Part I

Viscosity of Helium, Neon, and Nitrogen in the Dense Gaseous Region

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Viscosity measurements have been made for helium, neon, and nitrogen at 100°, 150°, and 200° C. and pressures up to 820 atm. using a transpiration-type viscometer. These viscosities are tabulated and are correlated with pressure to produce continuous relationships for each temperature. Values from these relationships are in good agreement with corresponding viscosities available in the literature. The residual viscosity, $\mu - \mu^*$, resulting from the values for each gas, has been related to its corresponding reduced density.

TO EXPAND the background concerning the viscosity behavior of substances in the dense gaseous region, it becomes necessary to obtain additional experimental information at elevated pressures. Viscosity measurements at elevated pressures are reported in the literature for helium by Flynn *et al.* (*6*), Kestin and Leidenfrost (*11*), Luker and Johnson (*13*), and Ross and Brown (*22*), but only by Flynn and coworkers (*6*) for neon. Aside from the work of Ross and Brown (*22*), who report viscosity measurements for helium up to 25° C. and pressures as high as 10,000 p.s.i.a. no other investigator has made measurements at these high pressures. For neon, the work of Flynn *et al.* (*6*) is confined to pressures below 2276 p.s.i.a. and temperatures below 100° C. Consequently, it became appropriate to obtain additional viscosity measurements for helium and neon at higher temperatures and pressures beyond 10,000 p.s.i.a. In addition, viscosity values for nitrogen at these conditions provide information on the capability of the equipment to produce reliable values. Since the effect of pressure on the viscosity of nitrogen is well established by a number of investigators (*9*, *11*, *17*, *22*), this gas has been used as a standard to test the reliability of the transpiration-type viscometer (*25*).

DETERMINATION OF VISCOSITIES AT HIGH PRESSURES

The experimental determination of viscosities at high pressures for gaseous helium, neon, and nitrogen was conducted in the unit designed and constructed by Shimotake and Thodos (*25*). This experimental unit was of the transpiration type and was operated under unsteady state conditions. In their work, this unit was calibrated with nitrogen and was then used to obtain the viscosity of gaseous ammonia for pressures up to 5000 p.s.i.a.

In the present study, two major changes were incorporated into this unit. To make this unit an absolute measuring device, the diameter and length of the capillary, as well as its other basic dimensions, were established directly. The diameter of the capillary was measured using three independent methods: plug gages, optical measurement, and mercury displacement.

Plug Gages. Representative stainless steel tubing (seamless-316) was cut into several small pieces with a circular carborundum saw. Carefully prepared plug gages were then used to determine the inside diameter of the tubing by inserting different sizes of these gages until one was found which would just not enter the capillary opening. By using this approach, a very close approximation of the inside diameter was possible. The average of several such measurements over a large number of pieces established the average inside diameter of the capillary tubing.

Optical Measurement. A cross-section of the tubing was mounted on bakelite and the magnification obtained from it with a microscope was projected onto a screen on which measurements were made.

Mercury Displacement. Mercury was forced into the capillary tubing until all of the air was displaced. The capillary completely filled with mercury was then weighed and the weight of the mercury was determined by difference. From the density of the mercury and the tube length, the average inside diameter was established.

These three methods produced average inside diameters that differed only by ±0.0005 cm. The average capillary tube diameter was 0.0248 cm. The basic capillary tube dimensions were as follows: inside radius, 0.01238 cm.; outside diameter, 0.1473 cm.; length, 317.9 cm.

To eliminate difficulties encountered at high pressures with the soapstone seals of the electrodes used by Shimotake and Thodos (*25*), these electrical probes were redesigned, and glass was used for electrical insulation and for effecting a pressure seal. This was accomplished by first surrounding a Kovar electrode with a glass liner, which was in turn surrounded by a metallic Kovar sleeve. One end of the Kovar sleeve was fused to the electrode with a glass bead to produce a hermetic seal between the Kovar sleeve and the electrode which extended beyond the fused glass seal. The other end of the Kovar sleeve was silver-soldered to a standard stainless steel tubing provided with a standard high pressure fitting. This arrangement permitted excellent electrical insulation without gas leakage for pressures as high as 15,000 p.s.i. and temperatures limited only by the melting point of the glass seal.

In the present study, when the viscometer was held in the vertical position, the tips of the electrodes were approximately on the same horizontal plane, and each was above the mercury meniscus present in each leg of the U-tube.

A typical run consisted of introducing a gas sample into the system and the time required for the mercury menisci in the manometer to traverse a prescribed distance, $h_1 - h_2$, was measured.

The experimental procedure in this study is the same as that outlined by Shimotake and Thodos (*25*) except for the means of operating the U-tube. In the present study, the manometer was tilted approximately 15 degrees from the vertical axis with the bypass valve open. The bypass valve then was closed and the U-tube was tilted to the same angle in the opposite side of the vertical. This procedure was repeated for the same temperature and different pressures ranging up to 12,000 p.s.i.g. The temperatures investigated were 100°, 150°, and 200° C. From these measurements, the viscosity was calculated using the approach outlined by Shimotake and Thodos (*25*), who developed, for this unsteady state flow, the relationship:

$$\theta = \frac{B}{2}\ln\frac{h_1}{h_2} + \frac{B}{2}\ \ln\frac{\left[(B^2+4Ch_2)^{1/2}+B\right]\left[(B^2+4Ch_1)^{1/2}-B\right]}{\left[(B^2+4Ch_2)^{1/2}-B\right]\left[(B^2+4Ch_1)^{1/2}+B\right]} + \left[(B^2+4Ch_1)^{1/2}-(B^2+4Ch_2)^{1/2}\right] \quad (1)$$

where $B = 4R^2L\mu/g(\rho_m-\rho_f)r^4$ and $C = mR^4\rho_f/4g(\rho_m-\rho_f)r^4$.

Pressure is expected to increase the length and radius of the capillary tubing. Of these effects, the change in radius is more significant. However, the relationship recommended by Lenoir and Comings (*12*) produced a correction for the radius which was negligibly small for 12,000 p.s.i.g., the maximum pressure encountered in this study. Hence, the radius was assumed to be independent of pressure. Similarly, the effect of temperature on the dimensions of the capillary indicated that this contribution was also insignificant for the maximum temperature of 200° C. Consequently, the dimensions of the viscometer were assumed to be independent of temperature and pressure within the range of the experimental conditions.

EXPERIMENTAL RESULTS

The nitrogen used in this study, obtained from The Matheson Company, was claimed to be 99.996% pure, while the neon and helium, obtained from the Linde Company, were each claimed to be 99.99% pure. The densities required by Equation 1 for the calculation of viscosity were obtained from literature sources. In this study, the mercury head differences in the U-tube, h_1 and h_2, depended on both temperature and pressure and were independent of the nature of the gas. These values of h_1 and h_2 and the duration of experimental runs are presented elsewhere (*21*) for temperatures of 100°, 150°, and 200° C. and pressures up to 12,000 p.s.i. The viscosities resulting from these measurements are listed for each temperature in Table I, and are plotted against pressure in Figures 1, 2, and 3 for helium, neon, and nitrogen, respectively. In these figures, the viscosities reported by other investigators are also included for comparative purposes.

In Figure 1, the viscosity measurements of helium at 100°, 150°, and 200° C. extend up to pressures of 12,035 p.s.i.a. The data of Ross and Brown (*22*) are not included in this figure, since the highest temperature reported by them is 25° C. which is below the lowest temperature of this study. The viscosities reported by Flynn and coworkers at 100° C. show a negative maximum deviation of 0.76% at their highest pressure of 2580 p.s.i.a. On the other hand, the viscosities reported by Kestin and Leidenfrost (*11*) have been interpolated to compare them with the values of this study and show a maximum positive deviation of 0.56% at 100° C. and 1015 p.s.i.a. The close agreement between experimental and literature values infers that the present measurements must be reliable.

The viscosities for neon were established in this investigation for temperatures of 100°, 150°, and 200° C. and pressures up to 12,045 p.s.i.a. These measurements produced

Table I. Experimental Data and Viscosity Values for Helium, Neon, and Nitrogen at High Pressures

Helium		Neon		Nitrogen	
P, P.S.I.A.	μ, Centipoises × 10⁵	*P*, P.S.I.A.	μ, Centipoises × 10⁵	*P*., P.S.I.A.	μ, Centipoises × 10⁵
100° C.					
1,045	2299	1,025	3689	1,035	2162
2,035	2311	2,045	3725	2,025	2283
3,035	2346	3,045	3771	3,030	2459
4,035	2359	4,035	3808	3,935	2603
5,025	2363	5,055	3854	5,045	2791
6,025	2378	6,045	3924	6,025	2935
7,035	2389	7,055	3987	7,030	3159
8,035	2394	8,035	4038	8,025	3362
9,035	2402	9,035	4100	9,015	3543
10,035	2409	10,035	4158	10,065	3740
11,025	2417	11,045	4214		
12,035	2423	12,035	4267		
150° C.					
1,035	2514	1,040	3993	1,060	2373
2,035	2519	2,035	4022	2,045	2459
3,035	2548	3,035	4054	3,035	2554
4,035	2552	4,045	4084	4,035	2715
5,025	2571	5,025	4111	5,050	2861
6,035	2580	6,035	4151	6,055	2985
7,025	2590	7.045	4202	7,035	3168
8,025	2594	8,035	4251	8,020	3310
9,035	2602	9,035	4306	9,035	3443
10,035	2614	10,025	4372	10,010	3581
11,045	2621	11,035	4396		
12,035	2623	12,045	4438		
200° C.					
1,035	2712	1,045	4255	1,035	2541
2,035	2733	2,040	4286	2,035	2600
3,025	2758	3,035	4310	3,035	2718
4,035	2766	4,035	4335	4,035	2830
5,025	2772	5,025	4360	5,035	2906
6,035	2782	6,035	4398	6,045	3046
7,035	2783	7,035	4444	7,045	3100
8,035	2796	8,045	4485	8,050	3298
9,035	2797	9,035	4546	9,040	3433
10,035	2795	10,015	4582	10,035	3557
11,035	2794	11,045	4614		
12,035	2796	12,035	4642		

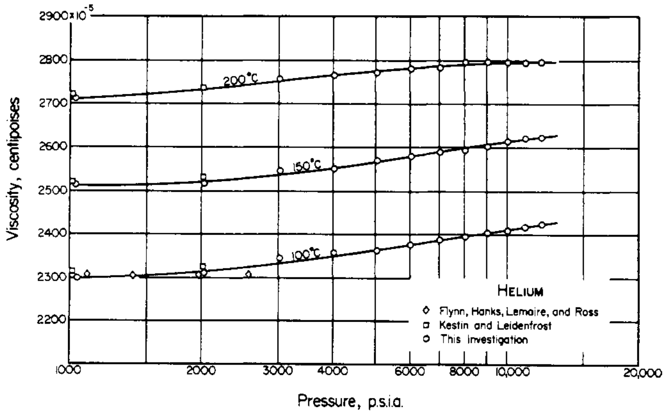

Figure 1. Effect of pressure on the viscosity of helium

with pressure the smooth relationships presented in Figure 2. In this figure are also presented the experimental measurements of Flynn *et al.* (*6*) available at 100° C. Their results lie somewhat above the 100° C. isotherm obtained from the data of this study. The maximum deviation between the values of Flynn and coworkers and the corresponding value from this isotherm is 0.53%.

Figure 3 presents the viscosities established for nitrogen at 100°, 150°, and 200° C. These isotherms, when plotted as viscosity *vs.* pressure, intersect at approximately 7000 p.s.i. In order to compare the results of this study with values available in the literature, each isotherm is presented separately. Five references (*2, 6, 7, 9, 23*) were used to compare these experimental viscosity measurements. From Figure 3, it is apparent that the values of this investigation are in good agreement with the average of the values reported by the other investigators. This agreement adds credence to the dependability of the experimental equipment to produce reliable values.

The viscosity values for helium, neon, and nitrogen determined in this study and those already presented in the literature were used to obtain residual viscosities, $\mu - \mu^*$, which have been correlated against their corresponding reduced densities. The atmospheric viscosity values, μ^*, reported by Shimotake and Thodos (*24*) for helium and neon and the corresponding values for nitrogen reported by Brebach and Thodos (*4*) were used. The resulting residual viscosity-density correlation for helium is presented in Figure 4. The densities of helium were obtained from the *PVT* measurements of Michels and Wouters (*19*) and Wiebe, Gaddy, and Heins (*26*). For helium, the experimental critical density, $\rho_c = 0.0693$ gram per cc., of Mathias, Crommelin, Kamerlingh Onnes, and Swallow (*16*) was used to reduce the densities corresponding to the experimental conditions. This correlation presents relationships that are temperature-dependent for the 150° and 200° C. viscosity values of this study. For the viscosity values at 100° C., negative residual viscosities resulted and these have not been included in Figure 4. In addition, the values of Flynn *et al.* (*6*) and Kestin and Leidenfrost (*11*) are also included in this figure. This high degree of irregularity may be explained partly by the fact that the viscosity of helium has a weak dependence on pressure as shown in Figure 1. Therefore, the corresponding residual quantities become extremely sensitive to such small fluctuations.

Figure 5 presents the residual viscosity-density behavior for neon. For this substance at 100° and 150° C., the experimental *PVT* measurements of Michels, Wassenaar, and Louwerse (*18*) were used while densities at 200° C. were taken from the reduced density correlation for neon presented by Hamrin and Thodos (*8*). For neon, the critical density, ρ_c = 0.484 gram per cc., obtained by Mathias, Crommelin, and Kamerlingh Onnes (*14*), was used. The isothermal relationships for neon exhibit a weaker tempera-

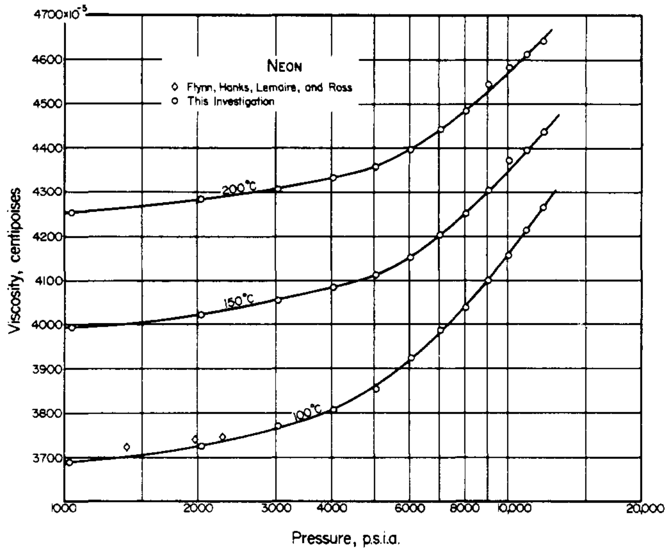

Figure 2. Effect of pressure on the viscosity of neon

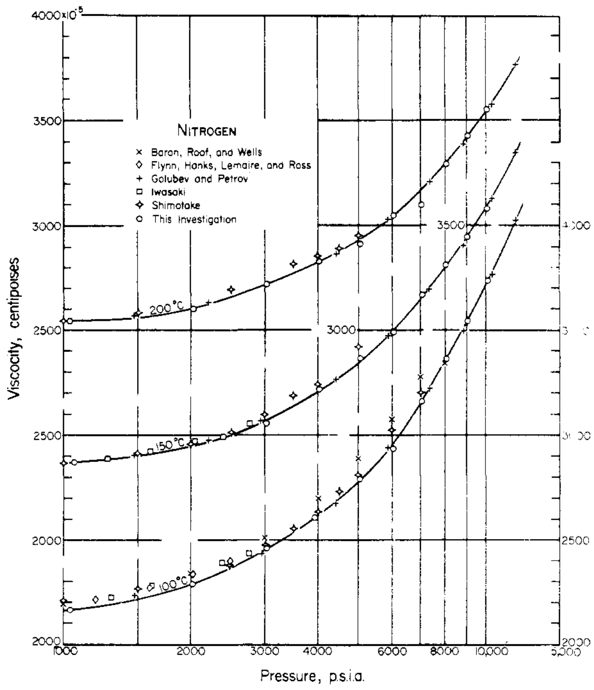

Figure 3. Effect of pressure on the viscosity of nitrogen

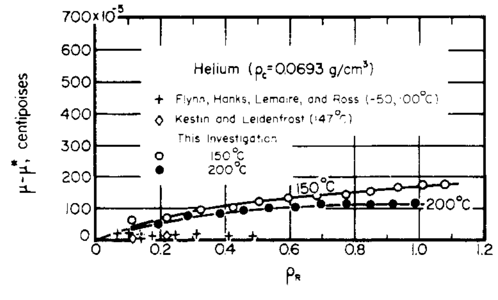

Figure 4. Residual viscosity-density relationships for helium

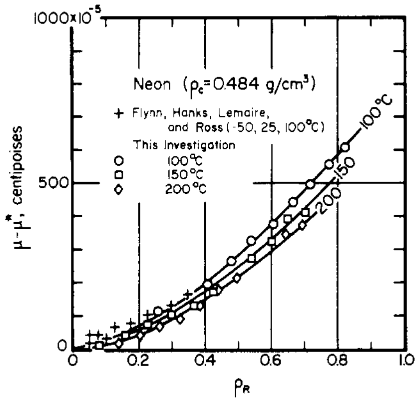

Figure 5. Residual viscosity-density relationships for neon

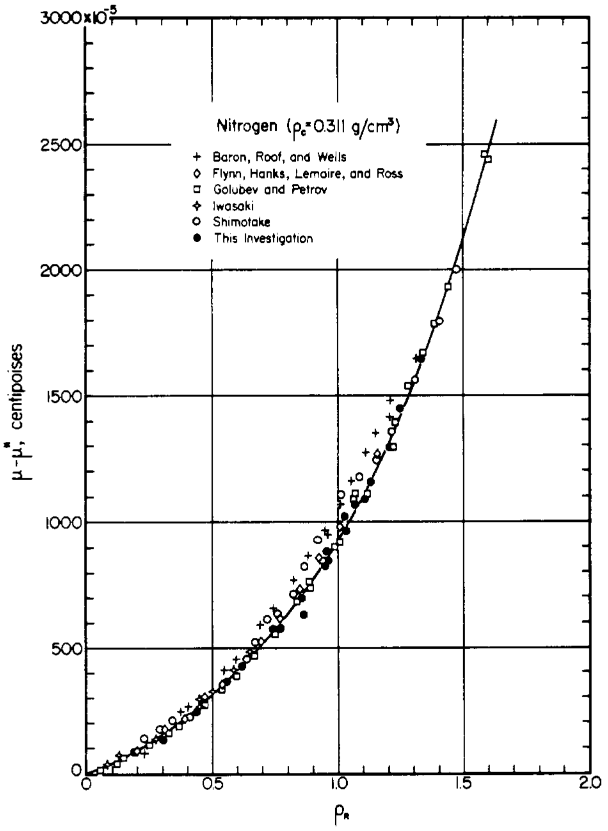

Figure 6. Residual viscosity-density relationship for nitrogen

ture dependence than was the case for helium. This behavior is consistent with the conclusions of Eakin and coworkers (*5*) that at low densities, the residual viscosity-density relationship is a weak function of temperature. For nitrogen this temperature dependence is not apparent and the results of this study and those of others presented in the literature produce in Figure 6 a single continuous relationship. The necessary density values for nitrogen at 100° and 150° C. were obtained from the *PVT* data of Michels, Wouters, and de Boer (*20*), while values at 200° C. were obtained from the measurements of Bartlett, Cupples, and Tremearne (*3*) and Amagat (*1*). The experimental critical density for nitrogen, ρ_c = 0.311 gram per cc., reported by Mathias, Kamerlingh Onnes, and Crommelin (*15*) was used to produce reduced densities for this substance. The anomalous behavior of neon and particularly that of helium needs further consideration, but may be qualitatively explained by their excessive quantum deviations which manifest to a behavior that is not consistent with ordinary substances (*10*).

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NOMENCLATURE

B = constant for Equation 1, $4R^2 L\mu/g(\rho_m - \rho_f)r^4$
C = constant for Equation 1, $mR^4\rho_f/4g(\rho_m - \rho_f)r^4$
g = acceleration constant, 980 cm. per second^2
h_1, h_2 = initial and final mercury head difference, respectively, cm.
L = length of capillary, cm.
m = correction coefficient for kinetic energy term
r = radius of capillary, cm.
R = radius of U-tube, cm.

Greek Letters

θ = time, seconds
μ = absolute viscosity, cp.
μ^* = viscosity at normal pressure, cp.
ρ = density, grams per cc.
ρ_c = critical density, grams per cc.
ρ_f = density of fluid, grams per cc.
ρ_m = density of mercury, grams per cc.
ρ_R = reduced density, ρ/ρ_c

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