Excess Transport Properties of Light Molecules

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A detailed study has been made of the excess viscosity of dense-phase aragon, deuterium, helium-3, helium-4, para and normal hydrogen, neon, and nitrogen and of the excess thermal conductivity of normal hydrogen. A definite temperature dependence for the excess viscosity vs. density has been shown to exist for argon, helium-4, hydrogen, and nitrogen and to be indicated for deuterium. The existing thermal conductivity data for hydrogen have been examined. A theoretical analysis for the qualitative behavior of excess thermal conductivity is given. The critical point viscosity values for all the species are given. Graphs, together with references to 1-atm. data, are presented for computation of the transport properties.

Reduced state and other correlations are often developed as aids to engineering. At times, approaches to convenience and simplification give rise to loss of important information. A detailed study has been made of the excess viscosity of dense-phase argon, deuterium, helium-3, helium-4, para and normal hydrogen, neon, and nitrogen and of the excess thermal conductivity of normal hydrogen. The excess transport property is defined as the transport property at a given pressure and temperature less that at the same temperature and 1 atm. Considerable detail is noted in the temperature dependence of the excess viscosity vs. density of argon, hydrogen, and nitrogen. The indications are that the excess viscosity of deuterium should also exhibit a temperature dependence.

The pressure dependence of viscosity and thermal conductivity particularly at low temperatures and in the dense phase is a generally known fact. However, there have been efforts to consider the excess or residual transport properties as a single monotonic function of density. The studies of this paper emphasize that when all the data available are considered, it becomes very clear that there is a significant temperature dependence which should not be neglected.

A characteristic temperature dependence for hydrogen of the excess viscosity vs. density relation was noticed by Rogers, Zeigler, and McWilliams (*44*) who made use of the near room temperature data of Michels, Schipper, and Rintoul (*37*). The work of Rogers et al. showed two curves, one for the liquid phase and another for the gas phase. The new work of Diller (*5*) substantiates this earlier conclusion drawn from more scant data.

A literature search for viscosity data of other molecular species exhibiting such temperature dependence was initiated. The results, whch are developed below, show that the temperature dependence of the excess viscosity was clearly indicated in the data of Zhdanova (*62, 63, 64*) and Rudenko and co-workers (*47, 56*).

The temperature dependence of the transport properties of low-temperature fluids was also found to vary from substance to substance with the reduced de Broglie wave length Λ^*. This quantity is the ratio to σ of the de Broglie wave length of relative motion of two interacting molecules whose kinetic energy of relative motion is ϵ, that is

$$\Lambda^* = \Lambda/\sigma \tag{1}$$

where

$$\Lambda = h/\sqrt{m\epsilon} \tag{2}$$

ϵ and σ are characteristic energy and distance parameters

TABLE 1. LENNARD-JONES FORCE CONSTANTS Λ^* AND REDUCED CRITICAL-POINT VISCOSITIES

Species	ϵ/k, °K.	σ, Å	Λ^*	μ_c^*
A	119.8	3.405	0.186	0.448
N_2	95.05	3.698	0.226	0.499
Ne	35.60	2.749	0.593	0.391
D_2	37.00	2.928	1.223	0.301*
H_2	37.00	2.928	1.731	0.233
He^4	10.22	2.556	2.68	0.211*
He^3	10.22	2.556	3.09	0.139

* From reference *23*.

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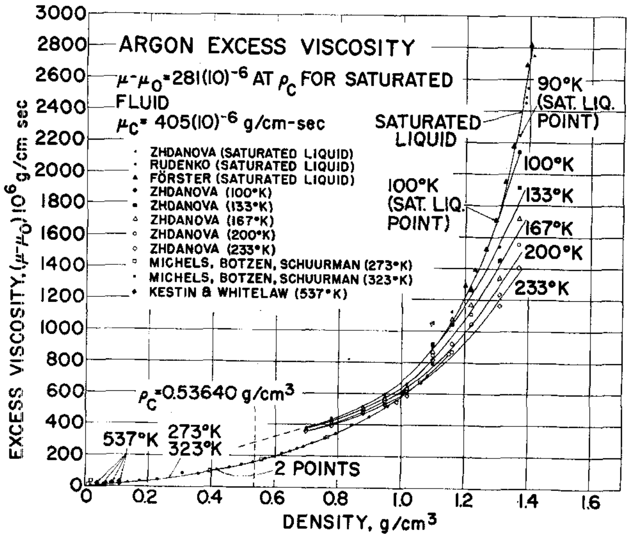

Fig. 1. Argon excess viscosity vs. density.

of the Lennard-Jones (*29*) intermolecular, potential energy function, $\varphi(r, \sigma) = 4\epsilon$. h is Planck's constant, and m is the mass of the species. Λ^* values are given in Table 1. Kerrisk, Rogers, and Hammel (*23*) demonstrated the importance of Λ^* as a correlating parameter for transport properties of light molecules. Their analysis of several low molecular weight species showed for molecules lighter than and including tritium that the thermal conductivities for the saturated liquids will exhibit a positive temperature coefficient and that the property can be correlated as a temperature-dependent function on the basis of the substance-dependent parameter Λ^*. Treatment of the excess thermal conductivity by others (*44, 48*), attributing to hydrogen only a negative temperature coefficient in the liquid state, was questioned by Rogers (*43*) and Rogers et al. (*45*).

The analysis that follows points up difficulties and inaccuracies of simple correlations for excess transport properties (*3, 44, 48, 50, 51*). Such simple correlations should be re-examined.

ARGON VISCOSITY

This entire study has been limited to fluid phases at pressures above 1 atm., including the liquid phase, and at temperatures up to values moderately above ambient. The data of Zhdanova (*62, 63*), Rudenko (*47*), Förster (*9*), Michels et al. (*33*), and Kestin and Whitelaw (*25*) were used for the dense-phase argon. One atmosphere data of Johnston and Grilly (*17*), and of references *25* and *33* were used to compute the excess viscosity. Figure 1 shows the excess viscosity of argon vs. density. The values for Zhdanova's data were read at constant temperatures from the smoothed isochores presented by Zhdanova. Despite the use of data from these smoothed curves, considerable scatter still exists in Figure 1. The data of Feleppova et al. (*8*) were examined. They show a temperature dependence similar to that of other observers; however, these data are low compared with those of Michels et al. (*33*), and as there are some internal inconsistencies and the data appear to be unreasonably low in the critical region, they are not included in Figure 1. The data of Michels et al. (*33*) and of Kestin and Whitelaw (*25*) from 273° to 537°K. form a single curve in Figure 1 and cross the 233°K. isotherm of Zhdanova (*62, 63*). This effect may be real as it also exists for nitrogen. The extrapolation of the saturated liquid curve to the critical density gives $405(10)^{-6}$ g./cm.-sec. for the viscosity at the critical point, instead of the value $285(10)^{-6}$ g./cm.-sec. obtained by Shimotake and Thodos (*50*). There is some evidence indicating that the data of Zhdanova (*62, 63*) and Rudenko (*47*) might be high near the critical-point density. Their data at 267°K. are high relative to those of Michels et al. (*33*) and Kestin and Whitelaw (*25*) at 273°K. Nevertheless, the temperature dependence of excess viscosity is evident in Figure 1, as are the differences between the excess viscosities of gas and saturated liquid at the same density for all densities equal to and greater than the critical density. It is significant that the saturated-liquid curve in Figure 1 and the dense-gas curve for 273° and 323°K. were determined by other investigators as well as Zhdanova.

The PVT data of Michels and co-workers (*35, 36*) were used to obtain densities for the viscosity-density correlation when densities were not given by the authors.

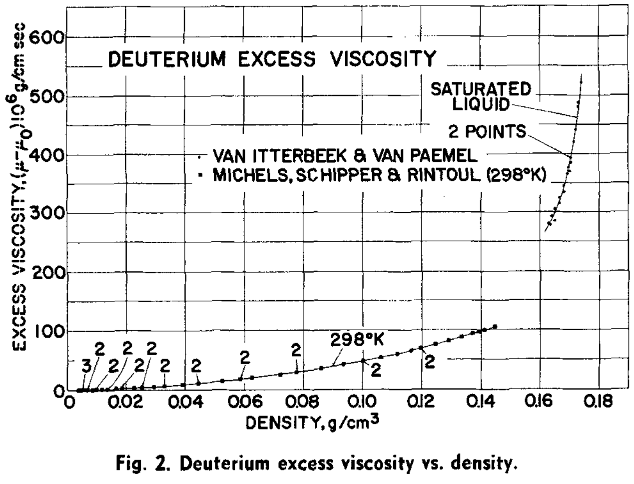

Fig. 2. Deuterium excess viscosity vs. density.

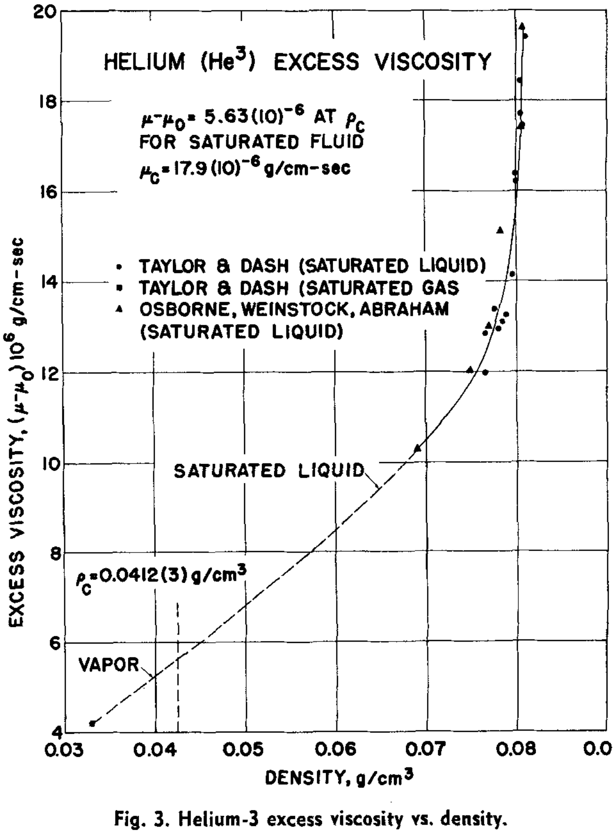

Fig. 3. Helium-3 excess viscosity vs. density.

DEUTERIUM VISCOSITY

Figure 2 was constructed from the data of van Itterbeek and van Paemel (*59*) for saturated liquid and the data of Michels et al. (*37*) for high-pressure gas. The small numbers associated with points in the figure indicate the multiplicity of data values represented by the plotted points. The 1-atm. data of van Itterbeek and van Paemel (*58*) and Coremans et al. (*4*) were used to compute the excess viscosity. Saturated liquid density data of Kerr (*20*) were used; densities for the gas were taken from the papers reporting the viscosity data. Figure 2 shows two curves, one for saturated liquid and one for room temperature gas, that cannot be extrapolated smoothly into each other to form a single curve as has been proposed (*51*). This is similar to the two curves for liquid and gas proposed for hydrogen (*44*). Undoubtedly, deuterium possesses a temperature-dependent excess viscosity similar to argon, nitrogen, and hydrogen.

HELIUM VISCOSITY

There are two isotopes of helium, He^3 and He^4, that must be treated separately. Table 1 shows the large differences between their reduced de Broglie wave lengths Λ^* and their critical point viscosities, indicating relatively large quantum effects in the various properties of the isotopes. The study here of liquid He^4 is limited to normal or liquid helium I above the so-called λ-transition line.

Figure 3 for He^3 shows the viscosity data of Osborne et al. (*38*) and Taylor and Dash (*54*), recomputed with the recent saturated fluid densities of Kerr and Taylor (*21*), Sherman and Edeskuty (corrected) (*49*), and Roberts, Sherman, and Sydoriak (*41*). One-atmosphere data of Becker et al. (*1*) were used to compute the excess viscosity. The interpolation between the single, gas-phase viscosity value and the liquid data covers a long range. A value, 17.9(10)$^{-6}$ g./cm.-sec., is obtained for the critical point viscosity which may be compared with 18.7(10)$^{-6}$ g./cm.-sec. in reference 23. These values are considered to be in good agreement. Two viscosity values of Taylor and Dash (*54*) reported for saturated liquid just below and for gas just above the critical point were not used since both are at temperatures near to and above the presently-accepted best value for the critical temperature (*53*). Additional unreported data (*54*) were used to obtain the single plotted point in Figure 3 for saturated gas.

Also, a new value for the critical density of He^3, 0.0412 (3) g./cc. (He^3 MW = 3.01603), was determined by the method of rectilinear diameters from the density data cited (*21, 41, 49*) and the critical temperature (*53*), T_c = 3.3240°K.

Figure 4 is a plot of the excess viscosity of He^4. Two curves are shown for saturated liquid, one for data of Taylor and Dash (*54*), believed to be more reliable, and the other for the data of Welber (*60*). The higher-density data of Welber for liquid He^4 are not plotted in Figure 4 because of a confusion in temperature scales in Welber's paper (see Figure 4 in reference *60*) and the complication in his method, the absorption of the energy of torsional oscillations of a quartz crystal, piezoelectrically excited, giving spurious absorption peaks. The dip down of the curve for saturated liquid at its high density end is a precursor of the lambda-point transition.

The high-density, liquid-phase points for Tjerkstra (55) were computed from the tabulated $\rho\mu$ (density times viscosity) data with the density data of Edeskuty and Sherman (*6*) and Keesom and Keesom* (*19*). It is evident from Figure 4 that the He^4 viscosity data are not amenable to a single curve correlation independent of temperature. The most reliable measurements (*24, 25*) of the viscosity of He^4 gas at room temperature and somewhat higher, to densities as high as 0.033 g./cc., show no significant density dependence. Density data from Kerr and Taylor (*22*) and from Edwards (*7*) were used. The 1-atm. viscosity values, for computing the excess viscosity, were obtained from van Itterbeek and Keesom (*57*) and references *4*, *17*, and *58*. The viscosity of He^4 at its critical point was previously estimated (*23*) to be 31.2(10)$^{-6}$ g./cm.-sec.

HYDROGEN VISCOSITY

The excess viscosity of para hydrogen versus density is shown in Figure 5. This figure is similar to that of Diller (*5*) with the addition of near ambient data. For clarity of presentation some of Diller's isotherms are omitted. Diller has, at most, found only a very small difference between the viscosities of saturated-liquid, normal hydrogen [his own work and that of Johns (*16*)] and para hydrogen when compared at the same density. Figure 5 also includes saturated-vapor values from the correlation of

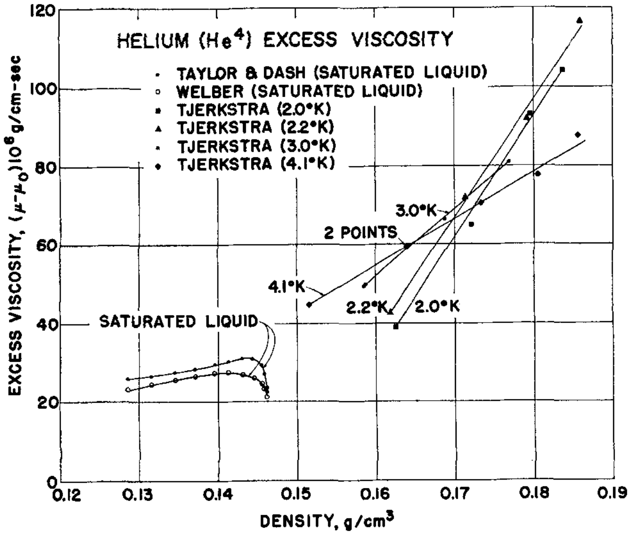

Fig. 4. Helium-4 excess viscosity vs. density.

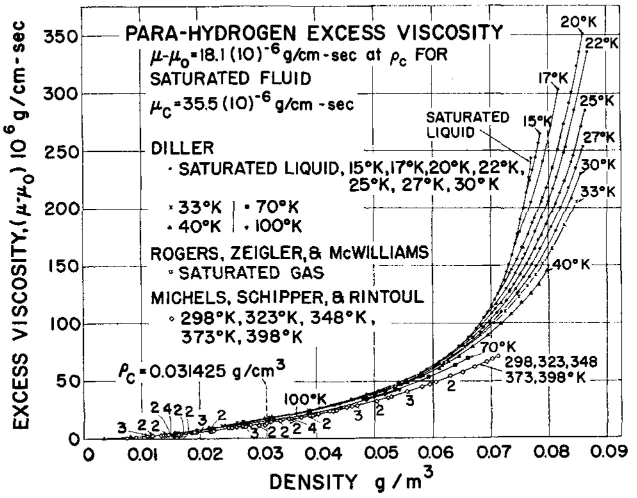

Fig. 5. Para hydrogen excess viscosity vs. density.

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* Adjusted to the corrected data of reference 6.

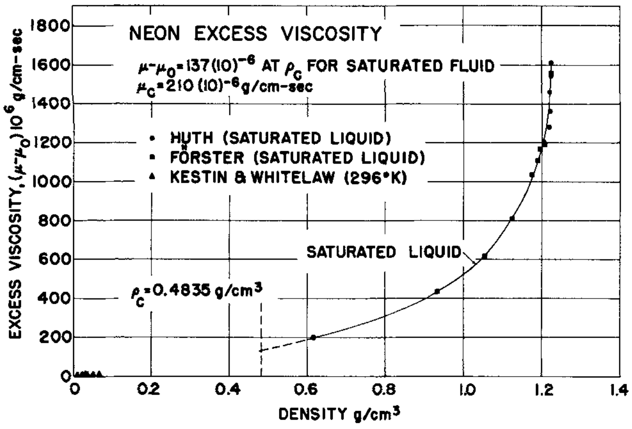

Fig. 6. Neon excess viscosity vs. density.

Rogers et al. (*44*). The saturated-fluid curve is interpolated between the data of Diller and Rogers et al. The critical point viscosity recommended by Diller is (35.5 ± 0.5) 10^{-6} g./cm.-sec. An empirical equation for the entire saturated fluid curve which reproduces the viscosity data within ± 1% from the triple to 1-atm. gas is

$$\mu = \left[\frac{-0.84407 - 45.722\rho + 515\rho^2}{-0.082066 + \rho}\right] 10^{-6}$$

The value for the viscosity calculated from this equation is $35.0(10)^{-6}$ g./cm.-sec. This is within the error specified for Diller's value and is in fair agreement with the Brebach and Thodos (*3*) value of $37.6(10)^{-6}$ g./cm.-sec., which they obtained indirectly by multiplying their value from an excess viscosity versus density graph by an appropriate factor. However, their dense-phase correlation of viscosities (*3, 51*) cannot be valid except for a limited range of saturated liquid. The data of Michels et al. (*37*) for normal hydrogen near room temperature are included in Figure 5; the data for para hydrogen at these temperatures would be the same. The isotherms of Figure 5 are similar to those for argon and nitrogen.

The 1-atm. viscosity correlation of reference *44* and also the equation recommended by Diller (*5*) were used to compute excess viscosity values. These equations give comparable values.

NEON VISCOSITY

There are not sufficient experimental viscosity data for neon for a reliable determination of the nature of the dense-phase isotherms. Figure 6 is a graph of excess viscosity of saturated liquid. The original data are from the investigations of Huth (*15*) and Förster (*9*). The gas-phase data in Figure 6 are from Kestin and Whitelaw (*25*). Only the lowest-temperature data of Kestin and Whitelaw are shown because the data up to temperatures of 520°K. coincide with those at 297°K. when plotted to the scale of Figure 6. The 1-atm. viscosity values for computing the excess viscosity were taken from references *4, 17, 25,* and *58* with preference given to the data of van Itterbeek and van Paemel (*58*) below 40°K. Extrapolation of the saturated liquid curve to the critical density gives a critical point viscosity of $210(10)^{-6}$ g./cm.-sec. This value is considerably higher than the value $168(10)^{-6}$ g./cm.-sec. obtained by Kerrick et al. (*23*) and by Shimotake and Thodos (*50*).

The densities of saturated liquid used in Figure 6 were taken from Mathias et al. (*31*), but these were corrected to the vapor pressure-temperature scale (equation) of Grilly (*13*).

The recent high-pressure, neon, gas-phase viscosity data of Trappeniers, Botzen, van den Berg, and van Oosten (*55a*) at 298°, 323°, and 348°K. are for densities up to 0.69 g./cc. The three isotherms show no significant temperature dependence among themselves. When plotted on Figure 6, these new viscosity values do show a considerable difference between the viscosities at near room temperature and saturated liquid both taken at the same densities.*

NITROGEN VISCOSITY

Figure 7 is a graph of the excess viscosity of nitrogen. The saturated liquid data of Rudenko and co-workers (*46*) and Förster (*9*) are in good agreement. Isotherms are shown for data from Zhdanova (*64*) including the work of Verkin and Rudenko (*56*), Michels and Gibson (*34*), and Lazarre and Vodar (*27*). The isotherm structure for nitrogen is similar to that for argon. The isotherms representing the data of Zhdanova at the higher densities are undoubtedly low as may be seen for the 75° and 100°K. isotherms, which, if extended, would not intersect the saturated-liquid curve in correct relationship with the 76.1° and 104.1°K. data points on the saturated liquid curve. At low densities, the extrapolations of the saturated-liquid curve and the 126°K. isotherm of Zhdanova intersect at a density in agreement with the expected critical density of nitrogen (T_c = 126.26°K.). This gives a critical-point viscosity of $285(10)^{-6}$ g./cm.-sec. as compared with $182(10)^{-6}$ g./cm.-sec. reported by Brebach and Thodos (*3*). As for argon, the moderate-temperature curve (300° to 450°K) for nitrogen crosses the higher-temperature data of Zhdanova at high densities. This kind of crossing is not found with the data for hydrogen of other investigators (see Figure 5). Additional measurements are needed to test its validity for argon and nitrogen. Only the 298°K. data of Michels and Gibson (*34*) are shown because their higher temperature data coincide with the 298°K. isotherm. The higher-density data of Lazarre and Vodar (*27*) form a natural extension of the 298°K. isotherm. Recent data of Goldman (*10*) (not shown) coincide closely with the 298°K. isotherm. These data cover the range of 195° to 298°K. below densities of ρ = 0.27 g./cc. and show no temperature dependence of excess viscosity. The data of Feleppova and Eshken (*8*)

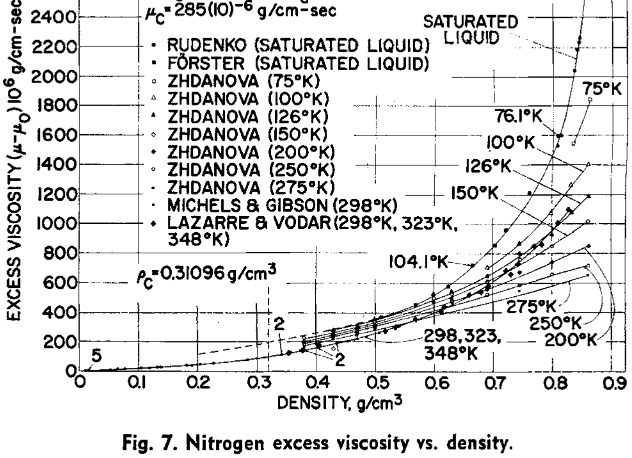

Fig. 7. Nitrogen excess viscosity vs. density.

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* This paragraph was added in revision.

were found to be lower, in general, than the data of Zhdanova, and their very high density-viscosity data were found to be internally inconsistent.

One-atmosphere values of viscosity for computing excess viscosity were obtained from the work of Johnston and co-workers (*18*) and references *25* and *27*. Density data not given with the viscosity data were taken from Strobridge (*52*), Mathias et al. (*32*), and Benedict (*2*).

Further investigatons and measurements of viscosity are needed to improve the excess viscosity-density relationship for nitrogen, but that temperature as a parameter is involved in this relation is evident from Figure 7.

Hydrogen Thermal Conductivity

The excess thermal conductivity vs. density of normal hydrogen is shown in Figure 8. The thermal conductivities of liquid para and liquid normal hydrogen are equal (*39*). The critical and triple points of normal hydrogen are indicated in Figure 8. A solid line is drawn through the saturated-liquid data of Powers et al. (*39*). The size of the plotted points represents the probable error in the liquid-phase measurements. The extrapolated, broken line for saturated liquid corresponds to the correlation and theoretical study by Kerrisk et al. (*23*).

Three isotherms are shown for the gas phase, representing the experimental data of Lenoir and Comings (*30*) and of Keyes (*26*). A single curve representing the gas phase over the range of temperature and pressure covered by these investigations is probably more realistic. The saturated liquid line in Figure 8 which recognizes the positive temperature coefficient of thermal conductivity of liquid hydrogen at low temperatures and high densities has a parallelism in the thermal conductivities of saturated liquid helium-3 (*28*), liquid helium-4 (*12*), and liquid deuterium (*40*). It has been predicted to occur for tritium (*23*). As the temperature of saturated liquid hydrogen approaches the critical point, the temperature coefficient of the thermal conductivity changes and becomes classical in sign.

The atmospheric thermal conductivities of gaseous hydrogen needed for computing excess conductivities were obtained from the correlation in reference *44*. Density data were obtained from Goodwin et al. (*11*) and Woolley et al. (*61*).

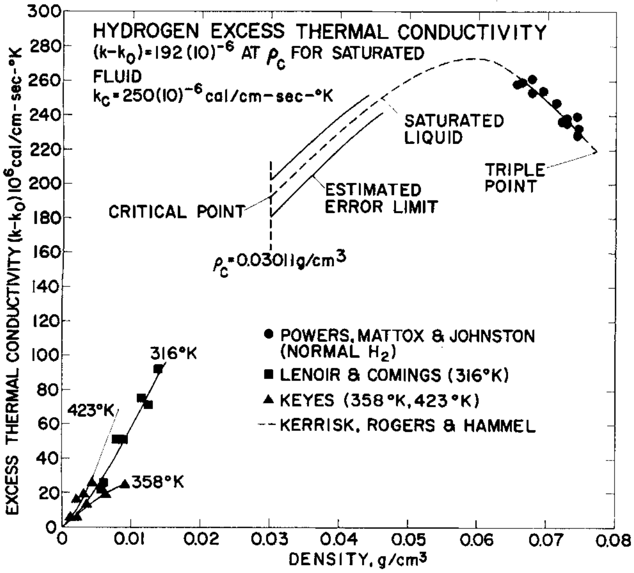

Fig. 8. Hydrogen excess thermal conductivity vs. density.

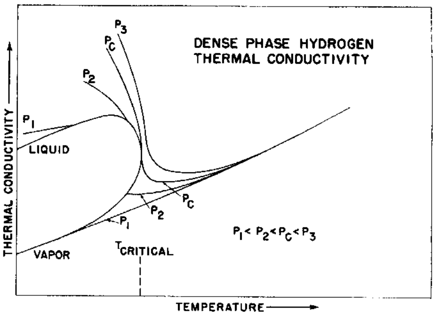

Fig. 9. Graphical representation of hydrogen thermal conductivity vs. temperature.

Figure 9 is a postulated schematic of the thermal conductivity of hydrogen vs. temperature based upon the papers of Kerrisk et al. (*23*) and Powers et al. (*39*). The isobars in Figure 9 of liquid hydrogen at low temperatures change from positive slope to negative slope with increasing pressure. The positive slope of the isobar P_1 is nonclassical for a liquid.

The differential with respect to the density of the thermal conductivity expressed as a function of pressure and temperature is

$$\frac{d(k-k_o)}{d\rho}=\left(\frac{\partial(k-k_o)}{\partial P}\right)_T\frac{dP}{d\rho}+\left(\frac{\partial(k-k_o)}{\partial T}\right)\frac{dT}{d\rho} \tag{4}$$

In Figure 9 it is seen that $(\partial k/\partial P)_T$ is always positive. $(dP/d\rho)_T$ is positive, and along an isotherm, $dT/d\rho = 0$. $(\partial k_o/\partial P)_T = 0$ by definition. Along an isotherm, therefore

$$\left[\frac{d(k-k_o)}{d\rho}\right]_T=\left(\frac{\partial k}{\partial P}\right)_T\left(\frac{dP}{d\rho}\right)_T>0 \tag{5}$$

Thus the isotherms of excess thermal conductivity plotted against density have a positive slope.

Along the saturation curve, thermal conductivity and density can be expressed as a function of a single variable, either the vapor pressure or the temperature. With temperature as the independent variable, the density derivative of excess thermal conductivity is

$$\left[\frac{d(k-k_o)}{d\rho}\right]_{sat}=\left[\frac{d(k-k_o)}{dT}\frac{dT}{d\rho}\right]_{sat} \tag{6a}$$

$$=\left[\frac{dk}{dT}\frac{dT}{d\rho}\right]_{sat}-\frac{dk_o}{dT}\left(\frac{dT}{d\rho}\right)_{sat} \tag{6b}$$

Along the saturation line $(dT/d\rho)_{sat}$ is negative for liquid and positive for vapor. Also, along the coexistence curve, as seen in Figure 9, $(dk/dT)_{sat}$ is positive everywhere for the vapor phase and is positive for saturated liquid at low temperatures. $(dk/dT)_{sat}$ is negative along the coexistence curve for the liquid phase in the vicinity of the critical region. Finally, from Figure 9, for an isobar such as P_1, dk_o/dT is positive. This information leads to an undetermined sign of the slope of the graph of excess thermal conductivity vs. density for the low temperature liquid phase along the coexistence curve; however, the experimental data of Powers et al. (*39*) shows this slope to be negative. Evidently the contribution of the last term of Equation (*6b*) is small. For the saturated liquid phase at higher temperatures and for saturated gas, the slope is positive.

The density-dependent differential equation for excess viscosity along the saturation line can also be expressed as a function of pressure to be

$$\left[\frac{d(k-k_o)}{d\rho}\right]_{\text{sat}} = \left[\frac{d(k-k_o)}{dP}\frac{dP}{d\rho}\right]_{\text{sat}} \qquad (7)$$

The values of the slopes of excess thermal conductivity vs. density graph remain to be determined. For the gas phase in the vicinity of the coexistence curve and for which $k \approx k_o$ at low pressures (see Figure 9) $(d(k - k_o)/dP)_{\text{sat}}$ of Equation (7) is greater than $(\partial(k - k_o)/\partial P)_T$ of Equation (5) at the saturation curve. The following simple phenomenological argument applies in this vapor region. The thermal conductivity will increase more rapidly along the saturation line with a pressure increment and its associated temperature increment than it will for the same pressure increment at constant temperature. Similarly, $(dP/d\rho)_{\text{sat}}$ exceeds $(dP/d\rho)_T$ at saturation. Consequently, for vapor $(k \approx k_o)$, $[d(k - k_o)/d\rho]_{\text{sat}} > [d(k - k_o)/d\rho]_T$, and the slope along the saturation curve of excess thermal conductivity vs. density graph is greater than the slope of the intersecting isotherms.

At the critical point $[d(k - k_o)/d\rho]_{\text{sat}}$ and $[d(k - k_o)/d\rho]_T$ are equal because $(dT/d\rho)_T = 0$ and the critical point isotherm is tangent to the coexistence curve. The plausible assumption is made that the excess thermal conductivity is a well-behaved function of density.

Figure 10 was constructed on the basis of above considerations. A qualitative description of the excess thermal conductivity characterized by the coexistence curve and intersecting isotherms is presented. The isotherms range from below to above the critical temperature.

Hamrin (*14*) indicates that the near-room temperature curve for the gas phase, excess thermal conductivity shows no temperature dependence between 0° to 75°C. and that it corresponds to the correlations of Rogers et al. (*44*) and Schaefer and Thodos (*48*) for density values up to those near the critical value. This would be similar to isotherm T_4. Roder (*42*) is measuring the dense-phase thermal conductivity of hydrogen below 100°K. The extent of agreement of his experimental data with this analysis will be of interest.

QUANTUM MECHANICAL TRENDS

The critical-point viscosity has been chosen to indicate the significance of quantum mechanical contributions to the viscosity of light molecules. Table 1 gives the Lennard-Jones force constants and the reduced de Broglie wave length Λ^* as used in reference 23 and the reduced critical-point viscosities. The viscosities are reduced by the molecular parameter $m^{1/2}\epsilon^{1/2}/\sigma^2$. The reduced critical-point viscosity decreases with increasing Λ^*. For low Λ^*, that is high molecular weight species, the reduced critical-point viscosities for ideal hard spheres should approach a constant limit as Λ^* approaches zero. Deviations exist because of nonideality. This accounts, at least in part, for the value for diatomic nitrogen in Table 1 not conforming to the pattern. The quantum mechanical trend for the critical-point viscosities with the substance dependent parameter Λ^* is clear cut. This behavior indicates the increasing contribution of the large zero-point energy and the more open fluid structure at low temperatures for the lighter molecular species.

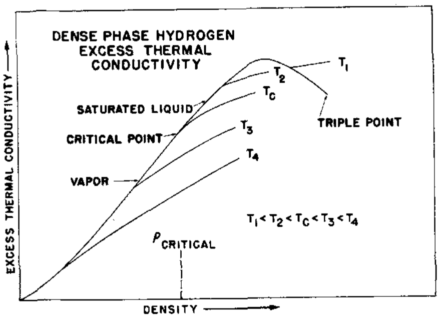

Fig. 10. Graphical representation of hydrogen excess thermal conductivity vs. density.

REMARKS AND CONCLUSIONS

The available data on the excess viscosities of argon, deuterium, helium-3, helium-4, para and normal hydrogen, neon, and nitrogen and the excess thermal conductivity of normal hydrogen in the liquid and dense-gas phases have been correlated as functions of density and temperature. The correlations extend from low densities to densities of the liquid at the triple point and from triple-point temperatures to temperatures of 400° to 500°K. For all these substances, the excess viscosity is dependent on temperature as well as density, and the same is probably true for the excess thermal conductivity of hydrogen. The dependence of the excess viscosity of argon, hydrogen, and nitrogen on density and temperature are similar as may be seen by comparing Figures 1, 5, and 7. This suggests a correspondence-law correlation of the excess viscosities of these and other substances.

The data on helium-3 are very limited, and liquid helium-4 shows a behavior connected with the λ transitions to the liquid helium-II phase which is a quantum state unique to helium-4 and not observed for any other liquid.

The correlation of excess viscosity with density, independent of temperature, with critical-point properties used for forming reduced variables as has been proposed (*3, 48, 50, 51*) simplifies the correlation for different class related substances. The present paper shows that this kind of temperature independent correlation of excess viscosity fails to recognize a demonstrable dependence of the excess viscosity on temperature at constant density which is significant at critical density and is quite large at higher densities. The curve for the excess viscosity of saturated liquid on an excess viscosity vs. density graph lies well above the curve for the dense-gas phase at high temperatures $(T >> T_c)$, see Figures 1, 5, and 7.

New values for the critical-point viscosities were deduced for argon, helium-3, para hydrogen, neon, and nitrogen from experimental data at other temperatures and pressures. The values for helium-3 and para hydrogen are close to previously deduced values (*3, 23*). The new values for argon, neon, and nitrogen are considerably higher than the older values (*3, 23, 50*). This might be explained on the basis of experimental error in the data used in the correlation, but in view of the new viscosity data for hydrogen (*5*) and the demonstration in Figure 5 of the dependence of the excess viscosity at critical density on temperature, higher values are to be expected for the deduced critical-point viscosities of these substances.

The correlations of excess transport properties, as given herein, can be used with the references to 1-atm. data for computation in the dense-phase regions. Whereas previous correlations have not looked at the detail of the viscosity behavior in the dense phase, these correlations now make possible more precise determinations of these properties with more complete cognizance of the overall density and temperature dependence. This is particularly true for argon, para-hydrogen, and nitrogen.

ACKNOWLEDGMENT

The authors wish to thank Keith Zeigler for doing the least-squares computation for Equation (3).

NOTATION

h = Planck's constant
k = thermal conductivity
m = mass of molecule
P = pressure
r = distance between interacting molecules
T = temperature

Greek Letters

ϵ = energy parameter
Λ = de Broglie wave length
Λ^* = reduced de Broglie wave length
μ = viscosity, g./cm.-sec.
φ = Lennard-Jones potential energy function
ρ = density, g./cc.
σ = distance parameter

Subscripts

c = critical-point conditions
o = 1-atm. pressure
sat = saturation curve

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