INTRODUCTION

The profession of chemical engineering was created to fill a pressing need. In the latter part of the nineteenth century the rapidly increasing growth complexity and size of the world’s chemical industries outstripped the abilities of chemists alone to meet their ever-increasing demands. It became apparent that an engineer working closely in concert with the chemist could be the key to the problem. This engineer was destined to be a chemical engineer.

From the earliest days of the profession, chemical engineering education has been characterized by an exceptionally strong grounding in both chemistry and chemical engineering. Over the years the approach to the latter has gradually evolved; at first, the chemical engineering program was built around the concept of studying individual processes (i.e., manufacture of sulfuric acid, soap, caustic, etc.). This approach, unit processes, was a good starting point and helped to get chemical engineering off to a running start.

After some time it became apparent to chemical engineering educators that the unit processes had many operations in common (heat transfer, distillation, filtration, etc.). This led to the concept of thoroughly grounding the chemical engineer in these specific operations and the introduction of the unit operations approach. Once again, this innovation served the profession well, giving its practitioners the understanding to cope with the ever-increasing complexities of the chemical and petroleum process industries.

As the educational process matured, gaining sophistication and insight, it became evident that the unit operations in themselves were mainly composed of a smaller subset of transport processes (momentum, energy, and mass transfer). This realization generated the transport phenomena approach — an approach
TRANSPORT PROCESSES AND TRANSPORT COEFFICIENTS

that owes much to the classic chemical engineering text of Bird, Stewart, and Lightfoot (1).

There is no doubt that modern chemical engineering is indebted to the transport phenomena approach. However, at the same time there is still much that is important and useful in the unit operations approach. Finally, there is another totally different need that confronts chemical engineering education — namely, the need for today’s undergraduates to have the ability to translate their formal education to engineering practice.

This text is designed to build on all of the foregoing. Its purpose is to thoroughly ground the student in basic principles (the transport processes); then to move from theoretical to semiempirical and empirical approaches (carefully and clearly indicating the rationale for these approaches); next, to synthesize an orderly approach to certain of the unit operations; and, finally, to move in the important direction of engineering practice by dealing with the analysis and design of equipment and processes.

THE PHENOMENOLOGICAL APPROACH; FLUXES, DRIVING FORCES, SYSTEMS COEFFICIENTS

In nature, the trained observer perceives that changes occur in response to imbalances or driving forces. For example, heat (energy in motion) flows from one point to another under the influence of a temperature difference. This, of course, is one of the basics of the engineering science of thermodynamics.

Likewise, we see other examples in such diverse cases as the flow of (respectively) mass, momentum, electrons, and neutrons.

Hence, simplistically we can say that a flux (see Figure 1-1) occurs when there is a driving force. Furthermore, the flux is related to a gradient by some characteristic of the system itself — the system or transport coefficient.

\[
\text{Flux} = \frac{\text{Flow quantity}}{(\text{Time})(\text{Area})} = (\text{Transport coefficient})(\text{Gradient}) \quad (1-1)
\]

The gradient for the case of temperature for one-dimensional (or directional) flow of heat is expressed as

\[
\text{Temperature gradient} = \frac{dT}{dY} \quad (1-2)
\]

The flux equations can be derived by considering simple one-dimensional models. Consider, for example, the case of energy or heat transfer in a slab (originally at a constant temperature, \(T_1\)) shown in Figure 1-2. Here, one of the opposite faces of the slab suddenly has its temperature increased to \(T_2\). The result is that heat flows from the higher to the lower temperature region. Over a period of time the temperature profile in the solid slab will change until the linear (steady-state) profile is reached (see Figure 1-2). At this point the rate of heat
flow \( Q \) per unit area \( A \) will be a function of the system’s transport coefficient (\( k \), thermal conductivity) and the driving force (temperature difference) divided by distance. Hence

\[
\frac{Q}{A} = k \frac{(T_1 - T_2)}{(X - O)}
\]  

(1-3)
If the above equation is put into differential form, the result is

\[ q_x = -k \frac{dT}{dx} \quad (1-4) \]

This result applies to gases and liquids as well as solids. It is the one-dimensional form of Fourier’s Law which also has \( y \) and \( z \) components

\[ q_y = -k \frac{dT}{dy} \quad (1-5) \]

\[ q_z = -k \frac{dT}{dz} \quad (1-6) \]

Thus heat flux is a vector. Units of the heat flux (depending on the system chosen) are BTU/hr ft\(^2\), calories/sec cm\(^2\), and W/m\(^2\).

Let us consider another situation: a liquid at rest between two plates (Figure 1-3). At a given time the bottom plate moves with a velocity \( V \). This causes the fluid in its vicinity to also move. After a period of time with unsteady flow we attain a linear velocity profile that is associated with steady-state flow. At steady state a constant force \( F \) is needed. In this situation

\[ \frac{F}{A} = -\mu \frac{O - V}{Y - O} \quad (1-7) \]

where \( \mu \) is the fluid’s viscosity (i.e., transport coefficient).

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**Figure 1-3.** Velocity profile development for steady laminar flow. (Adapted with permission from reference 1. Copyright 1960, John Wiley and Sons.)
Hence the $F/A$ term is the flux of momentum (because force $= d$(momentum)/$dt$). If we use the differential form (converting $F/A$ to a shear stress $\tau$), then we obtain

$$
\tau_{yx} = -\mu \frac{dV_x}{dy}
$$

(1-8)

Units of $\tau_{yx}$ are poundals/ft$^2$, dynes/cm$^2$, and Newtons/m$^2$.

This expression is known as Newton’s Law of Viscosity. Note that the shear stress is subscripted with two letters. The reason for this is that momentum transfer is not a vector (three components) but rather a tensor (nine components).

As such, momentum transport, except for special cases, differs considerably from heat transfer.

Finally, for the case of mass transfer because of concentration differences we cite Fick’s First Law for a binary system:

$$
J_{Ay} = -D_{AB} \frac{dC_A}{dy}
$$

(1-9)

where $J_{Ay}$ is the molar flux of component $A$ in the $y$ direction. $D_{AB}$, the diffusivity of $A$ in $B$ (the other component), is the applicable transport coefficient.

As with Fourier’s Law, Fick’s First Law has three components and is a vector. Because of this there are many analogies between heat and mass transfer as we will see later in the text. Units of the molar flux are lb moles/hr ft$^2$, g mole/sec cm$^2$, and kg mole/sec m$^2$.

THE TRANSPORT COEFFICIENTS

We have seen that the transport processes (momentum, heat, and mass) each involve a property of the system (viscosity, thermal conductivity, diffusivity). These properties are called the transport coefficients. As system properties they are functions of temperature and pressure.

Expressions for the behavior of these properties in low-density gases can be derived by using two approaches:

1. The kinetic theory of gases
2. Use of molecular interactions (Chapman–Enskog theory).

In the first case the molecules are rigid, nonattracting, and spherical. They have

1. A mass $m$ and a diameter $d$
2. A concentration $n$ (molecules/unit volume)
3. A distance of separation that is many times $d$. 
This approach gives the following expression for viscosity, thermal conductivity, and diffusivity:

\[ \mu = \frac{2}{3\pi^{3/2}} \frac{\sqrt{mKT}}{d^2} \]  

\[ k = \frac{1}{d^2} \sqrt{\frac{K^3T}{\pi^3m}} \]  

where the gas is monatomic.

\[ D_{AB} = \frac{2}{3} \left( \frac{K^3}{\pi^3} \right)^{1/2} \left( \frac{1}{2m_A} + \frac{1}{2m_B} \right)^{1/2} \frac{T^{3/2}}{P \left( \frac{d_A + d_B}{2} \right)^2} \]  

The subscripts A and B refer to gas A and gas B.

If molecular interactions are considered (i.e., the molecules can both attract and repel) a different set of relations are derived. This approach involves relating the force of interaction, \( F \), to the potential energy \( \phi \). The latter quantity is represented by the Lennard-Jones (6–12) potential (see Figure 1-4)

\[ \phi(r) = 4\epsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6} \right] \]

where \( \sigma \) is the collision diameter (a characteristic diameter) and \( \epsilon \) a characteristic energy of interaction (see Table A-3-3 in Appendix for values of \( \sigma \) and \( \epsilon \)).

The Lennard-Jones potential predicts weak molecular attraction at great distances and ultimately strong repulsion as the molecules draw closer.

Resulting equations for viscosity, thermal conductivity, and diffusivity using the Lennard-Jones potential are

\[ \mu = 2.6693 \times 10^{-6} \frac{\sqrt{MT}}{\sigma^2 \Omega \mu} \]  

where \( \mu \) is in units of kg/m sec or pascal-seconds, \( T \) is in °K, \( \sigma \) is in Å, the \( \Omega \mu \) is a function of \( KT/\epsilon \) (see Appendix), and \( M \) is molecular weight.

\[ k = 0.8322 \frac{\sqrt{T/M}}{\sigma^2 \Omega_k} \]  

where \( k \) is in W/m °K, \( \sigma \) is in Å, and \( \Omega_k = \Omega \mu \). The expression is for a monatomic gas.

\[ D_{AB} = 1.8583 \times 10^{-7} \frac{\sqrt{T^3(1/M_A + 1/M_B)}}{P \sigma_{AB}^2 \Omega D_{AB}} \]  

where \( \sigma_{AB} \) is the Lennard-Jones collision diameter (see Figure 1-4) and \( \Omega D_{AB} \) a function of the Lennard-Jones potential (see Appendix).
where $D_{AB}$ is units of $m^2/sec$, $P$ is in atmospheres, $\sigma_{AB} = \frac{1}{2}(\sigma_A + \sigma_B)$, $\varepsilon_{AB} = \varepsilon_A\varepsilon_B$, and $\Omega_{DAB}$ is a function of $KT/\varepsilon_{AB}$ (see Appendix B, Table A-3-4).

Example 1-1 The viscosity of isobutane at 23°C and atmospheric pressure is $7.6 \times 10^{-6}$ pascal-sec. Compare this value to that calculated by the Chapman–Enskog approach.

From Table A-3-3 of Appendix A we have

$$\sigma = 5.341 \text{ Å}, \quad \varepsilon/K = 313 \text{ K}$$

Then, $KT/\varepsilon = 296.16/313 = 0.946$ and from Table A-3-4 of Appendix B we obtain

$$\Omega_{\mu} = 1.634$$

$$\mu = 2.6693 \times 10^{-6} \frac{\sqrt{MT}}{\sigma^2 \Omega_{\mu}}$$

$$\mu = 2.6693 \times 10^{-6} \frac{\sqrt{(58.12)(296.16)}}{(5.341)^2(1.634)}$$
\[ \mu = 7.51 \times 10^{-6} \text{ pascal-sec} \]
\[ \% \text{ error} = \left[ \frac{(7.6 - 7.51)}{7.6} \right] \times 100 = 1.18\% \]

**Example 1-2** Calculate the diffusivity for the methane–ethane system at 104°F and 14.7 psia.

\[ T = \frac{104 + 460}{1.8} ^\circ \text{K} = 313^\circ \text{K} \]

Let methane be A and let ethane be B. Then,

\[ \left( \frac{1}{M_A} + \frac{1}{M_B} \right) = \left( \frac{1}{16.04} + \frac{1}{30.07} \right) = 0.0956 \]

From Table A in the Appendix we have

- \( \sigma_A = 3.822 \text{ Å} \)
- \( \sigma_B = 4.418 \text{ Å} \)
- \( \frac{\epsilon_A}{K} = 137^\circ \text{K} \)
- \( \frac{\epsilon_B}{K} = 230^\circ \text{K} \)
- \( \sigma_{AB} = \frac{1}{2}(\sigma_A + \sigma_B) = \frac{1}{2}(3.822 + 4.418) \text{ Å} = 4.120 \text{ Å} \)
- \( \frac{\epsilon_{AB}}{K} = \sqrt{\left( \frac{\epsilon_A}{K} \right) \left( \frac{\epsilon_B}{K} \right)} = \sqrt{(137^\circ \text{K})(230^\circ \text{K})} = 177.5^\circ \text{K} \)
- \( \frac{KT}{\epsilon_{AB}} = \frac{313}{177.5} = 1.763 \)

From Table A-3-4 in Appendix we have \( \Omega_{DAB} = 1.125 \)

\[ D_{AB} = \frac{1.8583 \times 10^{-7} \sqrt{T^3(1/M_A + 1/M_B)}}{P\sigma_{AB}^2\Omega_{DAB}} \]

\[ D_{AB} = \frac{1.8583 \times 10^{-7} \sqrt{(313^\circ \text{K})^3(0.0956)}}{(1)(4.120)^2(1.125)} \]

\[ D_{AB} = 1.66 \times 10^{-5} \text{ m}^2/\text{sec} \]

The actual value is \( 1.84 \times 10^{-5} \text{ m}^2/\text{sec} \). Percent error is 9.7 percent.

**TRANSPORT COEFFICIENT BEHAVIOR FOR HIGH DENSITY GASES AND MIXTURES OF GASES**

If gaseous systems have high densities, both the kinetic theory of gases and the Chapman–Enskog theory fail to properly describe the transport coefficients’ behavior. Furthermore, the previously derived expression for viscosity and
thermal conductivity apply only to pure gases and not to gas mixtures. The typical approach for such situations is to use the theory of corresponding states as a method of dealing with the problem.

Figures 1-5, 1-6, 1-7, and 1-8 give correlation for viscosity and the thermal conductivity of monatomic gases. One set (Figures 1-5 and 1-7) are plots of the
Figure 1-6. Modified reduced viscosity as a function of reduced temperature and pressure \((3)\). (Trans. Am. Inst. Mining, Metallurgical and Petroleum Engrs 201 1954 pp 264 ff; N. L. Carr, R. Kobayashi, D.B. Burrows.)

Reduced viscosity \(\mu/\mu_c\), where \(\mu_c\) is the viscosity at the critical point) or reduced thermal conductivity \(k/k_c\) versus \((T/T_c)\), reduced temperature, and \((p/p_c)\) reduced pressure. The other set are plots of viscosity and thermal conductivity divided by the values \((\mu_0, k_0)\) at atmospheric pressure and the same temperature.
Values of $\mu_c$ can be estimated from the empirical relations

\[ \mu_c = 61.6 \frac{(MT_c)^{1/2}}{(V_c)^{2/3}} \]  \hspace{1cm} (1-17)

\[ \mu_c = \frac{7.70 \, M^{1/2} \, P_c^{2/3}}{(T_c)^{1/6}} \]  \hspace{1cm} (1-18)
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Reduced pressure, \( p_r = p/p_c \)

Reduced thermal conductivity, \( k' = k/k_0 \)

Reduced pressure, \( p_r = p/p_c \)

Figure 1-8. Modified reduced thermal conductivity as a function of reduced temperature and pressure. (Reproduced with permission from reference 5. Copyright 1953, American Institute of Chemical Engineers.)

where \( \mu_c \) is in micropoises, \( T_c \) is in \( ^\circ \text{K} \), \( P_c \) in atmospheres, and \( \hat{V}_c \) is in \( \text{cm}^3/\text{g mole} \).

The viscosity and thermal conductivity behavior of mixtures of gases at low densities is described semiempirically by the relations derived by Wilke (6) for viscosity and by Mason and Saxena (7) for thermal conductivity:

\[
\mu_{\text{mix}} = \sum_{i=1}^{n} \frac{y_i \mu_i}{\sum_{j=1}^{n} y_j \Phi_{ij}} \quad (1-19)
\]

\[
\phi_{ij} = \frac{1}{8} \left( 1 + \frac{M_i}{M_j} \right)^{-1/2} \left[ 1 + \left( \frac{\mu_i}{\mu_j} \right)^{1/2} \left( \frac{M_j}{M_i} \right)^{1/4} \right] \quad (1-20)
\]

\[
k_{\text{mix}} = \sum_{i=1}^{n} \frac{y_i k_i}{\sum_{j=1}^{n} y_j \Phi_{ij}} \quad (1-21)
\]
The $$\Phi_{ij}$$’s in equation (1-21) are given by equation (1-20). The $$y$$’s refer to the mole fractions of the components.

For mixtures of dense gases the pseudocritical method is recommended. Here the critical properties for the mixture are given by

$$P'_{c} = \sum_{i=1}^{n} y_i P_{ci} \quad (1-22)$$

$$T'_{c} = \sum_{i=1}^{n} y_i T_{ci} \quad (1-23)$$

$$\mu'_{c} = \sum_{i=1}^{n} y_i \mu_{ci} \quad (1-24)$$

where $$y_i$$ is a mole fraction; $$P_{ci}$$, $$T_{ci}$$, and $$\mu_{ci}$$ are pure component values. These values are then used to determine the $$P_R$$ and $$T_R$$ values needed to obtain ($$\mu/\mu_i$$) from Figure 1-5.

The same approach can be used for the thermal conductivity with Figure 1-7 if $$k_c$$ data are available or by using a $$k^0$$ value determined from equation (1-15).

Behavior of diffusivities is not as easily handled as the other transport coefficients. The combination ($$D_{AB}$$) is essentially a constant up to about 150 atm pressure. Beyond that, the only available correlation is the one developed by Slattery and Bird (8). This, however, should be used only with great caution because it is based on very limited data (8).

**Example 1-3** Compare estimates of the viscosity of CO$_2$ at 114.6 atm and 40.3°C using

1. Figure 1-6 and an experimental viscosity value of $1800 \times 10^{-8}$ pascal-sec for CO$_2$ at 45.3 atm and 40.3°C
2. The Chapman–Enskog relation and Figure 1-6.

From Table A-3-3 of Appendix A, $$T_c = 304.2^\circ$$K and $$P_c = 72.9$$ atmospheres. For the first case we have

$$T_R = \frac{313.46}{304.2} = 1.03, \quad P_R = \frac{45.3}{72.9} = 0.622$$

so that $$\mu^0 = 1.12$$ and

$$\mu_0 = \frac{\mu}{\mu^0} = \frac{1800 \times 10^{-8}}{1.12} \text{ pascal-sec} = 1610 \times 10^{-8} \text{ pascal-sec}$$

For $$P = 114.6 \text{ atm}$$ we have

$$P_R = \frac{114.6}{72.9} = 1.57, \quad T_R = 1.03$$
so that \( \mu^* = 3.7 \) and

\[
\mu = \mu^* \mu_0 = (3.7)(1610 \times 10^{-8} \text{ pascal-sec}) = 6000 \times 10^{-8} \text{ pascal-sec}
\]

For the second case, from Table A-3-3 of Appendix we have

\[
M = 44.01, \quad \sigma = 3.996 \text{ Å}, \quad \frac{\varepsilon}{k} = 190\text{°K}
\]

and

\[
\frac{KT}{\varepsilon} = \frac{313.46}{190} = 1.65
\]

so that from Table A-3-4 of Appendix and \( \Omega_\mu = 1.264 \) we obtain

\[
\mu = 2.6693 \times 10^{-6} \frac{\sqrt{\frac{MT}{\sigma^2 \Omega_\mu}}}{1553 \times 10^{-8} \text{ pascal-sec}}
\]

\[
\mu = 2.6693 \times 10^{-6} \frac{(44.01)(313.46)}{(3.996)^2(1.264)} = 1553 \times 10^{-8} \text{ pascal-sec}
\]

From Figure 1-6, \( \mu^* \) is still 3.7 so that

\[
\mu = (3.7)(1553 \times 10 \text{ pascal-sec}) = 5746 \times 10^{-8} \text{ pascal-sec}
\]

The actual experimental value is \( 5800 \times 10^{-8} \text{ pascal-sec} \). Percent errors for case 1 and case 2 are 3.44\% and 0.93\%, respectively.

**Example 1-4** Estimate the viscosity of a gas mixture of CO\(_2\) \((y = 0.133)\); O\(_2\) \((y = 0.039)\); N\(_2\) \((y = 0.828)\) at 1 atm and 293\°K by using

1. Figure 1-5 and the pseudocritical concept
2. Equations (1-19) and (1-20) with pure component viscosities of 1462, 2031, and \( 1754 \times 10^{-8} \text{ pascal-sec} \), respectively, for CO\(_2\), O\(_2\), and N\(_2\).

In the first case the values of \( T_c, P_c, \) and \( \mu_c \) (from Table A-3-3 of Appendix) are as follows:

<table>
<thead>
<tr>
<th>( T_c (^\circ K) )</th>
<th>( P_c ) (atmospheres)</th>
<th>( \mu_c ) (pascal-seconds)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO(_2) 304.2</td>
<td>72.9</td>
<td>3430 \times 10^{-8}</td>
</tr>
<tr>
<td>O(_2) 154.4</td>
<td>49.7</td>
<td>2500 \times 10^{-8}</td>
</tr>
<tr>
<td>N(_2) 126.2</td>
<td>33.5</td>
<td>1800 \times 10^{-8}</td>
</tr>
</tbody>
</table>
TRANSPORT COEFFICIENT BEHAVIOR

\[ T'_c = (0.133)(304.2^\circ K) + (0.039)(154.4^\circ K) + (0.828)(126.2^\circ K) \]

\[ T'_c = 150.97^\circ K \]

\[ P'_c = [(0.133)(72.9) + (0.039)(49.7) + (0.828)(33.5)] \text{ atm} \]

\[ P'_c = 39.37 \text{ atmospheres} \]

\[ \mu'_c = [(0.133)(3430) + (0.039)(2500) + (0.828)(1800)] \times 10^{-8} \text{ pascal-sec} \]

\[ \mu'_c = 2044.1 \times 10^{-8} \text{ pascal-sec} \]

Then

\[ T'_R = \frac{293}{150.97} = 1.94, \quad P'_R = \frac{1}{39.37} = 0.025 \]

From Figure 1-5 we have

\[ \mu'_R = \frac{\mu}{\mu'_c} = 0.855 \]

\[ \mu = (0.855)(2044.1 \times 10^{-8} \text{ pascal-sec}) = 1747.7 \times 10^{-8} \text{ pascal-sec} \]

For case 2, let \( \text{CO}_2 = 1, \text{O}_2 = 2, \) and \( \text{N}_2 = 3. \) Then:

<table>
<thead>
<tr>
<th>( i )</th>
<th>( j )</th>
<th>( M_i/M_j )</th>
<th>( M_i/M_j )</th>
<th>( \Phi_{ij} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
</tr>
<tr>
<td>2</td>
<td>1.38</td>
<td>0.72</td>
<td>0.73</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>1.57</td>
<td>0.83</td>
<td>0.73</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>0.73</td>
<td>1.39</td>
<td>1.39</td>
</tr>
<tr>
<td>2</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>1.14</td>
<td>1.16</td>
<td>1.04</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>0.64</td>
<td>1.20</td>
<td>1.37</td>
</tr>
<tr>
<td>2</td>
<td>0.88</td>
<td>0.86</td>
<td>0.94</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
<td></td>
</tr>
</tbody>
</table>

\[
\mu_{\text{mix}} = \sum_{i=1}^{3} \frac{Y_i \mu_i}{\sum_{j=1}^{3} Y_j \Phi_{ij}}
\]

\[
\mu_{\text{mix}} = \left[ \frac{(0.133)(1462)}{(0.76)} + \frac{(0.039)(2031)}{(1.06)} + \frac{(0.828)(1754)}{(1.05)} \right] \times 10^{-8} \text{ pascal-sec}
\]

\[ \mu_{\text{mix}} = 1714 \times 10^{-8} \text{ pascal-sec} \]
Actual experimental value of the mixture viscosity is $1793 \times 10^{-8}$ pascal-sec. The percent errors are 2.51 and 4.41%, respectively, for cases 1 and 2.

**TRANSPORT COEFFICIENTS IN LIQUID AND SOLID SYSTEMS**

In general, the understanding of the behavior of transport coefficients in gases is far greater than that for liquid systems. This can be partially explained by seeing that liquids are much more dense than gases. Additionally, theoretical and experimental work for gases is far more voluminous than for liquids. In any case the net result is that approaches to transport coefficient behavior in liquid systems are mainly empirical in nature.

An approach used for liquid viscosities is based on an application of the Eyring (9,10) activated rate theory. This yields an expression of the form

$$\mu = \frac{Nh}{V} \exp \left(\frac{0.408\Delta U_{vap}}{RT} \right)$$

(1-25)

where $N$ is Avogadro’s number, $h$ is Planck’s constant, $V$ is the molar volume, and $\Delta U_{vap}$ is the molar internal energy change at the liquid’s normal boiling point.

The Eyring equation is at best an approximation; thus it is recommended that liquid viscosities be estimated using the nomograph given in Figure B-1 of the appendix.

For thermal conductivity the theory of Bridgman (11) yielded

$$k = 2.80 \left(\frac{\tilde{N}}{V}\right)^{2/3} \tilde{K} V_S$$

(1-26)

where $V_S$ the sonic velocity, is

$$V_S = \sqrt{\frac{C_P}{C_V} \left(\frac{\partial P}{\partial \rho} \right)_T}$$

(1-27)

The foregoing expressions for both viscosity and thermal conductivity are for pure liquids. For mixtures it is recommended that the pseudocritical method be used where possible with liquid regions of Figures 1-5 through 1-8.

Diffusivities in liquids can be treated by the Stokes–Einstein equation

$$\frac{D_{AB}\mu_B}{KT} = \frac{1}{4\pi R_A}$$

(1-28)

where $R_A$ is the diffusing species radius and $\mu_B$ is the solvent viscosity.
Table 1-1 Association Parameters

<table>
<thead>
<tr>
<th>Solvent System</th>
<th>$\psi_B$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>2.6</td>
</tr>
<tr>
<td>Methanol</td>
<td>1.9</td>
</tr>
<tr>
<td>Ethanol</td>
<td>1.5</td>
</tr>
<tr>
<td>Unassociated</td>
<td>1.0</td>
</tr>
<tr>
<td>Solvents (ether, benzene, etc.)</td>
<td></td>
</tr>
</tbody>
</table>

Another approach (for dilute solutions) is to use the correlation of Wilke and Chang (12):

$$D_{AB} = 7.4 \times 10^{-8} \frac{(\psi_B M_B)^{1/2} T}{\mu V_A^{0.6}}$$  \hspace{1cm} (1-29)

where $\hat{V}_A$ is the diffusing species molar volume at its normal boiling point, $\mu$ is the solution viscosity, and $\psi_B$ is an empirical parameter ("association parameter") as shown in Table 1-1.

Liquid diffusivities are highly concentration-dependent. The foregoing expressions should therefore be used only for dilute cases and of course for binaries.

For solid systems the reader should consult the text by Jakob (13) for thermal conductivities. Diffusivities in solid systems are given by references 14–17.

Example 1-5 Compare viscosity values for liquid water at 60°C as determined by

1. The Eyring equation (the $\Delta U_{\text{vap}}$ is $3.759 \times 10^7$ J/kg mole)
2. Using the nomograph in Figure B-1 and Table B-1 of Appendix

For case 1,

$$\hat{V} = \frac{M}{\rho} = \frac{18.02}{1000} \text{ m}^3/\text{kg mole} = 0.01802 \text{ m}^3/\text{kg mole}$$

$$\mu = \frac{\hat{N}h}{\hat{V}} \exp \left( \frac{0.408 \Delta U_{\text{vap}}}{RT} \right)$$

$$\mu = \frac{6.023 \times 10^{26}}{\text{kg mole}} \cdot \frac{6.62 \times 10^{34}}{\text{J sec}} \exp \left[ \frac{(0.408)(3.759 \times 10^7 \text{ m}^3/\text{kg mole})}{333.10^\circ \text{K}(8314.4 \text{ J/kg mole})} \right]$$

$$\mu = 0.00562 \text{ pascal-sec}$$

For case 2, the coordinates for water are (10.2, 13). Connecting 60°C with this point gives a viscosity of $4.70 \times 10^{-4}$ pascal-sec.

Actual experimental viscosity value is $4.67 \times 10^{-4}$ pascal-sec, which clearly indicates that the Eyring method is only an approximation.
Example 1-6  Estimate the thermal conductivity of liquid carbon tetrachloride (CCl₄) at 20°C and atmospheric pressure.

\[ \rho = 1595 \text{ kg/m}^3, \quad \frac{1}{\rho} \left( \frac{\partial \rho}{\partial P} \right)_T = 89.5 \times 10^{-11} \text{ m}^2/\text{N} \]

\[ \left( \frac{\partial P}{\partial \rho} \right)_T = \frac{1}{\rho} \left[ \frac{1}{\rho} \left( \frac{\partial \rho}{\partial P} \right)_T \right] = \frac{1}{(1595 \text{ kg/m}^3)(89.5 \times 10^{-11} \text{ m}^2/\text{J})} \approx 7 \times 10^5 \text{ m}^2/\text{sec}^2 \]

If it is assumed that \( C_P = C_V \) (a good assumption for the conditions) then

\[ V_s = \sqrt{\frac{C_P}{C_V} \left( \frac{\partial P}{\partial \rho} \right)_T} = \sqrt{(1)(7 \times 10^5 \text{ m}^2/\text{sec}^2)} = 837 \text{ m/sec} \]

The value of \( V \) is given by

\[ \hat{V} = \frac{M}{\rho} = \frac{153.84 \text{ m}^3}{1595 \text{ kg mole}} = 0.0965 \text{ m}^3/\text{kg mole} \]

\[ kV = 2.80 \left( \frac{\hat{V}}{V} \right)^{2/3} \]

\[ KV_i = 2.80 \left( \frac{6.023 \times 10^{26} \text{ kg mole}}{0.0965 \text{ m}^3} \right)^{2/3} \left( \frac{1.3805 \times 10^{-23} \text{ J}}{\text{K}} \right)(837 \text{ m/sec}) \]

\[ k = 0.112 \frac{\text{J}}{\text{m sec °K}} \]

The experimental value is 0.103 J/m sec °K. This gives a percent error of 8.74 percent.

Example 1-7  What is the diffusivity for a dilute solution of acetic acid in water at 12.5°C? The density of acetic acid at its normal boiling point is 0.937 g/cm³. The viscosity of water at 12.5°C is 1.22 cP.

Using the Wilke–Chang equation, we obtain

\[ D_{AB} = 7.4 \times 10^{-8} (\psi_B M_B)^{1/2} \left( \frac{T}{\mu_B V_A} \right)^{0.6} \]

\[ \hat{V}_A = \frac{M}{\rho} = \frac{60}{0.937} = 64.1 \text{ cm}^3/\text{g mole} \]

\[ \psi_B = 2.6 \text{ (from Table 1-1)} \]

\[ D_{AB} = 7.4 \times 10^{-8}(2.6 \times 18)^{1/2} \left( \frac{287.5\text{K}}{(1.22)(64.1 \text{ m}^3/\text{g mole})^{0.6}} \right) \]

\[ D_{AB} = 9.8 \times 10^{-6} \text{ cm}^2/\text{sec} = 9.8 \times 10^{-10} \text{ m}^2/\text{sec} \]
ONE-DIMENSIONAL EQUATION OF CHANGE; ANALOGIES

As was shown earlier, each of the three transport processes is a function of a driving force and a transport coefficient. It is also possible to make the equations even more similar by converting the transport coefficients to the forms of diffusivities. Fick’s First Law [equation (1-9)] already has its transport coefficient \(D_{AB}\) in this form. The forms for Fourier’s Law [equation (1-7)] and Newton’s Law of Viscosity [equation (1-8)] are

- Thermal diffusivity \(\alpha = \frac{k}{\rho C_p}\) \(\text{(1-30)}\)
- Momentum diffusivity \(\nu = \frac{\mu}{\rho}\) \(\text{(1-31)}\)

Units of all the diffusivities are \((\text{length})^2/\text{unit time}\) (i.e., cm\(^2\)/sec, m\(^2\)/sec, and ft\(^2\)/hr). Momentum diffusivity is also known as kinematic viscosity.

If the transport coefficients are thus converted, the equations of change in one dimension then become

\[
q_y = -\alpha \frac{d(\rho C_p T)}{dy} \quad \text{(1-32)}
\]
\[
\tau_{yx} = -\nu \frac{d(\rho V_x)}{dy} \quad \text{(1-33)}
\]
\[
J_{Ay} = -D_{AB} \frac{d(C_A)}{dy} \quad \text{(1-34)}
\]

This result indicates that these three processes are analogous in one-dimensional cases. Actually, heat and mass transfer will be analogous in even more complicated cases as we will demonstrate later. This is not true for momentum transfer whose analogous behavior only applies to one-dimensional cases.

SCALE-UP; DIMENSIONLESS GROUPS OR SCALING FACTORS

One of the most important characteristics of the chemical and process industries is the concept of scale-up. The use of this approach has enabled large-scale operations to be logically and effectively generated from laboratory-scale experiments. The philosophy of scale-up was probably best expressed by the highly productive chemist Leo Baekeland (the inventor of Bakelite and many other industrial products). Baekeland stated succinctly, “make your mistakes on a small scale and your profits on a large scale.”

Application of scale-up requires the use of the following:

1. Geometric similarity
2. Dynamic similarity
3. Boundary conditions
4. Dimensionless groups or scaling factors.
The first of these, geometric similarity, means that geometries on all scales must be of the same type. For example, if a spherically shaped process unit is used on a small scale, a similarly shaped unit must be used on a larger scale. Dynamic similarity implies that the relative values of temperature, pressure, velocity, and so on, in a system be the same on both scales. The boundary condition requirement fixes the condition(s) at the system’s boundaries. As an example, consider a small unit heated with electrical tape (i.e., constant heat flux). On a larger scale the use of a constant wall temperature (which is not constant heat flux) would be inappropriate.

Dimensionless groups or scaling factors are the means of sizing the units involved in scaling up (or down). They, in essence, represent ratios of forces, energy changes, or mass changes. Without them the scale-up process would be almost impossible.

Additionally, these groups are the way that we make use of semiempirical or empirical approaches to the transport processes. As we will see later, the theoretical/analytical approach cannot always be used, especially in complex situations. For such cases, dimensionless groups enable us to gain insights and to analyze and design systems and processes.

PROBLEMS

1-1. Estimate the viscosities of \( n \)-hexane at 200°C and toluene at 270°C. The gases are at low pressure.
1-2. What are the viscosities of methane, carbon dioxide, and nitrogen at 20°C and atmospheric pressure?
1-3. Estimate the viscosity of liquid benzene at 20°C.
1-4. Determine a value for the viscosity of ammonia at 150°C.
1-5. A young engineer finds a notation that the viscosity of nitrogen at 50°C and a “high pressure” is \( 1.89 \times 10^{-9} \) pascal-seconds. What is the pressure?
1-6. Available data for mixtures of hydrogen and dichlorofluoromethane at 25°C and atmospheric pressure are as follows:

<table>
<thead>
<tr>
<th>Mole Fraction Hydrogen</th>
<th>Viscosity of Mixture (( \times 10^5 ) pascal-sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>1.24</td>
</tr>
<tr>
<td>0.25</td>
<td>1.281</td>
</tr>
<tr>
<td>0.50</td>
<td>1.319</td>
</tr>
<tr>
<td>0.75</td>
<td>1.351</td>
</tr>
<tr>
<td>1.00</td>
<td>0.884</td>
</tr>
</tbody>
</table>

Compare calculated values to the experimental data at 0.25 and 0.75 mole fraction of hydrogen.

1-7. Estimate the viscosity of a 25-75 percent mole fraction mixture of ethane and ethylene at 300°C and a pressure of \( 2.026 \times 10^7 \) pascals.
1-8. Values of viscosity and specific heats, respectively, for nitric oxide and methane are (a) $1.929 \times 10^{-5}$ pascal-sec and $29.92$ kilojoules/(kg mole °K) and (b) $1.116 \times 10^{-5}$ pascal seconds and $35.77$ kilojoules/(kg mole °K). What are the thermal conductivities of the pure gases at $27^\circ$C?

1-9. Compare values of thermal conductivity for argon at atmospheric pressure and $100^\circ$C using equations (1-11) and (1-15), respectively.

1-10. A value of thermal conductivity for methane at $1.118 \times 10^7$ pascals is $0.0509$ joules/(sec m K). What is the temperature for this value?

1-11. Water at $40^\circ$C and a pressure of $4 \times 10^{12}$ pascals has a density of $993.8$ kg/m$^3$ and an isothermal compressibility $(\rho^{-1}(\partial \rho/\partial P)_T)$ of $3.8 \times 10^{-18}$ pascals$^{-1}$. What is its thermal conductivity?

1-12. What is the thermal conductivity of a mixture of methane (mole fraction of $0.486$) and propane at atmospheric pressure and $100^\circ$C?

1-13. Argon at $27^\circ$C and atmospheric pressure has values of viscosity and thermal conductivity of $2.27 \times 10^{-5}$ pascal-sec and $1.761 \times 10^{-4}$ Joules/(sec m °K) from each property respectively. Calculate molecular diameters and collision diameters, compare them, and evaluate.

1-14. Compute a value for $D_{AB}$ for a system of argon (A) and oxygen (B) at $294^\circ$K and atmospheric pressure.

1-15. The diffusivity for carbon dioxide and air at $293^\circ$K and atmospheric pressure is $1.51 \times 10^{-5}$ m$^2$/sec. Estimate the value at $1500^\circ$K using equations (1-12) and (1-16).

1-16. A dilute solution of methanol in water has a diffusivity of $1.28 \times 10^{-9}$ m$^2$/sec at $15^\circ$C. Estimate a value at $125^\circ$C.

1-17. Estimate a value of diffusivity for a mixture of 80 mole percent methane and 20 mole percent of ethane at $40^\circ$C and $1.379 \times 10^7$ pascals.

1-18. Determine a value of $D_{AB}$ for a dilute solution of 2,4,6-trinitrotoluene in benzene at $15^\circ$C.

1-19. Find values of $\sigma_{AB}$ and $\varepsilon_{AB}$ from the following data:

<table>
<thead>
<tr>
<th>$D_{AB}$ (m/sec)</th>
<th>$T$ (°K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1.51 \times 10^{-5}$</td>
<td>293</td>
</tr>
<tr>
<td>$2.73 \times 10^{-5}$</td>
<td>400</td>
</tr>
<tr>
<td>$5.55 \times 10^{-5}$</td>
<td>600</td>
</tr>
<tr>
<td>$9.15 \times 10^{-5}$</td>
<td>800</td>
</tr>
</tbody>
</table>

1-20. At $25^\circ$C, estimate the diffusivity of argon (mole fraction of 0.01) in a mixture of nitrogen, oxygen, and carbon dioxide (mole fractions of 0.78, 0.205, and 0.005, respectively).
REFERENCES