§1.3 Pressure and Temperature Dependence of Viscosity

Extensive data on viscosities of pure gases and liquids are available in various science and engineering handbooks. When experimental data are lacking and there is not time to obtain them, the viscosity can be estimated by empirical methods, making use of other data on the given substance. We present here a corresponding-states correlation, which facilitates such estimates and illustrates general trends of viscosity with temperature and pressure for ordinary fluids. The principle of corresponding states, which has a sound scientific basis, is widely used for correlating equation-of-state and thermodynamic data. Discussions of this principle can be found in textbooks on physical chemistry and thermodynamics.

The plot in Fig. 1.3-1 gives a global view of the pressure and temperature dependence of viscosity. The reduced viscosity $\mu_r = \mu / \mu_c$ is plotted versus the reduced temperature $T_r = T / T_c$, for various values of the reduced pressure $p_r = p / p_c$. A "reduced" quantity is one that has been made dimensionless by dividing by the corresponding quantity at the critical point. The chart shows that the viscosity of a gas approaches a limit (the low-density limit) as the pressure becomes smaller; for most gases, this limit is nearly attained at 1 atm pressure. The viscosity of a gas at low density increases with increasing temperature, whereas the viscosity of a liquid decreases with increasing temperature.

Experimental values of the critical viscosity $\mu_c$ are seldom available. However, $\mu_c$ may be estimated in one of the following ways: (i) if a value of viscosity is known at a given reduced pressure and temperature, preferably at conditions near to those of

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interest, then \( \mu_c \) can be calculated from \( \mu_c = \mu / \mu_r \); or (ii) if critical \( p-V-T \) data are available, then \( \mu_c \) may be estimated from these empirical relations:

\[
\mu_c = 61.6(MT_c^{1/2}(\bar{V}_c)^{-2/3} \quad \text{and} \quad \mu_c = 7.70M^{1/2}p_c^{2/3}T_c^{-1/6} \quad (1.3-1a, b)
\]

Here \( \mu_c \) is in micropoises, \( p_c \) in atm, \( T_c \) in K, and \( \bar{V}_c \) in cm³/g-mole. A tabulation of critical viscosities³ computed by method (i) is given in Appendix E.

Figure 1.3-1 can also be used for rough estimation of viscosities of mixtures. For \( N \)-component fluids with mole fractions \( x_a \), the "pseudocritical" properties⁴ are:

\[
p'_c = \sum_{a=1}^{N} x_a p_{ca} \quad T'_c = \sum_{a=1}^{N} x_a T_{ca} \quad \mu'_c = \sum_{a=1}^{N} x_a \mu_{ca} \quad (1.3-2a, b, c)
\]

That is, one uses the chart exactly as for pure fluids, but with the pseudocritical properties instead of the critical properties. This empirical procedure works reasonably well

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unless there are chemically dissimilar substances in the mixture or the critical properties of the components differ greatly.

There are many variants on the above method, as well as a number of other empiricisms. These can be found in the extensive compilation of Reid, Prausnitz, and Poling.\(^5\)

**EXAMPLE 1.3-1**

Estimate the viscosity of N\(_2\) at 50°C and 854 atm, given \(M = 28.0 \text{ g/g-mole}, p_c = 33.5 \text{ atm}, \text{ and } T_c = 126.2 \text{ K.} \)

**Estimation of Viscosity from Critical Properties**

**SOLUTION**

Using Eq. 1.3-1b, we get

\[
\mu_c = 7.70(28.0)^{1/2}(33.5)^{2/3}(126.2)^{-1/6} = 189 \text{ micropoises} = 189 \times 10^{-6} \text{ poise} \quad (1.3-3)
\]

The reduced temperature and pressure are

\[
T_r = \frac{273.2 + 50}{126.2} = 2.56; \quad p_r = \frac{854}{33.5} = 25.5 \quad (1.3-4a, b)
\]

From Fig. 1.3-1, we obtain \(\mu_r = \mu/\mu_c = 2.39\). Hence, the predicted value of the viscosity is

\[
\mu = \mu_c(\mu/\mu_c) = (189 \times 10^{-6})(2.39) = 452 \times 10^{-6} \text{ poise} \quad (1.3-5)
\]

The measured value\(^6\) is 455 \times 10^{-6} \text{ poise. This is unusually good agreement.}

**§1.4 MOLECULAR THEORY OF THE VISCOSITY OF GASES AT LOW DENSITY**

To get a better appreciation of the concept of molecular momentum transport, we examine this transport mechanism from the point of view of an elementary kinetic theory of gases.

We consider a pure gas composed of rigid, nonattracting spherical molecules of diameter \(d\) and mass \(m\), and the number density (number of molecules per unit volume) is taken to be \(n\). The concentration of gas molecules is presumed to be sufficiently small that the average distance between molecules is many times their diameter \(d\). In such a gas it is known\(^1\) that, at equilibrium, the molecular velocities are randomly directed and have an average magnitude given by (see Problem 1C.1)

\[
\bar{u} = \sqrt{\frac{8kT}{\pi m}} \quad (1.4-1)
\]

in which \(k\) is the Boltzmann constant (see Appendix F). The frequency of molecular bombardment per unit area on one side of any stationary surface exposed to the gas is

\[
Z = \frac{1}{2}n\bar{u} \quad (1.4-2)
\]

---


The average distance traveled by a molecule between successive collisions is the \textit{mean free path} \( \lambda \), given by

\[
\lambda = \frac{1}{\sqrt{2\pi d^2 n}}
\]

On the average, the molecules reaching a plane will have experienced their last collision at a distance \( a \) from the plane, where \( a \) is given very roughly by

\[
a = \frac{3}{2} \lambda
\]

The concept of the mean free path is intuitively appealing, but it is meaningful only when \( \lambda \) is large compared to the range of intermolecular forces. The concept is appropriate for the rigid-sphere molecular model considered here.

To determine the viscosity of a gas in terms of the molecular model parameters, we consider the behavior of the gas when it flows parallel to the \( xz \)-plane with a velocity gradient \( \frac{dv_x}{dy} \) (see Fig. 1.4-1). We assume that Eqs. 1.4-1 to 4 remain valid in this non-equilibrium situation, provided that all molecular velocities are calculated relative to the average velocity \( v \) in the region in which the given molecule had its last collision. The flux of \( x \)-momentum across any plane of constant \( y \) is found by summing the \( x \)-momenta of the molecules that cross in the positive \( y \) direction and subtracting the \( x \)-momenta of those that cross in the opposite direction, as follows:

\[
\tau_{yx} = Zmv_x|_{y-a} - Zmv_x|_{y+a}
\]

In writing this equation, we have assumed that all molecules have velocities representative of the region in which they last collided and that the velocity profile \( v_x(y) \) is essentially linear for a distance of several mean free paths. In view of the latter assumption, we may further write

\[
v_x|_{y+a} = v_x|_y \pm \frac{3}{2} \lambda \frac{dv_x}{dy}
\]

By combining Eqs. 1.4-2, 5, and 6 we get for the net flux of \( x \)-momentum in the positive \( y \) direction

\[
\tau_{yx} = -\frac{1}{3} n \bar{u} \lambda \frac{dv_x}{dy}
\]

This has the same form as Newton's law of viscosity given in Eq. 1.1-2. Comparing the two equations gives an equation for the viscosity

\[
\mu = \frac{1}{3} n \bar{u} \lambda = \frac{1}{3} \rho \bar{u} \lambda
\]
or, by combining Eqs. 1.4-1, 3, and 8

\[ \mu = \frac{2}{3} \sqrt{\frac{mkT}{\pi}} = \frac{2}{3} \pi \sqrt{\frac{mkT}{\pi}} \]

This expression for the viscosity was obtained by Maxwell\(^2\) in 1860. The quantity \( \pi d^2 \) is called the collision cross section (see Fig. 1.4-2).

The above derivation, which gives a qualitatively correct picture of momentum transfer in a gas at low density, makes it clear why we wished to introduce the term "momentum flux" for \( \tau_y \), in §1.1.

The prediction of Eq. 1.4-9 that \( \mu \) is independent of pressure agrees with experimental data up to about 10 atm at temperatures above the critical temperature (see Fig. 1.3-1). The predicted temperature dependence is less satisfactory; data for various gases indicate that \( \mu \) increases more rapidly than \( \sqrt{T} \). To better describe the temperature dependence of \( \mu \), it is necessary to replace the rigid-sphere model by one that portrays the attractive and repulsive forces more accurately. It is also necessary to abandon the mean free path theories and use the Boltzmann equation to obtain the molecular velocity distribution in nonequilibrium systems more accurately. Relegating the details to Appendix D, we present here the main results.\(^3\),\(^4\),\(^5\)

Fig. 1.4-2 When two rigid spheres of diameter \( d \) approach each other, the center of one sphere (at \( O' \)) "sees" a circle of area \( \pi d^2 \) about the center of the other sphere (at \( O \)), on which a collision can occur. The area \( \pi d^2 \) is referred to as the "collision cross section."

\(^2\) James Clerk Maxwell (1831–1879) was one of the greatest physicists of all time; he is particularly famous for his development of the field of electromagnetism and his contributions to the kinetic theory of gases. In connection with the latter, see J. C. Maxwell, Phil. Mag., 19, 19, Prop. XIII (1860); S. G. Brush, Am. J. Phys, 30, 269–281 (1962). There is some controversy concerning Eqs. 1.4-4 and 1.4-9 (see S. Chapman and T. G. Cowling, The Mathematical Theory of Non-Uniform Gases, Cambridge University Press, 3rd edition 1970), p. 98; R. E. Cunningham and R. J. J. Williams, Diffusion in Gases and Porous Media, Plenum Press, New York (1980), §6.4.


\(^4\) The Curtiss-Hirschfelder\(^4\) extension of the Chapman-Enskog theory to multicomponent gas mixtures, as well as the development of useful tables for computation, can be found in J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, Molecular Theory of Gases and Liquids, Wiley, New York, 2nd corrected printing (1964). See also C. F. Curtiss, J. Chem. Phys., 49, 2917–2919 (1968), as well as references given in Appendix E.

\(^5\) Joseph Oakland Hirschfelder (1911–1990), founding director of the Theoretical Chemistry Institute at the University of Wisconsin, specialized in intermolecular forces and applications of kinetic theory.
A rigorous kinetic theory of monatomic gases at low density was developed early in the twentieth century by Chapman in England and independently by Enskog in Sweden. The Chapman–Enskog theory gives expressions for the transport properties in terms of the intermolecular potential energy $\varphi(r)$, where $r$ is the distance between a pair of molecules undergoing a collision. The intermolecular force is then given by $F(r) = -d\varphi/dr$. The exact functional form of $\varphi(r)$ is not known; however, for nonpolar molecules a satisfactory empirical expression is the Lennard-Jones (6-12) potential given by

$$\varphi(r) = 4\varepsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6} \right]$$

(1.4-10)

in which $\sigma$ is a characteristic diameter of the molecules, often called the collision diameter and $\varepsilon$ is a characteristic energy, actually the maximum energy of attraction between a pair of molecules. This function, shown in Fig. 1.4-3, exhibits the characteristic features of intermolecular forces: weak attractions at large separations and strong repulsions at small separations. Values of the parameters $\sigma$ and $\varepsilon$ are known for many substances; a partial list is given in Table E.1, and a more extensive list is available elsewhere.\(^6\) When $\sigma$ and $\varepsilon$ are not known, they may be estimated from properties of the fluid at the critical point ($c$), the liquid at the normal boiling point ($b$), or the solid at the melting point ($m$), by means of the following empirical relations:\(^4\)

- $\varepsilon/\kappa = 0.77 T_c$ \quad $\sigma = 0.84 V_{b, \text{liq}}^{1/3}$ or $\sigma = 2.44 (T_c/p_c)^{1/3}$ (1.4-11a, b, c)
- $\varepsilon/\kappa = 1.15 T_b$ \quad $\sigma = 1.166 V_{b, \text{liq}}^{1/3}$ (1.4-12a, b)
- $\varepsilon/\kappa = 1.92 T_m$ \quad $\sigma = 1.222 V_{m, \text{sol}}^{1/3}$ (1.4-13a, b)

Here $\varepsilon/\kappa$ and $T$ are in K, $\sigma$ is in Ångström units ($1 \text{ Å} = 10^{-10} \text{ m}$), $V$ is in $\text{cm}^3/\text{g-mole}$, and $p_c$ is in atmospheres.

The viscosity of a pure monatomic gas of molecular weight $M$ may be written in terms of the Lennard-Jones parameters as

$$\mu = \frac{5}{16} \frac{\sqrt{\pi n k T}}{\pi \sigma^3 \Omega_n} \quad \text{or} \quad \mu = 2.6693 \times 10^{-5} \frac{\sqrt{MT}}{\sigma^3 \Omega_n}$$

(1.4-14)

---

In the second form of this equation, if \( T [= K \) and \( \sigma [= \text{Å} \), then \( \mu [= \text{g/cm} \cdot \text{s} \). The dimensionless quantity \( \Omega_\alpha \) is a slowly varying function of the dimensionless temperature \( kT/\varepsilon \), of the order of magnitude of unity, given in Table E.2. It is called the "collision integral for viscosity," because it accounts for the details of the paths that the molecules take during a binary collision. If the gas were made up of rigid spheres of diameter \( \sigma \) (instead of real molecules with attractive and repulsive forces), then \( \Omega_\mu \) would be exactly unity. Hence the function \( \Omega_\mu \) may be interpreted as describing the deviation from rigid-sphere behavior.

Although Eq. 1.4-14 is a result of the kinetic theory of monatomic gases, it has been found to be remarkably good for polyatomic gases as well. The reason for this is that, in the equation of conservation of momentum for a collision between polyatomic molecules, the center of mass coordinates are more important than the internal coordinates [see §0.3(b)]. The temperature dependence predicted by Eq. 1.4-14 is in good agreement with that found from the low-density line in the empirical correlation of Fig. 1.3-1. The viscosity of gases at low density increases with temperature, roughly as the 0.6 to 1.0 power of the absolute temperature, and is independent of the pressure.

To calculate the viscosity of a gas mixture, the multicomponent extension of the Chapman–Enskog theory can be used. Alternatively, one can use the following very satisfactory semiempirical formula:

\[
\mu_{\text{mix}} = \frac{x_\alpha \mu_\alpha}{\sum \mu_\beta \Phi_{\alpha\beta}}
\]

in which the dimensionless quantities \( \Phi_{\alpha\beta} \) are

\[
\Phi_{\alpha\beta} = \frac{1}{\sqrt{8}} \left( 1 + \frac{M_\alpha}{M_\beta} \right)^{-1/2} \left[ 1 + \left( \frac{\mu_\alpha}{\mu_\beta} \right)^{1/2} \left( \frac{M_\beta}{M_\alpha} \right)^{1/4} \right]^2
\]

Here \( N \) is the number of chemical species in the mixture, \( x_\alpha \) is the mole fraction of species \( \alpha \), \( \mu_\alpha \) is the viscosity of pure species \( \alpha \) at the system temperature and pressure, and \( M_\alpha \) is the molecular weight of species \( \alpha \). Equation 1.4-16 has been shown to reproduce measured values of the viscosities of mixtures within an average deviation of about 2%. The dependence of mixture viscosity on composition is extremely nonlinear for some mixtures, particularly mixtures of light and heavy gases (see Problem 1A.2).

To summarize, Eqs. 1.4-14, 15, and 16 are useful formulas for computing viscosities of nonpolar gases and gas mixtures at low density from tabulated values of the intermolecular force parameters \( \sigma \) and \( \varepsilon/k \). They will not give reliable results for gases consisting of polar or highly elongated molecules because of the angle-dependent force fields that exist between such molecules. For polar vapors, such as \( \text{H}_2\text{O}, \text{NH}_3, \text{CHOH}, \) and \( \text{NOCl} \), an angle-dependent modification of Eq. 1.4-10 has given good results. For the light gases \( \text{H}_2 \) and \( \text{He} \) below about 100K, quantum effects have to be taken into account.

Many additional empiricisms are available for estimating viscosities of gases and gas mixtures. A standard reference is that of Reid, Prausnitz, and Poling.\(^{10}\)

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Compute the viscosity of CO₂ at 200, 300, and 800 K and 1 atm.

**SOLUTION**

Use Eq. 1.4-14. From Table E.1, we find the Lennard-Jones parameters for CO₂ to be \( \varepsilon/\kappa = 190 \) K and \( \sigma = 3.996 \) Å. The molecular weight of CO₂ is 44.01. Substitution of \( M \) and \( \sigma \) into Eq. 1.4-14 gives

\[
\mu = 2.6693 \times 10^{-5} \frac{\sqrt{44.01T}}{(3.996^2\Omega_\mu)} = 1.109 \times 10^{-5} \frac{\sqrt{T}}{\Omega_\mu}
\]

in which \( \mu \) [=] g/cm · s and \( T \) [=] K. The remaining calculations may be displayed in a table.

<table>
<thead>
<tr>
<th>( T ) (K)</th>
<th>( \kappa T/\epsilon )</th>
<th>( \Omega_\mu )</th>
<th>( \sqrt{T} )</th>
<th>Predicted</th>
<th>Observed(^{11})</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td>1.053</td>
<td>1.548</td>
<td>14.14</td>
<td>1.013 \times 10^{-4}</td>
<td>1.015 \times 10^{-4}</td>
</tr>
<tr>
<td>300</td>
<td>1.582</td>
<td>1.286</td>
<td>17.32</td>
<td>1.494 \times 10^{-4}</td>
<td>1.495 \times 10^{-4}</td>
</tr>
<tr>
<td>800</td>
<td>4.212</td>
<td>0.9595</td>
<td>28.28</td>
<td>3.269 \times 10^{-4}</td>
<td>⋯</td>
</tr>
</tbody>
</table>

Experimental data are shown in the last column for comparison. The good agreement is to be expected, since the Lennard-Jones parameters of Table E.1 were derived from viscosity data.

Estimate the viscosity of the following gas mixture at 1 atm and 293 K from the given data on the pure components at the same pressure and temperature:

<table>
<thead>
<tr>
<th>Species ( \alpha )</th>
<th>Mole fraction, ( x_\alpha )</th>
<th>Molecular weight, ( M_\alpha ) (g/cm · s)</th>
<th>Viscosity, ( \mu_\alpha ) (g/cm · s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. CO₂</td>
<td>0.133</td>
<td>44.01</td>
<td>1462 \times 10^{-7}</td>
</tr>
<tr>
<td>2. O₂</td>
<td>0.039</td>
<td>32.00</td>
<td>2031 \times 10^{-7}</td>
</tr>
<tr>
<td>3. N₂</td>
<td>0.828</td>
<td>28.02</td>
<td>1754 \times 10^{-7}</td>
</tr>
</tbody>
</table>

**SOLUTION**

Use Eqs. 1.4-16 and 15 (in that order). The calculations can be systematized in tabular form, thus:

\[
\begin{align*}
\alpha & \quad \beta & \quad M_\alpha/M_\beta & \quad \mu_\alpha/\mu_\beta & \quad \Phi_{\alpha\beta} & \quad \sum_{\beta=1}^{3} x_\beta \Phi_{\alpha\beta} \\
1. & \quad 1 & \quad 1.00 & \quad 1.00 & \quad 1.00 & \quad 1.00 \\
2. & \quad 1 & \quad 1.375 & \quad 0.720 & \quad 0.730 & \quad 0.763 \\
3. & \quad 1 & \quad 1.571 & \quad 0.834 & \quad 0.727 & \quad 0.763 \\
1. & \quad 2 & \quad 0.727 & \quad 1.389 & \quad 1.394 & \quad 1.057 \\
2. & \quad 2 & \quad 1.00 & \quad 1.00 & \quad 1.00 & \quad 1.006 \\
3. & \quad 2 & \quad 1.142 & \quad 1.158 & \quad 1.006 & \quad 1.006 \\
1. & \quad 3 & \quad 0.637 & \quad 1.200 & \quad 1.370 & \quad 1.049 \\
2. & \quad 3 & \quad 0.876 & \quad 0.864 & \quad 0.993 & \quad 1.049 \\
3. & \quad 3 & \quad 1.000 & \quad 1.000 & \quad 1.000 & \quad 1.000 \\
\end{align*}
\]

\[ \mu = \frac{(0.1333)(1462)(10^{-7})}{0.763} + \frac{(0.039)(2031)(10^{-7})}{1.057} + \frac{(0.828)(1754)(10^{-7})}{1.049} \]
\[ = 1714 \times 10^{-7} \text{ g/cm} \cdot \text{s} \]

The observed value \(^1\) is \(1793 \times 10^{-7} \text{ g/cm} \cdot \text{s}\).

§1.5 MOLECULAR THEORY OF THE VISCOSITY OF LIQUIDS

A rigorous kinetic theory of the transport properties of monatomic liquids was developed by Kirkwood and coworkers.\(^1\) However this theory does not lead to easy-to-use results. An older theory, developed by Eyring\(^2\) and coworkers, although less well grounded theoretically, does give a qualitative picture of the mechanism of momentum transport in liquids and permits rough estimation of the viscosity from other physical properties. We discuss this theory briefly.

In a pure liquid at rest the individual molecules are constantly in motion. However, because of the close packing, the motion is largely confined to a vibration of each molecule within a “cage” formed by its nearest neighbors. This cage is represented by an energy barrier of height \(\Delta G_0^*/N\), in which \(\Delta G_0^*\) is the molar free energy of activation for escape from the cage in the stationary fluid (see Fig. 1.5-1). According to Eyring, a liquid at rest continually undergoes rearrangements, in which one molecule at a time escapes from its “cage” into an adjoining “hole,” and that the molecules thus move in each of the


coordinate directions in jumps of length \( a \) at a frequency \( \nu \) per molecule. The frequency is given by the rate equation

\[
\nu = \frac{kT}{h} \exp\left(-\frac{\Delta G_0^+}{RT}\right)
\]  

(1.5-1)

In which \( k \) and \( h \) are the Boltzmann and Planck constants, \( \tilde{N} \) is the Avogadro number, and \( R = \tilde{N}k \) is the gas constant (see Appendix F).

In a fluid that is flowing in the \( x \) direction with a velocity gradient \( dv_x/dy \), the frequency of molecular rearrangements is increased. The effect can be explained by considering the potential energy barrier as distorted under the applied stress \( \tau_{yx} \) (see Fig. 1.5-1), so that

\[
-\Delta \tilde{G}^+ = -\Delta G_0^+ \pm \left( \frac{a}{\delta} \right) \left( \tau_{yx} \frac{\tilde{V}}{2} \right)
\]  

(1.5-2)

where \( \tilde{V} \) is the volume of a mole of liquid, and \( \pm (a/\delta)(\tau_{yx} \tilde{V}/2) \) is an approximation to the work done on the molecules as they move to the top of the energy barrier, moving with the applied shear stress (plus sign) or against the applied shear stress (minus sign). We now define \( \nu_+ \) as the frequency of forward jumps and \( \nu_- \) as the frequency of backward jumps. Then from Eqs. 1.5-1 and 1.5-2 we find that

\[
\nu_+ = \frac{kT}{h} \exp\left(-\frac{\Delta G_0^+}{RT}\right) \exp\left(\pm a\tau_{yx} \tilde{V}/2\delta RT\right)
\]  

(1.5-3)

The net velocity with which molecules in layer \( A \) slip ahead of those in layer \( B \) (Fig. 1.5-1) is just the distance traveled per jump \( a \) times the net frequency of forward jumps \( (\nu_+ - \nu_-) \); this gives

\[
v_{v_A} - v_{v_B} = a(\nu_+ - \nu_-)
\]  

(1.5-4)

The velocity profile can be considered to be linear over the very small distance \( \delta \) between the layers \( A \) and \( B \), so that

\[
-\frac{dv_x}{dy} = a \left( \frac{\nu_+ - \nu_-}{\delta} \right)
\]  

(1.5-5)

By combining Eqs. 1.5-3 and 5, we obtain finally

\[
-\frac{dv_x}{dy} = \left( \frac{a}{\delta} \right) \left( \frac{kT}{h} \exp\left(-\frac{\Delta G_0^+}{RT}\right) \right) \left( \exp\left(\pm a\tau_{yx} \tilde{V}/2\delta RT\right) - \exp\left(-a\tau_{yx} \tilde{V}/2\delta RT\right) \right)
\]  

(1.5-6)

This predicts a nonlinear relation between the shear stress (momentum flux) and the velocity gradient—that is, non-Newtonian flow. Such nonlinear behavior is discussed further in Chapter 8.

The usual situation, however, is that \( a\tau_{yx} \tilde{V}/2\delta RT << 1 \). Then we can use the Taylor series (see §C.2) \( \sinh x = x + (1/3!)x^3 + (1/5!)x^5 + \cdots \) and retain only one term. Equation 1.5-6 is then of the form of Eq. 1.1-2, with the viscosity being given by

\[
\mu = \left( \frac{\delta}{a} \right)^2 \frac{\tilde{N}h}{\tilde{V}} \exp\left(\Delta G_0^+ / RT\right)
\]  

(1.5-7)

The factor \( \delta/a \) can be taken to be unity; this simplification involves no loss of accuracy, since \( \Delta G_0^+ \) is usually determined empirically to make the equation agree with experimental viscosity data.

It has been found that free energies of activation, \( \Delta G_0^+ \), determined by fitting Eq. 1.5-7 to experimental data on viscosity versus temperature, are almost constant for a given
§1.6 Viscosity of Suspensions and Emulsions

fluid and are simply related to the internal energy of vaporization at the normal boiling point, as follows:3

\[ \Delta \tilde{G}_V = 0.408 \Delta \tilde{U}_{\text{vap}} \]  

(1.5-8)

By using this empiricism and setting \( \delta /a = 1 \), Eq. 1.5-7 becomes

\[ \mu = \frac{\tilde{N}h}{V} \exp \left( 0.408 \frac{\Delta \tilde{U}_{\text{vap}}}{RT} \right) \]  

(1.5-9)

The energy of vaporization at the normal boiling point can be estimated roughly from Trouton's rule

\[ \Delta \tilde{U}_{\text{vap}} \approx \Delta H_{\text{vap}} - RT_b = 9.4RT_b \]  

(1.5-10)

With this further approximation, Eq. 1.5-9 becomes

\[ \mu = \frac{\tilde{N}h}{V} \exp (3.8T_b/T) \]  

(1.5-11)

Equations 1.5-9 and 11 are in agreement with the long-used and apparently successful empiricism \( \mu = A \exp(B/T) \). The theory, although only approximate in nature, does give the observed decrease of viscosity with temperature, but errors of as much as 30% are common when Eqs. 1.5-9 and 11 are used. They should not be used for very long slender molecules, such as \( \text{n-C}_{25}\text{H}_{42} \).

There are, in addition, many empirical formulas available for predicting the viscosity of liquids and liquid mixtures. For these, physical chemistry and chemical engineering textbooks should be consulted.4

Estimate the viscosity of liquid benzene, \( \text{C}_6\text{H}_6 \), at 20°C (293.2K).

**SOLUTION**

Use Eq. 1.5-11 with the following information:

\[ \tilde{V} = 89.0 \text{ cm}^3/\text{g} - \text{mole} \]
\[ T_b = 80.1^\circ \text{C} \]

Since this information is given in c.g.s. units, we use the values of Avogadro's number and Planck's constant in the same set of units. Substituting into Eq. 1.5-11 gives:

\[ \mu = \frac{(6.023 \times 10^{23})(6.624 \times 10^{-27})}{(89.0)} \exp \left( \frac{3.8 \times (273.2 + 80.1)}{293.2} \right) \]

\[ = 4.5 \times 10^{-3} \text{ g/cm} \cdot \text{s} \text{ or } 4.5 \times 10^{-4} \text{ Pa} \cdot \text{s} \text{ or } 0.45 \text{ mPa} \cdot \text{s} \]

§1.6 VISCOSITY OF SUSPENSIONS AND EMULSIONS

Up to this point we have been discussing fluids that consist of a single homogeneous phase. We now turn our attention briefly to two-phase systems. The complete description of such systems is, of course, quite complex, but it is often useful to replace the suspension or emulsion by a hypothetical one-phase system, which we then describe by

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