330.6	- 2.72	327.4	- 1.50	328.0	- 2.13	330.4	- 3.15
8000	354.0	- 2.26	348.2	- 0.92	347.1	- 0.95	348.1	- 2.33
				Methane				
100	118.9	+ 0.25[b]	129.7	- 0.23[b]	138.2	- 0.43[b]	146.5	- 0.55[b]
500	123.3	- 0.65[b]	134.0	- 2.16[b]	142.7	- 3.22[b]	151.1	- 3.48[b]
1000	132.9	- 3.46[b]	141.1	- 4.54[b]	149.0	- 5.97[b]	157.0	- 6.94[b]
2000	159.3	+ 1.63	161.7	+ 3.46	165.8	+ 3.38	171.3	+ 2.86
3000	190.9	- 0.68	187.4	+ 0.59	187.2	+ 0.06	188.9	- 0.16
4000	221.0	- 0.32	214.3	- 0.28	211.4	- 1.61	208.5	- 1.53
5000	251.1	- 0.04	241.0	+ 0.25	234.9	- 1.66	228.7	- 1.84
6000	281.0	- 0.11	267.0	0.00	257.0	- 1.01	248.8	- 1.45
7000	308.1	+ 0.13	292.4	+ 0.24	278.7	- 0.25	268.2	- 0.63
8000	332.9	+ 0.80	315.8	+ 0.79	300.0	+ 0.40	287.0	0.00
				Ethane				
100	100	+ 3.30[b]	108	+ 2.22[b]	117	+ 1.62[b]	127	+ 2.20[b]
500	112	- 9.82	118	- 7.63	126	- 7.14	134	- 4.48
1000	228	+ 0.88	156	+ 3.21	151	- 0.66	150	0.00
2000	452	- 1.11	346	- 2.60	260	+ 1.54	225	+ 0.89
3000	547	+ 0.55	454	- 1.54	372	- 2.42	310	- 0.32
4000	620	+ 0.65	533	- 0.94	452	- 1.99	381	+ 0.52
5000	678	+ 1.33	598	- 0.67	519	- 2.12	440	+ 1.14
6000	730	+ 1.51	654	- 0.31	574	- 1.57	492	+ 1.83
7000	780	+ 1.15	704	- 0.43	622	- 1.61	537	+ 2.61
8000	822	+ 1.38	747	- 0.13	664	- 1.81	578	+ 2.94
				Propane				
100	90	+ 8.99[b]	97	+ 6.25[b]	103	+ 6.18[b]	110	+ 4.59[b]
500	730	+ 21.9	496	+ 32.0	126	+ 1.59	122	+ 3.28
1000	796	+ 29.9	630	+ 22.5	422	- 5.21	211	- 5.43
2000	912	+ 30.4	765	+ 19.2	608	- 3.95	462	+ 1.54
3000	1012	+ 31.4	868	+ 20.4	723	- 4.56	578	+ 0.69
4000	1106	+ 29.2	960	+ 20.3	815	- 4.66	669	+ 0.75
5000	1192	+ 28.2	1048	+ 19.3	897	- 4.57	738	- 0.41
6000	1279	+ 26.4	1128	+ 18.6	965	- 4.97	800	- 1.50
7000	1364	+ 24.8	1201	+ 17.9	1032	- 4.75	860	- 1.74
8000	1446	+ 23.1	1272	+ 17.2	1098	- 4.46	918	- 1.63

[a] $D = (\eta_{theor.} - \eta_{exp.})/\eta_{exp.}$; expressed as %.

[b] Calculated by Method A; all others by Method B.

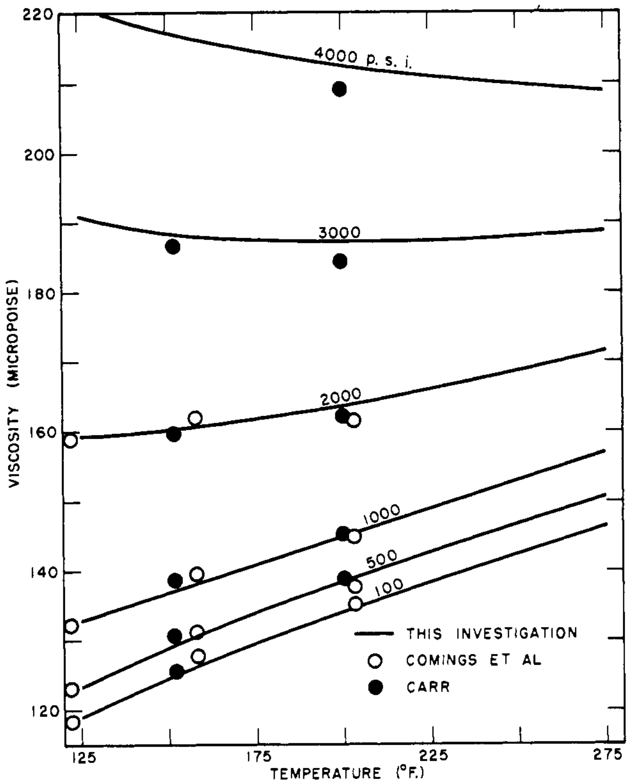

Figure 4. Comparison of methane viscosity

COMMENTS ON METHOD

The Rankine viscometer has not previously been used in measurements on fluids over the present range of temperature and pressure, and few data obtained by other methods are available for comparison; so the accuracy of the data is unknown. Comparisons show discrepancies for both nitrogen and propane. At lower pressures the viscosity reported here for nitrogen is lower than that obtained at three other laboratories, although it agrees well with Iwasaki's results. The observed rise in viscosity with increasing pressure is greater than previously reported. However, it may be pertinent that two laboratories which have recently reported on the viscosity of nitrogen at room temperature by an oscillating disk (*13*) and by a transpiration method (*8*) found a slope of viscosity *vs.* pressure greater than that obtained by Michels and Gibson.

The differences in results on propane obtained here and those obtained on rolling-ball or falling-needle viscometers are not readily explained. One factor may be turbulence, which can occur in such viscometers at even moderate values of the Reynolds number. Errors can occur at higher temperatures and pressures unless the relative thermal expansion of the cylinder and of the falling body and the pressure dilation of the cylinder are known precisely. On the other hand, the Rankine viscometer may be suspect. If the mercury pellet should tend to descend inside a tube of fluid, the pellet would be lengthened and the quantity of fluid being driven through the capillary would be decreased, both factors tending to give a low value of viscosity. Deviations would then be expected to increase with increasing fluid density —i.e., at lower temperatures for a given pressure, or at higher pressures for a given temperature. This trend is not observed for these results relative to published data.

As a qualitative check on the suggested tendency for the mercury to bypass high-density fluids, the viscosity was determined at room temperature for water and for heptane. The instrument could not be thermostated below about 110° F., so runs were made at a fluctuating ambient temperature of 76.5° ± 0.7° F. For both liquids the plot of sin ω *vs.* $1/t$ was very nearly linear. The viscosity of water was found to be 9015 micropoises, which is approximately 0.28% higher than the value interpolated from tables (*11*), as corrected (*24*). The viscosity of a heptane sample as determined in this viscometer was 2.37% lower than the value obtained with a certified Ostwald viscometer.

The differences between the present and previous results on nitrogen and propane cannot be explained solely by assuming that dense fluids per se cause low experimental values on the Rankine viscometer. If these results are in error, another or supplementary explanation is required.

CORRESPONDING-STATES CORRELATION

Several correlations of viscosity based on the principle of corresponding states have been published. These have generally been prepared from viscosity data from several sources of varying reliability. The viscosity of a fluid at its critical state is seldom known, so use of the reduced viscosity η/η_c is not a practical correlating factor. Instead, the charts usually show the value of the ratio of the viscosity to its value at the same temperature but at atmospheric pressure η/η_1 as functions of reduced temperature T/T_c and reduced pressure p/p_c. Such chart has been prepared from the data reported herein, covering the following ranges of variables: η/η_1, 1 to 16; T/T_c, 0.9 to 3.2; p/p_c, 0.4 to 15. It is in general agreement with published charts (*4,5,7,12,15*) except that where comparisons are possible, this chart gives values of η/η_1 that are generally but not consistently higher than are given elsewhere. Detailed comparison on a small-scale figure is not feasible; upon request to the authors, a 9 × 11-inch copy of the chart on full grid will be mailed.

DENSE-GAS THEORY CORRELATION

The results can be correlated on the basis of the Enskog dense-gas theory, many aspects of which have been discussed by Hirschfelder, Curtiss, and Bird (*10*).

Consideration of the collisions between molecules in a dense gas has led to an equation for the relative viscosity at elevated pressure:

$$\eta/\eta_1 = \frac{b_0}{\bar{V}}\left[\frac{1}{y} + 0.8 + 0.761y\right] \qquad (2)$$

Table II. Co-volume and Molecular Diameter

Temp., °F.	b_0, Cu. Ft./Lb.-mole Method A	 Method B	σ, A.[a]
	Nitrogen		
125	0.808	. . .	3.42
175	0.797	. . .	3.40
225	0.788	. . .	3.39
275	0.779	. . .	3.39
	Methane		
125	0.940	1.037	3.11
175	0.884	1.003	3.14
225	0.843	0.971	3.12
275	0.814	0.944	3.10
	Ethane		
125	3.050	2.185	3.94
175	2.600	2.084	3.92
225	2.275	1.931	3.81
275	2.039	1.794	3.75
	Propane		
125	6.28	4.76	6.48
175	5.06	3.94	5.55
225	4.21	3.31	4.78
275	3.52	2.88	4.05

[a] For nitrogen, σ from Equation 3. For hydrocarbons, σ from Equation 7.

where y is a thermodynamic function of the substance and where the co-volume of the molecules of diameter σ is given by

$$b_0 = \frac{2}{3}\pi\tilde{N}\sigma^3 \tag{3}$$

For real gases y is calculated from P-V-T data by use of the relation

$$y = \frac{\tilde{V}}{R}\left(\frac{\partial p}{\partial T}\right)_{\rho} - 1 \tag{4}$$

If reliable P-V-T data are available to be used directly, or preferably in the form of an equation of state to eliminate significant irregularities in the partial derivative caused by small experimental errors, it is possible to calculate η/η_1 by Equation 2 as soon as b_0 is available. The equation of state proposed by Benedict, Webb, and Rubin (*1*) was used for calculation of y. The eight sets of constants for the equation were assigned the values derived by Opfell, Schlinger, and Sage (*17*) for the hydrocarbons, while the values reported in Table 4.2-4 of (*10*) were used for nitrogen. [The value of C_0 for ethane was corrected (*19*) to 3334.26×10^6.]

Two approaches to the estimation of b_0 were used.

Method A. If η_0 is to be the low-pressure limit of η, it is necessary (*10*) that $\lim_{\rho \to 0} yV = b_0$. Plots of yV *vs.* ρ were extrapolated to zero density to obtain b_0 for each gas at the four temperatures.

Method B. It can be shown (*10*) that a plot of η/ρ as a function of y or of ρ exhibits a minimum if the range of experimental conditions is sufficiently great. The minimum occurs at $y = 1.146$, at which point

$$(\eta/\rho)_{\min} \times \frac{M}{\eta_0 b_0} = 2.545 \tag{5}$$

Values of b_0 calculated by these two methods are included in Table II.

Michels and Gibson (*16*) could use Method B on nitrogen because of their ranges of pressure and temperature. At 125° F. and above, the minimum for nitrogen occurs at pressures in excess of 8000 p.s.i. Because of this limited pressure range, only Method A could be used for nitrogen. The viscosity so calculated was less than the observed value at elevated pressures, with the greatest difference occurring in the mid-range of pressure.

For the hydrocarbons, Method A gave reasonably good predictions only at the lowest pressures, whereas Method B was useful at higher pressures. Except where noted, the calculated viscosities used in preparing Table I were obtained by Method B. The percentage difference reported is by the method which shows the lesser deviation from the observed value.

The values for the hydrocarbons are in agreement at higher pressures with prediction of viscosity by the Enskog dense-gas theory, based on the minimum in isothermal plots of η/ρ *vs.* ρ. At pressures of 3000 p.s.i. and greater, deviations in excess of 3% were observed only for propane at the three lowest temperatures. The critical temperature of propane is about 206° F. Whereas Method A was unsatisfactory for the hydrocarbons, it predicted the viscosity for nitrogen, which has a low critical temperature (−233° F.), with deviations of not over 4.4% from the observed values.

These data further evidence the inherent validity of the dense-gas theory in predictions of the viscosity of gases at elevated pressures when the temperature is somewhat above the critical temperature.

The Enskog theory also permits an estimation of the diameter of the molecules, considered as smooth rigid elastic spheres, from the minimum value of η/ρ. Equations 3 and 5 and the following equation given by Chapman and Cowling (*6*)

$$\eta = 0.1792(kmT)^{1/2}/\sigma^2 \tag{6}$$

can be used to arrive at an expression (*16*) for the diameter

$$\sigma = \frac{1}{0.955}(M/RT)^{1/2}(\eta/\rho)_{\min} \tag{7}$$

Values of σ for the hydrocarbons calculated by Equation 7 are included in Table II. For nitrogen, σ was calculated from Equation 3, with the value of b_0 determined by Method A. Because of this difference in method of calculation, the molecular diameter of nitrogen is not directly comparable with that of the hydrocarbons. Except for the unexplained value of σ for methane at 125° F., the effective diameter decreases with rising temperature. The extent to which σ varies smoothly with temperature is perhaps an indication of the internal consistency of the basic data.

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