Viscosity: Reduced-State Correlation for the Inert Gases

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A reduced-state viscosity correlation has been constructed from the available data of the inert gases. For the development of this correlation, the fragmentary experimental data for argon were utilized along the lines proposed for thermal conductivities by Owens and Thodos (21) in order to determine the effect of pressure on viscosity. In addition, the only available low-pressure viscosity data for neon and helium have been incorporated in this correlation to produce for the first time the effect of subatmospheric pressures. This correlation covers the range of pressures included between $P_R = 40$ and $P_R = 0.015 \times 10^{-4}$ and extends up to temperatures of $T_R = 100$. It has been found that the effect of subatmospheric pressures on viscosity does not become significant above pressures of 1 mm. of mercury. However, at lower pressures, viscosity is found to decrease rapidly, particularly in the regions below absolute pressures of 0.01 mm. of mercury.

Viscosities calculated with the reduced state correlation produce an average over-all deviation of 0.93% for neon, argon, krypton, and xenon. In these comparisons the available viscosity data for the gaseous and liquid states of these substances have been included. Deviations of the same order of magnitude are produced for helium in the gaseous state; however, these deviations become excessive for viscosities of helium in the liquid state.

The application of the final reduced state correlation has been extended to a number of diatomic and polyatomic gases and found to apply well to the diatomic gases only.

The current advances in the field of transport properties by Hirschfelder, Curtiss, and Bird (9) through the use of quantum and statistical mechanic principles, in conjunction with the recent developments on thermal conductivities by Owens and Thodos (21), make possible the extension of studies for the establishment of reduced-state viscosity correlations. The thermal conductivity studies of Owens and Thodos were restricted to the inert gas family, to obtain a background representative of substances possessing the simplest molecular constitution. In their studies the effect of pressure on thermal conductivity was accounted for from the single continuous correlation resulting when the residual thermal conductivity $k - k^*$ was correlated with ρ, the corresponding density of the substance. This relationship proved unique in defining thermal conductivities for the gaseous and liquid states.

In 1943 Uyehara and Watson (30) developed a generalized reduced-state correlation for which they claimed expected deviations on viscosity of less than 20%. They used the available viscosity information for a large number of substances in order to develop their compromising generalized reduced-state correlation. Despite the fact that the Uyehara-Watson correlation has proved quite valuable in its present form, particularly for engineering calculations, the recent advances of concepts on transport properties make necessary an examination of this field to find whether viscosity can be treated along the same lines as thermal conductivity for the development of similar correlations. In this study, this objective has been achieved through the utilization of the available high-pressure viscosity data for argon. These permitted the establishment of the high-pressure and liquid regions of the reduced-state correlation for the inert gases. In addition, the available subatmospheric viscosity data for neon and helium made possible for the first time the extension of this reduced-state correlation in the low-pressure region.

VISCOSITY AT MODERATE PRESSURES

Atmospheric-pressure viscosity data available in the literature for the inert gases have been correlated with reduced temperature to produce the relationships presented in Figure 1. The critical temperatures of the inert gases (16) used to produce the reduced temperatures and literature sources of the viscosity data are presented in Table 1. The curved relationships of Figure 1 are essentially parallel to each other, with the exception of helium. This behavior strongly suggests that the theorem of corresponding states should apply alike for neon, argon, krypton, and xenon. The different behavior for helium is expected and is consistent with deviations found in the correlations of compressibility factors (20) and thermal conductivities (21).

By an approach comparable to that utilized for thermal conductivities (21), the viscosity ratio $\mu^*/\mu_{T_c}^*$ was correlated with the reduced temperature T_R to produce the single relationship presented in Figure 2. The value $\mu_{T_c}^*$ represents the viscosity at atmospheric pressure resulting from Figure 1 at the critical temperature $T_R = 1.0$. In order to bring the viscosity data of helium in line with the relationship of Figure 2, it becomes necessary to assign to it the pseudocritical temperatures $T_c' = 5.3 + 2.03 = 7.33$°K. for $T > 10$°K. and $T_c' = 5.3 - 0.54 = 4.76$°K. for temperatures below 10°K.

The relationship of Figure 2 is unique and applies to all the inert gases for moderate absolute pressures ranging from 1 mm. of mercury up to pressures well above 10 atm. In addition, this relationship is found to be linear for $T_R \leq 1.0$ and $T_R \geq 3.5$. Therefore, the viscosity ratio for these regions can be expressed in equation form as follows:

$$\frac{\mu^*}{\mu_{T_c}^*} = T_R^{0.917} \qquad \text{for } T_R \leq 1.0 \quad (1)$$

$$\frac{\mu^*}{\mu_{T_c}^*} = 1.276 T_R^{0.645} \quad \text{for } T_R \geq 3.5 \quad (2)$$

For reduced temperatures, $1 \leq T_R \leq 3.5$, the viscosity ratios must be obtained directly from Figure 2.

The recent theoretical developments of

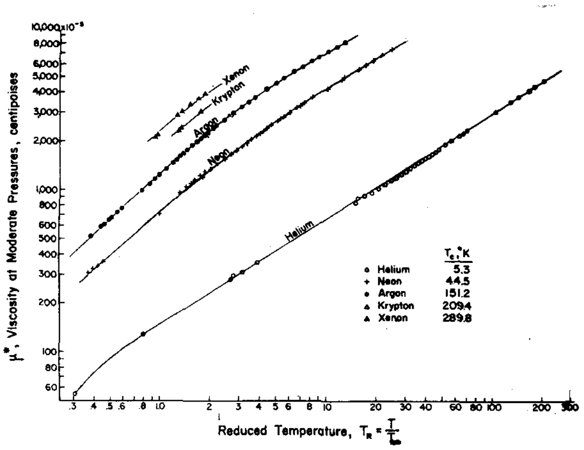


Fig. 1. Relationships of viscosity at moderate pressures and reduced temperature from literature data for the inert gases.

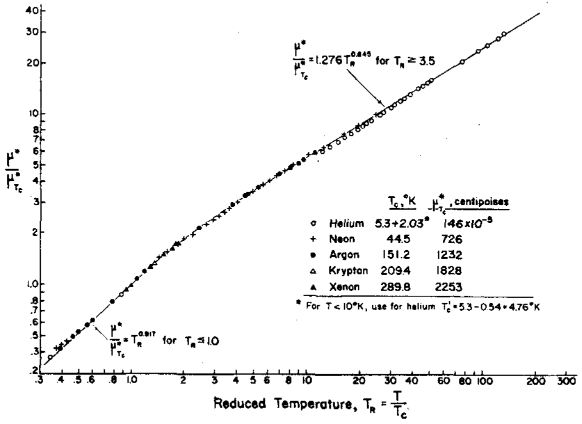


Fig. 2. Relationship of viscosity ratio and reduced temperature from the literature data for the inert gases at moderate pressures.

Hirschfelder, Curtiss, and Bird (*9*) in the field of transport properties utilize the Lennard-Jones potential parameters to define coefficients of thermal conductivity, viscosity, and self-diffusion. In this connection they propose for the first approximation of viscosity at moderate pressures,

$$[\mu]_1 = 2.6693 \times 10^{-5} \frac{\sqrt{MT}}{\sigma^2 \Omega^{(2,2)*}[T_N]} \quad (3)$$

Values of the constants σ and ϵ/κ for a number of substances are available (*9*). With these constants and the tabulated values of $\Omega^{(2,2)*}[T_N]$, the generalized collision integral function (*9*), the viscosity for the first approximation can be evaluated with Equation (3). For the kth approximation, the viscosity coefficient is given by

$$[\mu]_k = f_\mu^{(k)} [\mu]_1 \quad (4)$$

Values through the third approximation $f_\mu^{(3)}$ are presented by Hirschfelder, Curtiss, and Bird (*9*). Therefore, with Equations (3) and (4), the viscosity of gases for the third approximation $[\mu]_3$ can be calculated for any temperature and for the moderate pressures ranging from 1 mm. of mercury to 10 atm. The values of σ and ϵ/κ presented by Hirschfelder, Curtiss, and Bird (*9*) and appearing in Table 1 have been used with Equations (3) and (4) to produce the calculated viscosities μ^*. The viscosity at the critical temperature $\mu_{T_c}{}^*$ has been specifically calculated and used to produce the ratios $\mu^*/\mu_{T_c}{}^*$. These ratios, when correlated with reduced temperature, produced the relationship presented in Figure 3. The calculated values $\mu_{T_c}{}^*$ used to define these ratios are also presented in Table 1. The relationship of Figure 3 is similar to that presented in Figure 2 and also shows the existence of linear relationships for reduced temperatures $T_R \leq 1.0$ and $T_R \geq 3.5$. For these regions the viscosity ratio can be defined in equation form as

$$\frac{\mu^*}{\mu_{T_c}{}^*} = T_R \qquad \text{for } T_R \leq 1.0 \quad (5)$$

$$\frac{\mu^*}{\mu_{T_c}{}^*} = 1.276 T_R{}^{0.645} \text{ for } T_R \geq 3.5 \quad (6)$$

The striking resemblance between Figures 2 and 3 is significant and proves helpful

TABLE 1. FUNDAMENTAL CONSTANTS FOR THE INERT GASES AND LITERATURE SOURCES OF VISCOSITY DATA AT MODERATE PRESSURES

				Lennard-Jones potential parameters		$\mu_{T_c}{}^*$, centipoises			
	Molecular wt.	T_c, °K.	P_c, atm.	σ, Å.	ϵ/κ, °K.	Experimental, Figure 1	Calculated, Equation (3)	μ_c, centipoises	Literature sources
Helium	4.00	5.3	2.26	2.576	10.22	146×10^{-5}	113×10^{-5}	272×10^{-5}	*6, 8, 10, 12, 15, 22, 28, 29, 33*
Neon	20.18	44.5	26.9	2.789	35.7	726	723	1681	*4, 12, 15, 22, 27, 28, 33*
Argon	39.94	151.2	48.0	3.418	124	1232	1237	2852	*3, 11, 14, 15, 17, 22, 23, 24, 28, 31, 33*
Krypton	83.8	209.4	54.3	3.61	190	1828	1790	4232	*19, 22*
Xenon	131.3	289.8	58.0	4.055	229	2253	2238	5216	*19, 22, 26*

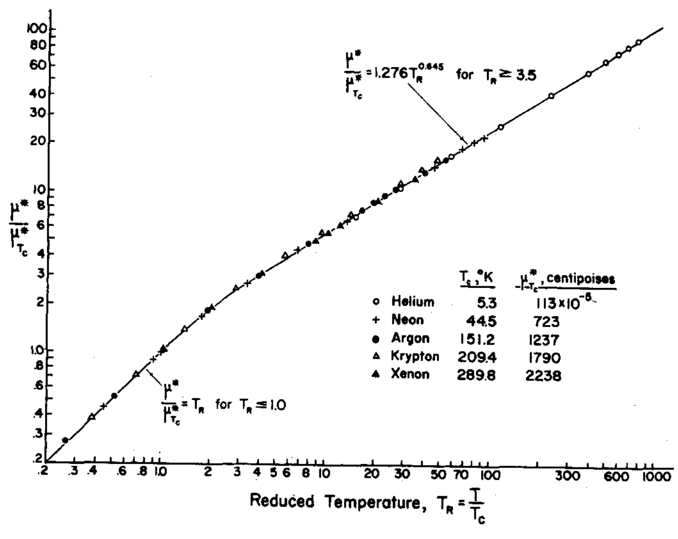


Fig. 3. Relationship of viscosity ratio and reduced temperature at moderate pressures (calculated with the Hirschfelder, Curtiss, and Bird equation).

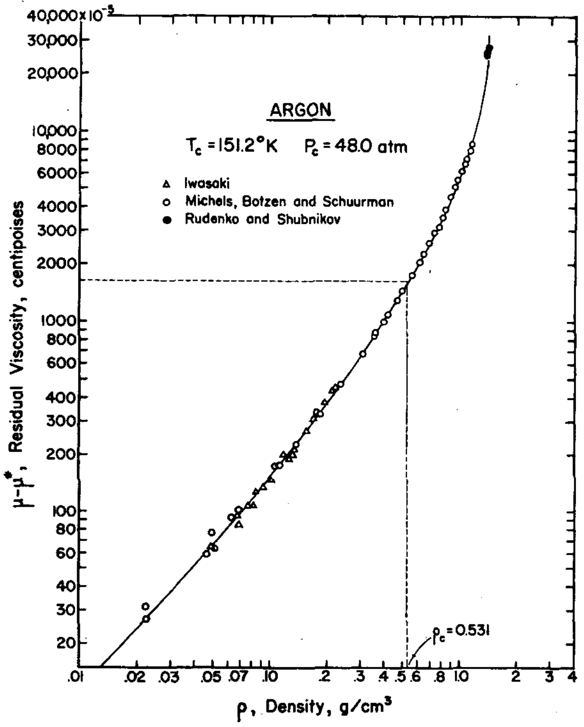


Fig. 4. Residual-viscosity–density relationship for argon in the gaseous and liquid states.

in extrapolating the relationship produced from the experimental values into the high-temperature region. Furthermore, these relationships are unique for the establishment of viscosities at any temperature, if limited to moderate pressures of less than 10 atm. For the treatment of viscosity at high pressures, the approach utilized for the thermal conductivity studies of the inert gases (*21*) has been applied to this study.

VISCOSITY AT HIGH PRESSURES

The equation of Enskog (*5*) for the calculation of viscosity at elevated pressures not only proves unwieldy and cumbersome to use but is found to be of limited accuracy and utility. To circumvent this situation in the comparable studies on thermal conductivities, Owens and Thodos (*21*) took advantage of the correlation proposed by Abas-Zade (*1*) to produce a single unique and continuous function for both gases and liquids when the residual thermal conductivity $k - k^*$ is correlated with ρ, the corresponding density of the substance. Following a parallel approach and utilizing the only available high-pressure data of Michels, Botzen, and Schuurman (*17*) and Iwasaki (*7*) for argon in the gaseous state, and those of Rudenko and Shubinkov (*23*) for the liquid state, the authors have developed a residual viscosity correlation involving $\mu - \mu^*$ and ρ, which is presented in Figure 4. As was shown to be the case for thermal conductivities, this viscosity correlation is also consistent and permits the calculation of viscosities at high pressures from the density of argon at the prevailing temperature and pressure conditions.

A residual viscosity at the critical point is readily available from Figure 4 and the critical density of argon $\rho_c = 0.531$ g./cc. The residual viscosity at the critical point, $(\mu - \mu^*)_c = 1620 \times 10^{-5}$ centipoises, in conjunction with the viscosity at atmospheric pressure and the critical temperature, $\mu_{T_c}{}^* = 1232 \times 10^{-5}$ centipoises, establishes the viscosity of argon at the critical point to be $\mu_c = 2{,}852 \times 10^{-5}$ centipoises. With these values, the ratio of $\mu^*/\mu_{T_c}{}^*$ becomes $(2{,}852 \times 10^{-5})/(1{,}232 \times 10^{-5}) = 2.315$ and thus establishes the constant applicable to this homologous series. Therefore, the relationship involving the viscosity at the critical point for the inert gases becomes

$$\mu_c = 2.315 \mu_{T_c}{}^* \qquad (7)$$

With the values $\mu_{T_c}{}^*$ presented in Table 1, critical viscosities have been produced with Equation (7) for the other inert gases, also presented in Table 1. With the critical viscosities defined for all the members of this series, all available high-pressure viscosity data found only for argon have been reduced to produce the high-pressure region of the correlation presented in Figure 5.

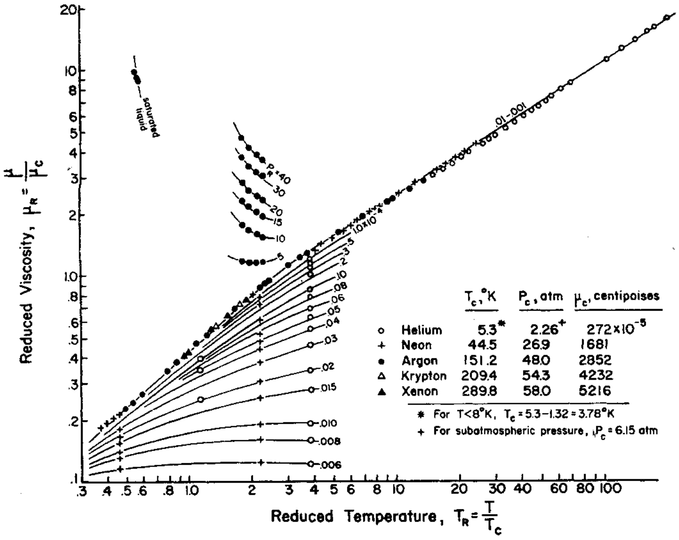


Fig. 5. Reduced-state correlation for the inert gases developed from available data.

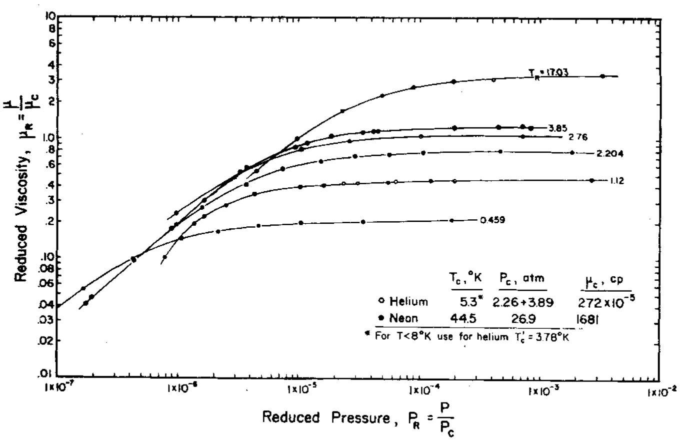


Fig. 6. Effect of subatmospheric pressures on the viscosity of helium and neon.

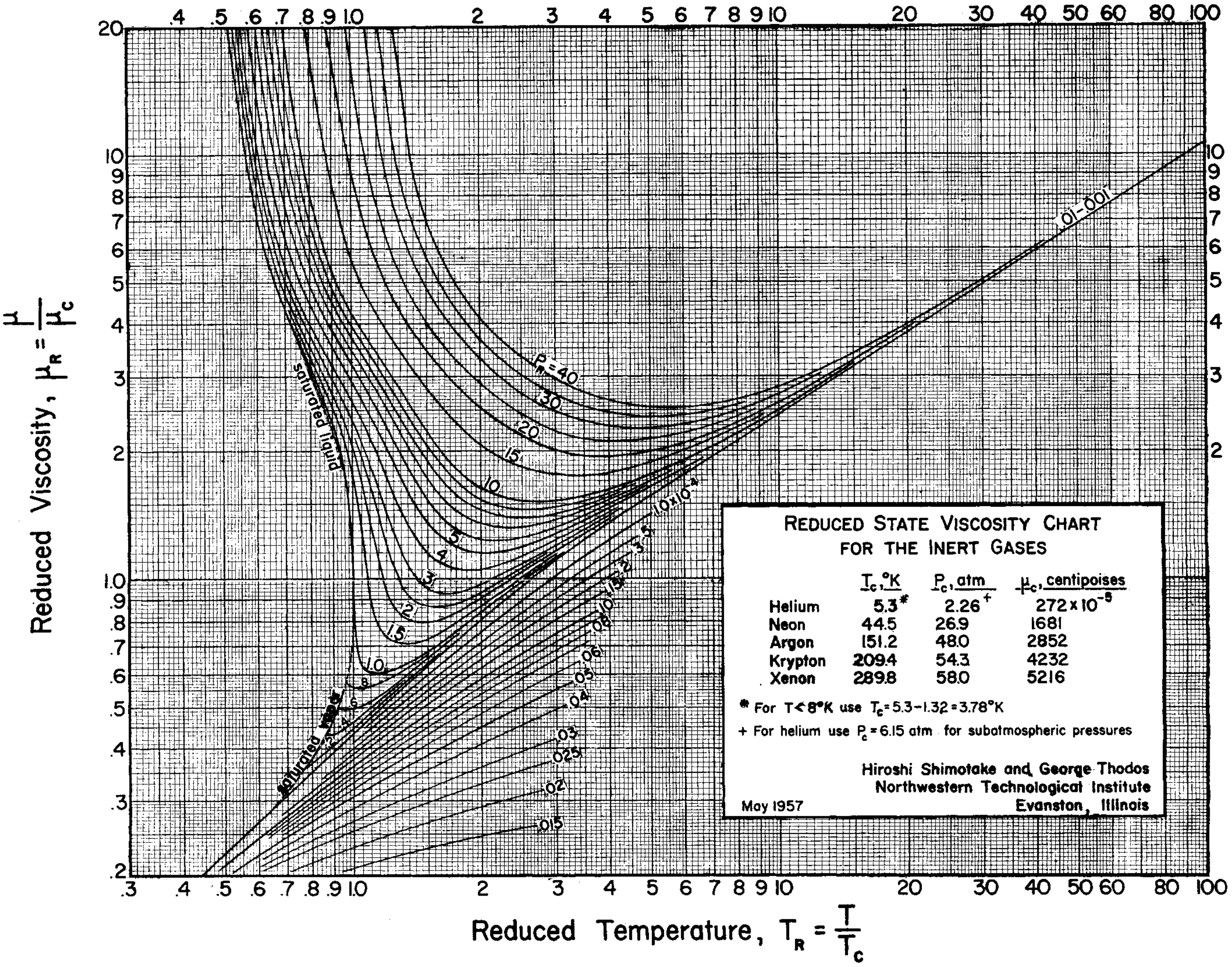
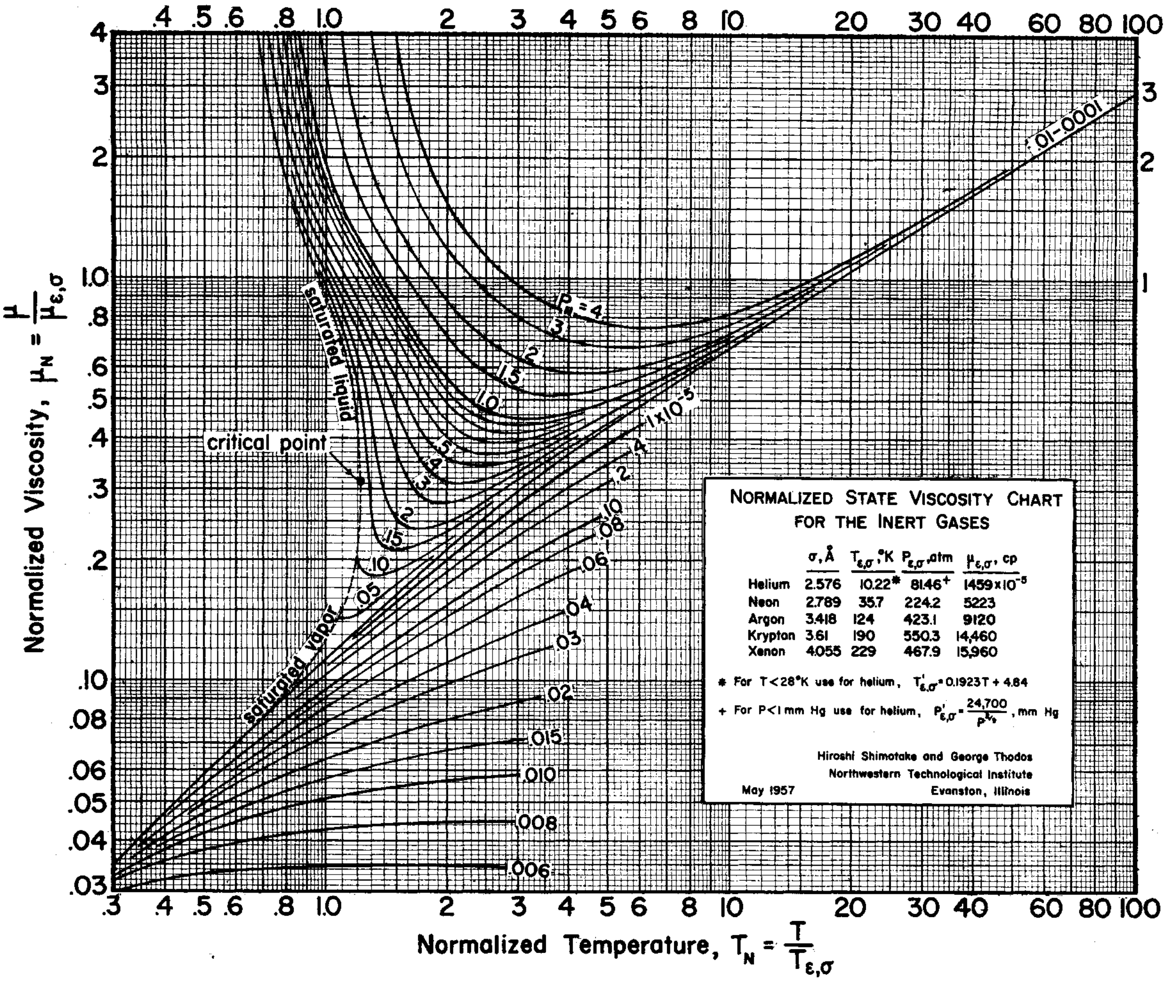


Fig. 7. Reduced-state viscosity correlation for the inert gases. (An 8-1/2-by 11-in. reproduction of this figure is available from the Chemical Engineering Department, Northwestern University, Evanston, Illinois.)



NORMALIZED STATE VISCOSITY CHART FOR THE INERT GASES

	σ, Å	$T_{\varepsilon,\sigma}$, °K	$P_{\varepsilon,\sigma}$, atm	$\mu_{\varepsilon,\sigma}$, cp
Helium	2.576	10.22*	81.46+	1459×10^{-5}
Neon	2.789	35.7	224.2	5223
Argon	3.418	124	423.1	9120
Krypton	3.61	190	550.3	14,460
Xenon	4.055	229	467.9	15,960

* For T < 28°K use for helium, $T'_{\varepsilon,\sigma} = 0.1923T + 4.84$

\+ For P < 1 mm Hg use for helium, $P'_{\varepsilon,\sigma} = \frac{24,700}{P^{4/3}}$, mm Hg

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Fig. 8. Normalized-state viscosity correlation for the inert gases.

VISCOSITY AT LOW PRESSURES

The low-pressure viscosity data of van Itterbeek and van Paemel for neon (*12*) have been used as the basis to extend the correlation of Figure 5 in the low-pressure region. In this connection the low-pressure data for helium (*10, 12*) have also been incorporated to establish this region. The variation of viscosity with pressure for both neon and helium is presented for several fixed temperatures in Figure 6. The experimental data show that viscosity does not begin to decrease until the absolute pressure is reduced below 1 mm. of mercury. This effect, when translated into Figure 5 for both neon and helium, produces the subatmospheric-pressure region existing below the moderate-pressure isobar ($0.001 \leq P_R \leq 0.01$).

CONSTRUCTION OF REDUCED STATE CORRELATION

Residual viscosities $\mu - \mu^*$ produced from Figure 4 have permitted the construction of the high-pressure gaseous- and liquid-state regions of the reduced-state correlation presented in Figure 7. The construction of this figure was made possible by adopting the following procedure. For a defined temperature and pressure, the density of argon was obtained from an enlarged plot presented elsewhere (*21*) and applicable to both the gaseous and liquid regions. With this density value, the residual viscosity $\mu - \mu^*$, obtained from Figure 4 and used in conjunction with the corresponding moderate-pressure viscosity μ^*, obtained from Figure 2, produced the viscosity at the defined temperature and pressure. The critical viscosity for argon $\mu_c = 2852 \times 10^{-5}$ centipoises produces, for this calculated value, the reduced viscosity $\mu_R = \mu/\mu_c$. Reduced viscosities have been calculated for several isobars to produce the high-pressure region of the reduced-state correlation presented in Figure 7. The low-pressure region of Figure 7 is the same developed for Figure 5.

TABLE 2. COMPARISON OF VISCOSITIES CALCULATED FROM REDUCED-STATE CORRELATION WITH EXPERIMENTAL VALUES FOR THE INERT GASES

			Low-pressure region			Moderate-pressure region			High-pressure region			Liquid region		
			Experimental points	Deviation, % Maximum	Deviation, % Average	Experimental points	Deviation, % Maximum	Deviation, % Average	Experimental points	Deviation, % Maximum	Deviation, % Average	Experimental points	Deviation, % Maximum	Deviation, % Average
	T_R	P_R												
Helium	0.3 -100	$8.9 \times 10^{-6} - 0.425$	65	27.60	13.4	61	9.00	2.31						
Neon	0.4 -25	0.0372	23	4.50	1.09	61	6.24	1.60						
Argon	0.4 -15	0.066-40				132	2.88	0.04	148	2.34	0.82	4	2.32	1.57
Krypton	1.3 -1.8	0.0185				4	0.765	0.49						
Xenon	0.95-1.9	0.0175				10	1.67	0.88						

NORMALIZED STATE VISCOSITY CORRELATION

The developments of Hirschfelder, Curtiss, and Bird (*9*) on transport properties extend into the dense-phase region through the introduction of reference states for temperature, pressure, and viscosity, defined as follows

$$T_{\epsilon,\sigma} = \frac{\epsilon}{\kappa} \qquad (8)$$

$$P_{\epsilon,\sigma} = \frac{\epsilon}{\sigma^3} \qquad (9)$$

$$\mu_{\epsilon,\sigma} = \frac{\sqrt{m\epsilon}}{\sigma^2} \qquad (10)$$

The reference temperature $T_{\epsilon,\sigma}$ possesses the dimension of absolute temperature, in degrees Kelvin, and therefore can be used directly; however, the expressions defining the reference pressure $P_{\epsilon,\sigma}$ and reference viscosity $\mu_{\epsilon,\sigma}$ must be changed into the forms

$$P_{\epsilon,\sigma} = 0.9869 \times 10^{18} \frac{\epsilon}{\sigma^3}, \quad \text{atm.} \qquad (11)$$

$$\mu_{\epsilon,\sigma} = 12.885 \times 10^5 \frac{\sqrt{M\epsilon}}{\sigma^2}, \quad \text{centipoises} \qquad (12)$$

in order to define the pressure $P_{\epsilon,\sigma}$ in atmospheres and the viscosity $\mu_{\epsilon,\sigma}$ in centipoises. In Equations (11) and (12) ϵ and σ are the same Lennard-Jones potential parameters defining Equations (8), (9), and (10). The reference temperatures $T_{\epsilon,\sigma}$ and calculated values of $P_{\epsilon,\sigma}$ and $\mu_{\epsilon,\sigma}$ are presented in Figure 8 for the inert gases. Equations (8), (11), and (12) are used to define the normalized temperature, pressure, and viscosity as followed:

$$T_N = \frac{T}{T_{\epsilon,\sigma}} \qquad (13)$$

$$P_N = \frac{P}{P_{\epsilon,\sigma}} \qquad (14)$$

$$\mu_N = \frac{\mu}{\mu_{\epsilon,\sigma}}. \qquad (15)$$

The dimensionless viscosity ratio $\mu/\mu_{\epsilon,\sigma}$ has been used to produce the normalized-state correlation of Figure 8. This was accomplished through the transformation of reduced-state values obtained from Figure 7 with Equations (13), (14), and (15). Therefore, Figure 8 is equivalent to Figure 7 and is presented in view of the current interest on transport properties defined in terms of the fundamental and basic potential parameters.

APPLICATION OF REDUCED-STATE CORRELATION

Viscosities have been calculated with the reduced correlation of Figure 7 and checked with the available literature values of the inert gases used in this study. Altogether, 152 viscosity values have been considered and produce an average deviation of less than 1% for argon in the liquid state and the gaseous high-pressure regions. In addition, the deviations for the low-pressure region are found to be 1.09% for neon and 13.4% for helium. A summary of the deviations resulting from the available data of the inert gases is presented in Table 2 for both the gaseous- and liquid-state regions. In these comparisons helium produces excessive deviations despite the fact that adjustments have been imposed on its critical temperature and pressure. This behavior indicates that helium must be treated by itself for the development of a viscosity correlation in which its actual critical constants are utilized. Inasmuch as high-pressure viscosity data for gaseous helium are not yet available, the construction of such a correlation will have to be postponed until this information becomes accessible.

The reduced-state correlation of Figure 7 has been applied to several diatomic and polyatomic gases. The high-pressure gaseous data of Michels and Gibson (*18*) and also those of Iwasaki (*13*), in conjunction with the high-temperature data of Vasilesco (*32*) at moderate pressures, have produced with Figure 7 an average deviation of 3.3% for nitrogen. Likewise, the high-pressure gaseous state data of Golubev (*7*) produced an average deviation of 3.1% for oxygen. A similar comparison with the high-pressure gaseous- and liquid-state data produced an average deviation of 11.5% for carbon dioxide (*25*). The high-pressure data for methane (*2*) and those for propane (*2*) produced average deviations of 4.1 and 16%, respectively. These results indicate that the reduced-state correlation of Figure 7 can be applied with good accuracy to the inert and diatomic gases but fails to produce reliable viscosity values for triatomic and polyatomic gases.

NOTATION

$f_\mu^{(k)}$ = viscosity correction factor for the kth approximation
m = mass of molecule, grams
M = molecular weight
T = absolute temperature, °K.
T_N = normalized temperature $T/(\epsilon/\kappa)$

Greek Letters

ϵ = characteristic energy for Lennard-Jones potential function, ergs
κ = Boltzmann constant, 1.38047×10^{-16} ergs/°K.
μ = viscosity, poises, g./(cm.)(sec.)
ϵ/κ = reference temperature, °K.
σ = characteristic length for Lennard-Jones potential function, Å
$\Omega^{(2,2)*}[T_N]$ = collision intergral function of the Lennard-Jones potential

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