# chap. 34 Transport Phenomena

㊱ Quiz 4

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- general: what is transport?
- mass transport: diffusion

When a perturbation is applied to a System
⇒ a property is shifted away from equilibrium
perturbation removed: system goes back to equil.

<u>transport</u>: evolution of a system property back to equilibrium distribution

<u>Transp.</u> table of such properties

fi transport: spatial non-equilibrium distribution of a property

gas particles: equil.: same distribution everywhere in the container

non-equilibrium particle no. density $d = \tilde{N}$ for gases

<u>Transp.</u> $d_{left} > d_{right}$

⇒ particles flow from left → right to get their number density $\tilde{N}$ equal everywhere

flux: quantity transferred / (area · time)

flux = no. of particles ~~trans~~ transported through an area in a time through a partitioning

$$\text{flux } J_x = -\alpha \frac{d(\text{property})}{dx}$$

$$\text{units: } \frac{[\text{property}]}{[\text{area}]\cdot[\text{time}]}$$

$\frac{d(\text{property})}{dx}$: spatial gradient of the property

assumption: very small displacement from equil.

flux happens opposite to the gradient

**TABLE 34.1 Transported Properties and the Corresponding Transport Process**

| Property Transported | Transport Process |
|---|---|
| Matter | Diffusion |
| Energy | Thermal conductivity |
| Linear momentum | Viscosity |
| Charge | Ionic conductivity |

In order for a system property to
erty must be different from the distril
particles in which the equilibrium sp:
same particle number density throu
particle number density were greate
would expect the gas particles to mc
density throughout the container. Th
tion of the system property that is co

A central concept in transport ph
through a given area in a given amou
or gradient exists for a system prope
ent. In the example just discussed, ir
partition and counting the number of
to the other side, as illustrated in Figu
of particles that move through the p:
of *all* of the transport processes listed
tial gradient in a system property wi
relationship between flux and the sp:

$$J_x$$

In Equation (34.1), $J_x$ is the flux
derivative in Equation (34.1) repres
(mass, energy, etc.). The linear relati
ent is reasonable when the displacer
modest displacement of the system
remainder of this chapter.

The negative sign in Equation (
direction of the gradient; therefore
external action is not taken to main
tained at a constant value, the f
Figure 34.1, which presents a grapl
and flux. The gas density is greatest
particle density increases as one g
According to Equation (34.1), parti
gradient in an attempt to make the
quantity of interest in Equation (3
serves as the proportionality consta
the **transport coefficient.** In the f
coefficients for the processes listed
involving these various transport ph
property will look different, it is imp

direction of the gradient; therefore, flux will result in a reduction of the gradient external action is not taken to maintain the gradient. If the gradient is externally mai tained at a constant value, the flux will also remain constant. Again, consid Figure 34.1, which presents a graphical example of the relationship between gradie and flux. The gas density is greatest on the left-hand side of the container such that t particle density increases as one goes from the right side of the container to the le According to Equation (34.1), particle flux occurs in opposition to the number densi gradient in an attempt to make the particle density spatially homogeneous. The fin quantity of interest in Equation (34.1) is the factor $\alpha$. Mathematically, this quanti serves as the proportionality constant between the gradient and flux and is referred to the **transport coefficient.** In the following sections, we will determine the transpc coefficients for the processes listed in Table 34.1 and derive the expressions for flu involving these various transport phenomena. Although the derivations for each transpc property will look different, it is important to note that all originate from Equation (34.1 That is, the underlying principle behind all transport phenomena is the relationsh between flux and gradient.

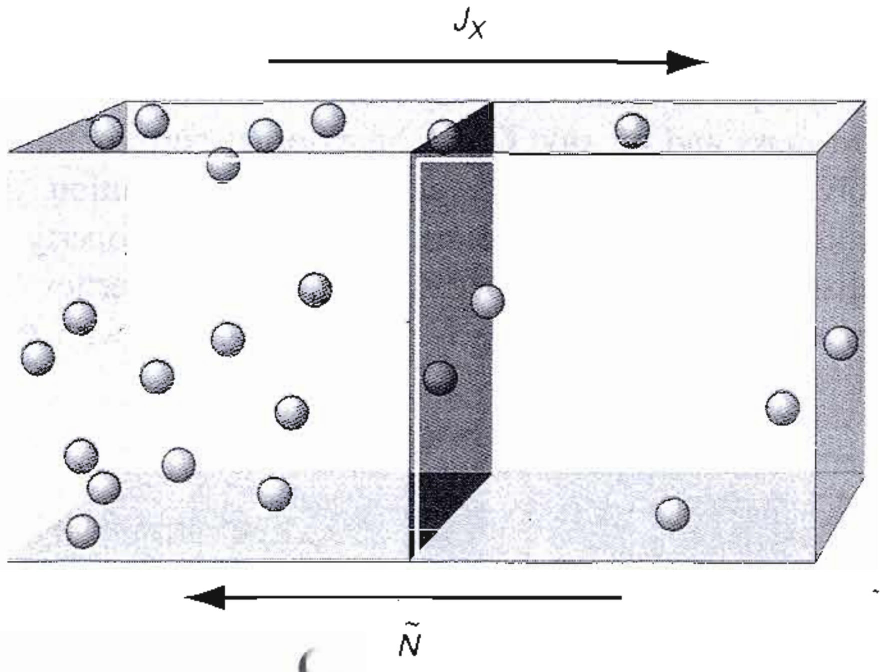

**FIGURE 34.1**
Illustration of flux. The flux $J_x$ of gas particles is in opposition to the gradient in particle number density $\tilde{N}$.

gradient: low $\tilde{N}$ to high $\tilde{N}$

flux: ~~to~~ high $\tilde{N}$ to low $\tilde{N}$

⇒ the flux leads to reduction of the gradient

if externally gradient is kept const. → flux = const.

$\tilde{N}$: increase from left to right

→ flux from right to left

$\alpha$: proportionality constant between flux and grad

$\alpha$ = transport coefficient

the above equation: underlying principle of all transport

## Mass transports: Diffusion

Evolution of particle density against a gradient

≙ gradient of chemical potential

Transp. grad. in no. density (particles) $\tilde{N}$

gas particle no. density: $\tilde{N}$

f'ux: flow of particles per time and area through a non-real plane (aerea a) at x = 0: flux plane

2 other (also non-real) planes are located at x = ±λ, the mean free path length away from x = 0, left and right of x = 0

λ: the path a particle travels on average between 2 collisions:

$$\lambda = \frac{RT}{\sqrt{2}\, P N_A \sigma} \quad \sigma\text{: cross section } \pi d^2$$

(spherical particles of diameter d)

$$k_B = \frac{R}{N_A} \quad \text{here: } \frac{d\tilde{N}}{dx} \neq 0 \text{ in x direction}$$

nality constant $\alpha$. This quantity is referred to as the diffusion coefficient for mass ansport. To determine this constant, consider the particle number density at $\pm\lambda$:

$$\widetilde{N}(-\lambda) = \widetilde{N}(0) - \lambda\left(\frac{d\widetilde{N}}{dx}\right)_{x=0} \tag{34.2}$$

$$\widetilde{N}(\lambda) = \widetilde{N}(0) + \lambda\left(\frac{d\widetilde{N}}{dx}\right)_{x=0} \tag{34.3}$$

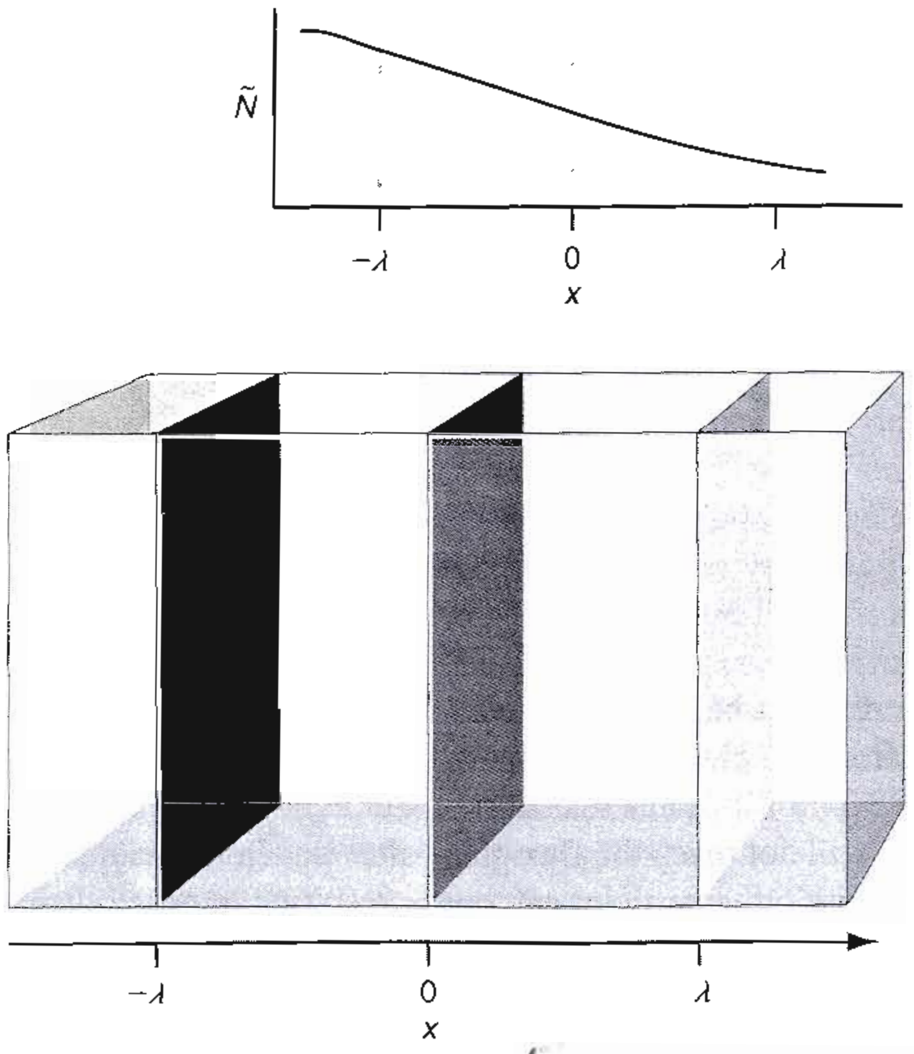

**FIGURE 34.2**
Model used to describe gas diffusion. The gradient in number density $\widetilde{N}$ results in particles diffusing from $-x$ to $+x$. The plane located at $x = 0$ is where the flux of particles in response to the gradient is calculated (the *flux plane*). Two planes, located one mean free path distance away ($\pm\lambda$) are considered with particles traveling from either of these planes to the flux plane. The total flux through the flux plane is equal to the difference in flux from the planes located at $\pm\lambda$.

if $\frac{d\tilde{N}}{dx} = 0 \Rightarrow$ flux $J_x = 0$

does not mean that the particles do not move, only that the same no. of particles crosses $x = 0$ left to right and right to left

flux to left $\oplus$ ~~since~~, flux to right $\ominus$

$\alpha$ for diffusion: diffusion coefficient for mass transport

$\tilde{N}$ at $x = \pm\lambda$:

$$\tilde{N}(x=-\lambda) = \tilde{N}(x=0) - \lambda\left(\frac{d\tilde{N}}{dx}\right)_{x=0}$$

$$\tilde{N}(x=\lambda) = \tilde{N}(x=0) + \lambda\left(\frac{d\tilde{N}}{dx}\right)_{x=0}$$

= Taylor series expansions of $\tilde{N}$ with respect to distance but only first two terms kept (modest displacement)

$\tilde{N}(\pm\lambda) = \tilde{N}(0) \pm$ term = change in concentration when going to the $\pm\lambda$ planes

$\lambda$ should be small enough that higher order terms in the series can be neglected

no. of particles that hit an area A in unit time:

$$\frac{dN}{dt} = J_x \cdot A$$

flux of particles from the $x = -\lambda$ plane to the flux plane: We need the no. of particles hitting the flux plane per unit time

→ we count only particles moving towards the flux plane

this no. of particles = $\tilde{N}$ · average speed in x direction

→ flux in x direction:

$$J_x = \tilde{N} \int_0^\infty v_x f(v_x)\, dv_x$$

$f(v_x)$ Maxwell distribution in 1 dimension $(x)$:

$$f(v_x) = \sqrt{\frac{m}{2\pi k_B T}} \exp\left[-\frac{m v_x^2}{2k_B T}\right]$$

$$J_x = \tilde{N} \int_0^{\infty} v_x \sqrt{\frac{m}{2\pi k_B T}}\, e^{-\frac{m v_x^2}{2k_B T}}\, dv_x$$

$$= \tilde{N} \sqrt{\frac{k_B T}{2\pi m}} = \frac{\tilde{N}}{4} V_{av} \text{ (average)}$$

$$V_{av} = \sqrt{\frac{8 k_B T}{\pi m}} = 2\sqrt{\frac{2 k_B T}{\pi m}} = 2\sqrt{\frac{2 \cdot 2 k_B T}{2\pi m}}$$

$$= 4\sqrt{\frac{k_B T}{2\pi m}}$$

→ flux from $x = \pm\lambda$ planes to $x = 0$ plane:

$$J_{-\lambda \to 0} = \frac{1}{4} V_{av} \tilde{N}(-\lambda) = \frac{1}{4} V_{av} \left[\tilde{N}(0) - \lambda \left(\frac{d\tilde{N}}{dx}\right)_{x=0}\right]$$

$$J_{+\lambda \to 0} = \frac{1}{4} V_{av} \tilde{N}(\lambda) = \frac{1}{4} V_{av} \left[\tilde{N}(0) + \lambda \left(\frac{d\tilde{N}}{dx}\right)_{x=0}\right]$$

total flux through $x=0$ plane is the difference of the 2 equations:

$$J_{tot} = J_{-\lambda \to 0} - J_{+\lambda \to 0} = \frac{1}{4} V_{av} \left[-2\lambda \left(\frac{d\tilde{N}}{dx}\right)_{x=0}\right]$$

$$= -\frac{1}{2} V_{av} \lambda \left(\frac{d\tilde{N}}{dx}\right)_{x=0}$$

an assumption which must be corrected:
particles move from the $x = \pm\lambda$ plane directly to $x=0$ along x

Transp. particle path not parallel to x, then in one free path $\lambda$ the particle will not reach $x=0$, but will be deflected by collission

where the number of particles traveling towar
number density and the average velocity in t
approach, the flux in the $+x$ direction is given

$$J_x = \widetilde{N}\int_0^\infty \mathrm{v}_x f(\mathrm{v}_x)\, d\mathrm{v}_x$$

$$= \widetilde{N}\int_0^\infty \mathrm{v}_x\left(\frac{m}{2\pi kT}\right)$$

$$= \widetilde{N}\left(\frac{kT}{2\pi m}\right)^{1/2}$$

$$= \frac{\widetilde{N}}{4}\nu_{ave}$$

In this equation, we have employed the definiti
Substituting Equation (34.2) and (34.3) into the
flux from the planes located at $-\lambda$ and $\lambda$ is giv

$$J_{-\lambda,0} = \frac{1}{4}\nu_{ave}\widetilde{N}(-\lambda) = \frac{1}{4}\nu_{av}$$

$$J_{\lambda,0} = \frac{1}{4}\nu_{ave}\widetilde{N}(\lambda) = \frac{1}{4}\nu_{ave}\left[\right.$$

The total flux through the flux plane is s
planes at $\pm\lambda$:

$$J_{Total} = J_{-\lambda,0} - J_{\lambda,0} = \frac{1}{4}$$

$$= -\frac{1}{2}\nu_{ave}\lambda\left(\frac{d\widetilde{N}}{dx}\right)_x$$

One correction remains before the derivatio
particles move from the planes located at $\pm\lambda$
However, Figure 34.3 illustrates that if the p
axis, the particle will not reach the flux plane
point, collisions with other particles can occu
tories away from the flux plane; therefore, the
Inclusion of these trajectories requires one to

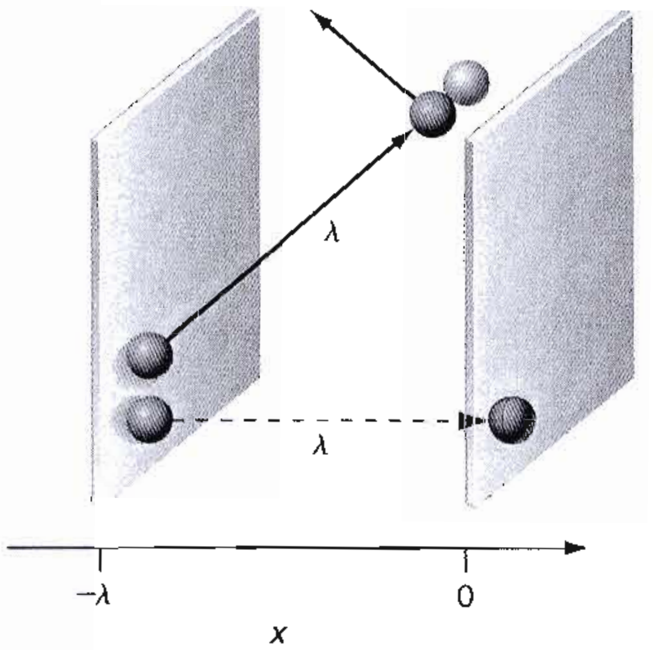

**FIGURE 34.3**
Particle trajectories aligned with the $x$ axis (dashed line) result in the particle traveling between planes without collision. However, trajectories not aligned with the $x$ axis (solid line) result in the particle not reaching the flux plane before a collision with another particle occurs. This collision may result in the particle being directed away from the flux plane.

=) an orientational average of the mean free path is necessary

=) reduction of the flux by factor 2/3

$$J_{tot} = -\frac{1}{3} v_{av}\,\lambda\left(\frac{d\tilde{N}}{dx}\right)_{x=0}$$

=) The diffusion coefficient D is the factor at the gradient: $D = \frac{1}{3} v_{av}\,\lambda$

$$J_{tot} = -D\left(\frac{d\tilde{N}}{dx}\right)_{x=0}$$

Fick's first law of diffusion

$v_{av}, \lambda$ : derived from kinetic gas theory

<u>example</u> What is D for Ar at 298 K and 1.00 atm

cross section: $\sigma_{Ar} = 3.6\cdot 10^{-19}\,m^2$, $M_{Ar} = 0.040\,\frac{kg}{mol}$

$$D_{Ar} = \frac{1}{3} v_{av}\,\lambda$$

$$v_{av} = \sqrt{\frac{8k_BT}{\pi m}} = \sqrt{\frac{8RT}{\pi M_{Ar}}} \qquad \frac{k_B}{m} = \frac{N_A k_B}{N_A m} = \frac{R}{M}$$

$$\lambda_{Ar} = \frac{RT}{PN_A\sqrt{2}\,\sigma_{Ar}} = \frac{k_BT}{\sqrt{2}\,\pi d^2 P} \qquad \sigma = \pi d^2, \quad k_B = \frac{R}{N_A}$$

$$D_{Ar} = \frac{1}{3}\sqrt{\frac{8RT}{\pi M_{Ar}}}\cdot\frac{RT}{PN_A\sqrt{2}\,\sigma_{Ar}}$$

$$= \frac{1}{3}\sqrt{\frac{8\cdot 8.314\,\frac{J}{K\,mol}\cdot 298K}{\pi\cdot 0.040\,kg/mol}}\cdot\frac{8.314\,\frac{J}{K\,mol}\cdot 298\,K}{101{,}325\,Pa\cdot 6.022\cdot 10^{23}\,mol^{-1}\cdot\sqrt{2}\cdot 3.6\cdot 10^{-19}\,m^2}$$

$$= \frac{1}{3}\,397\,\frac{m}{s}\cdot 7.98\cdot 10^{-8}\,m$$

$$= 1.1\cdot 10^{-8}\,\frac{m^2}{s}$$

parameters like $v_{av}$ from equilibrium distributions are now applied to non-equilibrium systems.
But, the non-equilibrium displacement is assumed to be very small (modest)
only then it is ok to use equilibrium expressions
to apply non-equilibrium distributions is mathematically too complex to be discussed here.
When D is known, also ~~at~~ particle size can be determined as cross section $\sigma$

At the same P, T what is the ratio of the cross sections of He and Ar when $D_{He} \approx 4 D_{Ar}$?

$$\frac{D_{He}}{D_{Ar}} = \frac{v_{av,He}\ \lambda_{He}}{v_{Av,Ar}\ \lambda_{Ar}} = 4$$

$$= \frac{\sqrt{\frac{8RT}{\pi M_{He}}}\ \frac{RT}{P_{\cancel{He}}\ N_A \sqrt{2}\ \sigma_{He}}}{\sqrt{\frac{8RT}{\pi M_{Ar}}}\ \frac{RT}{P\ N_A \sqrt{2}\ \sigma_{Ar}}}$$

$$\cancel{\frac{D_{He}}{D_{Ar}}} = \sqrt{\frac{M_{Ar}}{M_{He}}}\ \frac{\sigma_{Ar}}{\sigma_{He}} = 4$$

$$\frac{\sigma_{He}}{\sigma_{Ar}} = \frac{1}{4}\sqrt{\frac{M_{Ar}}{M_{He}}} = \frac{1}{4}\sqrt{\frac{39.9\ g/mol}{4.00\ g/mol}} = 0.79$$

$\underline{\sigma = \pi d^2}$, so that $\frac{\sigma_{He}}{\sigma_{Ar}}$ (from D) is ~~consistent with~~
$d_{He} = 0.89\ d_{Ar}$ (~~[illegible]~~)
from ~~atm~~ atomic radii tables: $d_{Ar} = 2.5\ d_{He}$ or $d_{He} = 0.4\ d_{Ar}$
reasons: hard-sphere approximation is used ~~for~~ here
~~such tables!~~

- Time Evolution of a Concentration Gradient

Fick's 1. Law useful to determine the time scale of diffusion:

flux : $\mathcal{J}_x = -D \dfrac{d\tilde{N}(x)}{dx}$

flux through a plane in position x

flux " " " " " x + dx, also 1. Law

$$\mathcal{J}_{x+dx} = -D \frac{d\tilde{N}(x+dx)}{dx}$$

particle density $\tilde{N}(x+dx)$ is related to $\tilde{N}(x)$:

again Taylor series expansion in x and only 2 terms are kept (small displacement from equilibrium):

$$\tilde{N}(x+dx) = \tilde{N}(x) + \left(\frac{d\tilde{N}(x)}{dx}\right)dx$$

$$\rightarrow \mathcal{J}_{x+dx} = -D\left[\frac{d\tilde{N}(x)}{dx} + \left(\frac{d^2\tilde{N}(x)}{dx^2}\right)dx\right]$$

the change of particle density between the 2 planes depends on flux difference through the planes

2 fluxes same → $\tilde{N}$ will not change

flux difference → time evolution of $\tilde{N}$

flux = no. of particles passing ~~the~~ through a given area in unit time

if it is the same area on both planes then

flux difference ~ $\Delta\tilde{N}$

⇒ relation between time dependence of no. density and flux difference is given as:

$$\frac{D_{He}}{D_{Ar}} = 4 = \frac{\nu_{ave,He}\lambda_{He}}{\nu_{ave,Ar}\lambda_{Ar}}$$

$$= \frac{\left(\frac{8RT}{\pi M_{He}}\right)^{1/2}\left(\right.}{\left(\frac{8RT}{\pi M_{Ar}}\right)^{1/2}\left(\right.}$$

$$= \left(\frac{M_{Ar}}{M_{He}}\right)^{1/2}\left(\frac{\sigma_{A}}{\sigma_{H}}\right.$$

$$\left(\frac{\sigma_{He}}{\sigma_{Ar}}\right) = \frac{1}{4}\left(\frac{M_{Ar}}{M_{He}}\right)^{1/2} =$$

Recall from Section 33.6 that the collisi
$\pi d^2$ where $d$ is the diameter of a gas partic
determined using the diffusion coefficients, i
smaller than that of Ar. However, the diam
radii is roughly 2.5 times greater than that o
traced to the hard-sphere approximation for i

## 34.3 The Time Evolut a Concentration

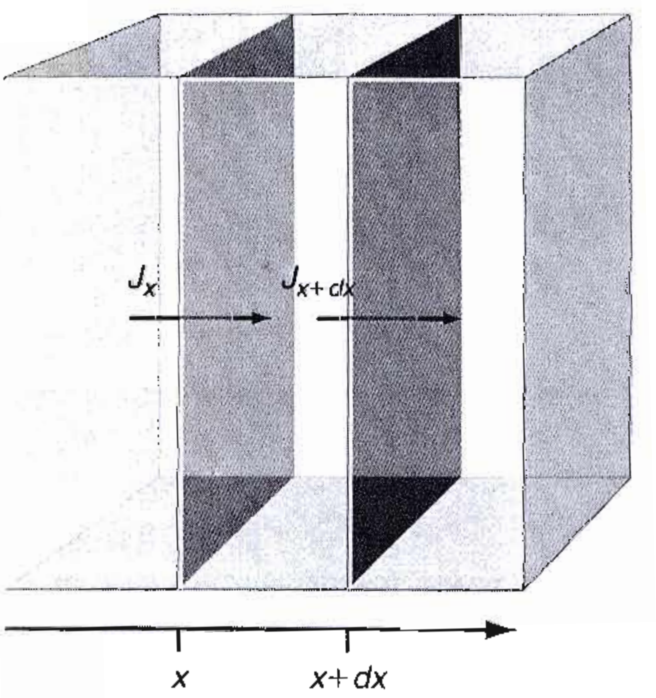

**FIGURE 34.4**
Depiction of flux through two separate planes. If $J_x = J_{x+dx}$, then the concentration between the planes will not change. However, if the fluxes are unequal, then the concentration will change with time.

As illustrated in the previous section, the exis
particle diffusion. What is the timescale for dif
a given amount of time? These questions are
can be derived as follows. Beginning with Fic

$$J_x = -D\Big($$

The quantity $J_x$ in Equation (34.12) is the flux
in Figure 34.4. The flux at location $x + dx$ c

$$J_{x+dx} = -D\Big(\frac{d}{}$$

The particle density at $(x + dx)$ is related to t

$$\widetilde{N}(x + dx) = \widetilde{N}(x) -$$

This equation is derived by keeping the first tw
number density with distance equivalent to the

$$\frac{\partial \tilde{N}(x,t)}{\partial t} = \frac{\partial (J_x - J_{x+dx})}{\partial x}$$

$$= D\frac{\partial}{\partial x}\left[-\left(\frac{\partial \tilde{N}(x,t)}{\partial x}\right) - \left(-\left(\left(\frac{\partial \tilde{N}(x,t)}{\partial x}\right) + \left(\frac{\partial^2 \tilde{N}(x,t)}{\partial x^2}\right) dx\right)\right)\right]$$

$$\rightarrow \quad \frac{\partial \tilde{N}(x,t)}{\partial t} = D\,\frac{\partial^2 \tilde{N}(x,t)}{\partial x^2}$$

diffusion equation: Fick's 2. law

$\tilde{N}$ depends on position and on time

time evolution of a concentration gradient

~ 2. derivative of the spatial ~~gradient~~ distribution

⇒ the ~~faster~~ larger the curvature of the distribution ~~concentration gradient~~ the faster ~~do~~ the relaxation will be.

Ficks 2. law: partial differential equation of 1. order in time and 2. order in space

a solution is only possible with a set of initial conditions:

$$\tilde{N}(x,t) = \frac{N_0}{2A\sqrt{\pi D t}}\, e^{-x^2/(4Dt)}$$

$N_0$: initial no. of solutes confined on a plane at $t=0$ and $x=0$

A: area of that plane

x: distance from the plane

D: diffusion coefficient

$\tilde{N}(x,t)$: distribution function which describes the probability of finding a solute at time t at a plane a distance x away from the ~~plane~~ initial plane at $t=0$

Transp. example for $D = 10^{-5}\,\frac{m^2}{s} \simeq D_{Ar}$ at 298 K, $P = 1$ atm : $\tilde{N}(x,t)/(n_0/A)$

increasing time → $\tilde{N}$ increases at further and further distances from the initial plane, as solutes diffuse into the solution

metric, or benchmark to describe $\tilde{N}(x,t)$: root mean square (rms) displacement

$$x_{rms} = \sqrt{\langle x^2 \rangle} = \sqrt{\frac{A}{N_0}\int_{-\infty}^{\infty} x^2\,\tilde{N}(x,t)\,dx}$$

$$= \sqrt{\frac{A}{N_0}\int_{-\infty}^{\infty} \frac{x^2 N_0}{2A\sqrt{\pi D t}}\, e^{-x^2/4Dt}\,dx}$$

$$= \sqrt{\frac{1}{2\sqrt{\pi D t}}\int_{-\infty}^{\infty} x^2\, e^{-x^2/4Dt}\,dx}$$

integration by parts → $x_{rms} = \sqrt{2Dt}$

$x_{rms}$ increases as $\sqrt{Dt}$

$x_{rms} = \sqrt{2Dt}$ is for 1 dimension (x) only!

in 3 dimensions (x, y, z):

diffusion is equivalent in all 3 dimensions

→ $r_{rms} = \sqrt{6Dt}$

until now only gases were treated, but the relations can be applied to liquids also

What is $x_{rms}$ for a solute with $D = 1.00 \cdot 10^{-5}\,\frac{m^2}{s}$ for t = 1000 and t = 10000 s ?

$$\left(\frac{\partial \tilde{N}(x,t)}{\partial x}\right) + \left(\frac{\partial^2 \tilde{N}(x,t)}{\partial x^2}\right)\partial x \Bigg)\Bigg)\Bigg]$$

$$\tag{34.16}$$

on, and is also known as **Fick's second** n position $x$ and time $t$. Equation (34.16) entration gradient is proportional to the oncentration. That is, the greater the e faster the relaxation will proceed. an be solved using standard techniques n the Further Reading section at the end sion for $\tilde{N}(x,t)$:

$$\frac{\quad}{)^{1/2}}e^{-x^2/4Dt} \tag{34.17}$$

ber of molecules confined to a plane at ay from the plane, and $D$ is the diffusion a distribution function that describes the e located a distance $x$ away from the ini- ariation in $\tilde{N}$ versus time is provided in roughly equivalent to the diffusion coef- onstrates that with an increase in time, $\tilde{N}$ l plane (located at 0 m in Figure 34.5). ntered thus far, it is more convenient to s a measure of $\tilde{N}(x,t)$ as opposed to n[illegible]ric employed to describe $\tilde{N}(x,t)$ is rmined using what should by now be a

$$x^2\tilde{N}(x,t)dx \Bigg]^{1/2}$$

$$\frac{\quad}{)^{1/2}}e^{-x^2/4Dt}\,dx \Bigg]^{1/2}$$

$$^{-x^2/4Dt}\,dx \Bigg]^{1/2} \tag{34.18}$$

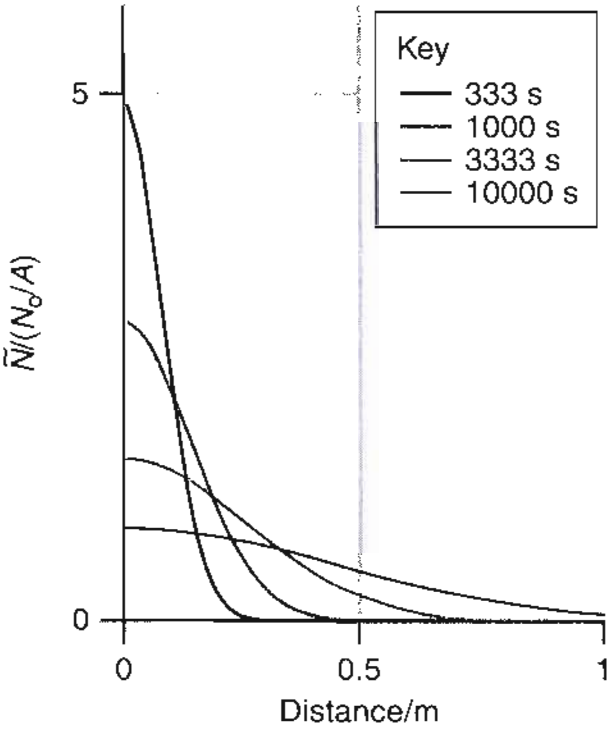

FIGURE 34.5
The spatial variation in particle number density $\tilde{N}(x,t)$ as a function of time. The number density is defined with respect to $N_0/A$, the number of particles confined to a plane located at $x = 0$ of area $A$. In this example, $D = 10^{-5}\text{m}^2\text{s}^{-1}$, a typical value for a gas at 1 atm and 298 K (see Example Problem 34.1). The corresponding diffusion time for a given concentration profile is indicated.

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$$x_{rms,\,1000s} = \sqrt{2Dt} = \sqrt{2 \cdot 1{,}00 \cdot 10^{-5}\,\frac{m^2}{s} \cdot 1000s}$$

$$= 0.141\ m$$

$$x_{rms,\,10000s} = \sqrt{10}\ x_{rms,\,1000s} = 0{,}447\ m$$

Maxwell Distribution of Molecular Speeds

~~show~~ you should know, but will not be asked

total particle speed v (length of the particle velocity vector)

(38) -5

$$v = \sqrt{v_x^2 + v_y^2 + v_z^2}$$

velocity : vector describing (length) the magnitude of movement and the direction of movement

speed: ~~giv~~ sccalar describing the magnitude of movement ~~l~~ $\frac{\text{distance}}{\text{time needed to travel}}$

only not the direction

speed distribution of particles F(v) is defined in terms of the one-dimensional velocity components along all 3 directions

$$F(v)\,dv = f(v_x)\,f(v_y)\,f(v_z)\,dv_x\,dv_y\,dv_z$$

$$= \left[\sqrt{\frac{m}{2\pi kT}}\;e^{-mv_x^2/2kT}\right]\cdot$$

$$\left[\sqrt{\frac{m}{2\pi kT}}\;e^{-mv_y^2/2kT}\right]\cdot$$

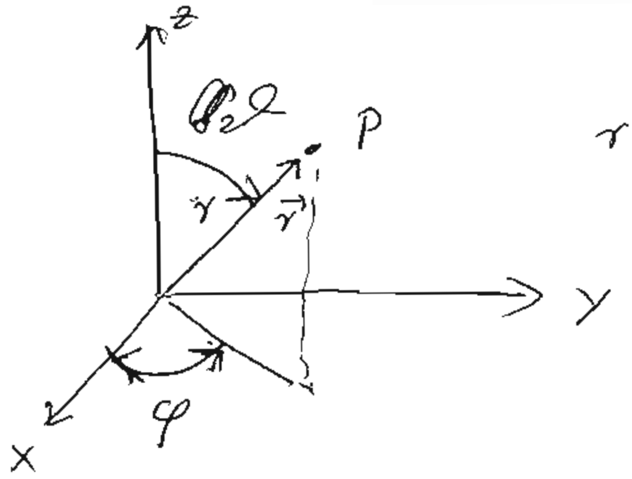
$$\left[\sqrt{\frac{m}{2\pi kT}}\;e^{-mv_z^2/2kT}\right]$$

$$= \left(\frac{m}{2\pi kT}\right)^{3/2} e^{-m(v_x^2+v_y^2+v_z^2)/2kT}\,dv_x\,dv_y\,dv_z$$

integration over angular coordinates

$\rightarrow dv_x\,dv_y\,dv_z = 4\pi v^2\,dv$

angular coordinates,



$r = \sqrt{\underline{r}^2}$

$$F(v)\,dv = 4\pi \left(\frac{m}{2\pi kT}\right)^{3/2} v^2 e^{-mv^2/2kT}\,dv$$

$R = N_A k$   molar mass $M = \overset{\uparrow \text{ particle mass}}{m} \cdot N_A$

in the root, put $k = \frac{R}{N_A}$ → $N_A$ goes into the nominater yielding $m N_A = M$

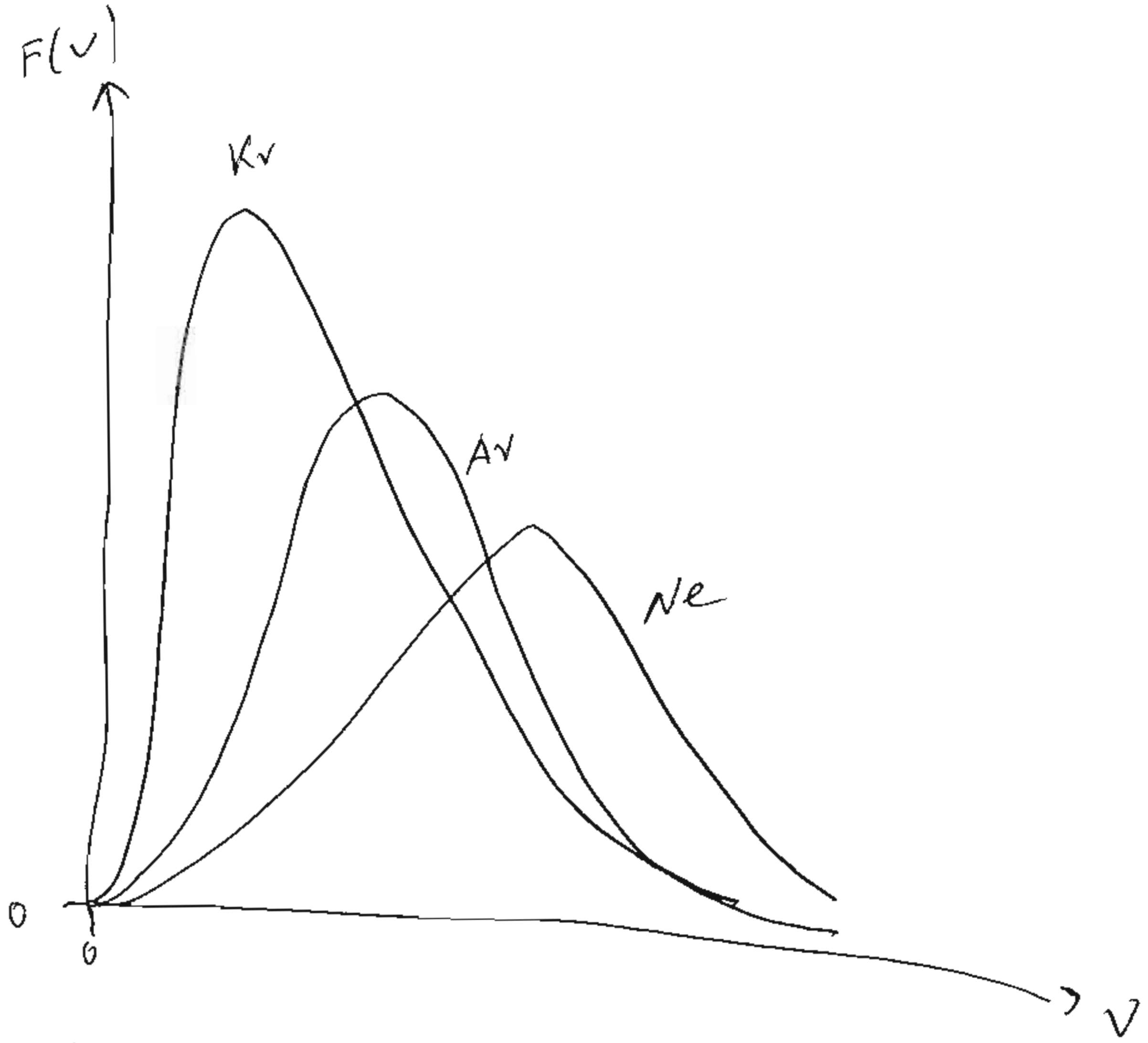
$$F(v)\,dv = 4\pi \left(\frac{M}{2\pi RT}\right)^{3/2} v^2 e^{-Mv^2/2RT}\,dv$$

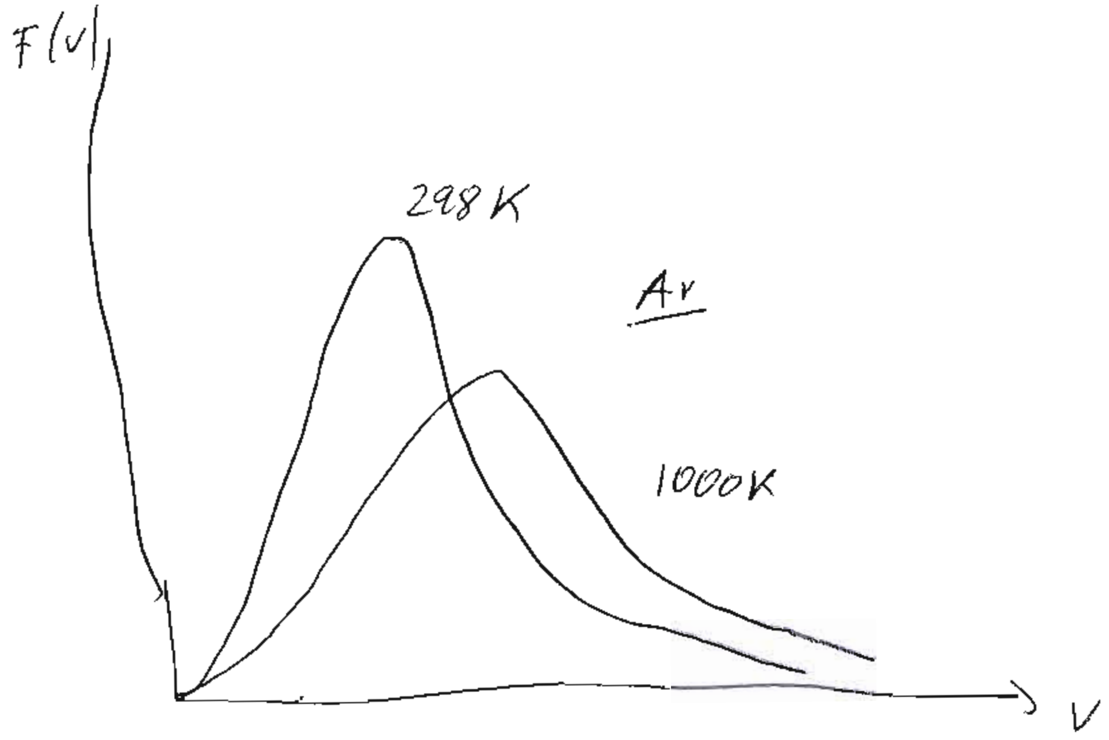
also in the exponent $\frac{m}{k} = \frac{M}{R}$

= Maxwell speed distribution
probability distribution for a moleculle to have a speed between v and v+dv
velocities can be positive or negative for +x or -x direction flight
speeds v must be positive and in F(v)

$0 \leq v \leq \infty$

Transp, Maxwell distributions
for 2 different T
for Kr, Ar, and Ne


F(v)
Kr
Ar
Ne
0
0
v


F(v)
298 K
Ar
1000 K
v

(38) −7

1) distribution not symmetric around maximum because at low speeds the $v^2$ factor dominates, at high speeds the exponential

2) T increase: lower maximum at higher speed ($E_k$ increase) area under normalized curves equal. normalitation = area = $1 \frac{m}{s}$

3) for h$\overset{a}{e}$vier atoms (Kr) peak at lower speeds when T is same (298 K for all 3)

$E_K$ (average) $= \frac{3}{2} kT$ depends only on T

but $E_k = \frac{1}{2} m v^2$

$\Rightarrow$ for larger mass (Kr) the average speed must be lower for same $E_k$ (average) at all masses ($\frac{3}{2} kT$)

Transp. measured no. of atoms at given speeds in a gas for K(g), measured at 466 K
+ Maxwell distribution curve
agreement excellent p. 864 top

$V_{mp}$ most probable speed:

maximum of distribution

$$\Rightarrow \frac{dF(v)}{dv} = 0$$

$$\frac{dF(v)}{dv} = \frac{d}{dv}\left[4\pi \left(\frac{m}{2\pi kT}\right)^{3/2} v^2 e^{-mv^2/2kT}\right]$$

(38) -8

$$= 4\pi \left(\frac{m}{2\pi kT}\right)^{3/2} \frac{d}{dv}\left[v^2 e^{-mv^2/2kT}\right]$$

$$= 4\pi \left(\frac{m}{2\pi kT}\right)^{3/2} e^{-mv^2/2kT}\left[2v - \frac{mv^3}{kT}\right]$$

for $v_{mp}$ : $\left.\frac{dF(v)}{dv}\right|_{v=v_{mp}} = 0$

$$\longrightarrow 2v_{mp} - \frac{m v_{mp}^3}{kT} = 0$$

$$\Rightarrow \quad v_{mp} = \sqrt{\frac{2kT}{m}}$$

$m = \frac{M}{N_A}$ $\quad k = \frac{R}{N_A}$ $\quad N_A$ cancels

$$v_{mp} = \sqrt{\frac{2RT}{M}}$$

average speed is given by multiplication of $v$ with the distribution and integration from 0 to $\infty$

$$v_{ave} = \int_0^\infty v F(v)\, dv$$

$$= \int_0^\infty v\left[4\pi\left(\frac{m}{2\pi kT}\right)^{3/2} v^2 e^{-mv^2/2kT}\right] dv$$

$$= \left(\frac{8kT}{\pi m}\right)^{1/2} = \left(\frac{8RT}{\pi M}\right)^{1/2}$$

root mean square speed $v_{rms}$ is the square root of the average of $v^2$

$$v_{rms} = \sqrt{\frac{3kT}{m}} = \sqrt{\frac{3RT}{M}}$$

Transp. Ar at 298 K:

$v_{mp} > v_{ave} > v_{rms}$

calculate $v_{mp}$, $v_{ave}$, $v_{rms}$ for Ar at 298 K

$$M_{Ar} = 0{,}040\ kg/mol$$

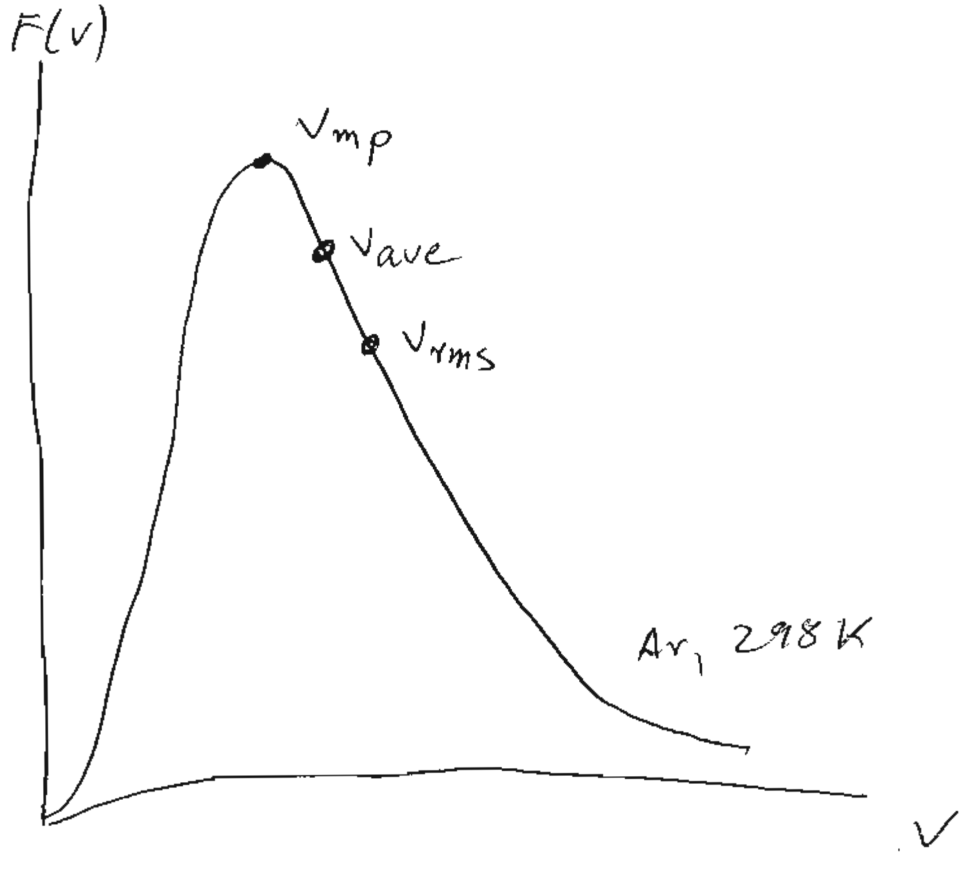
$$v_{mp} = \sqrt{\frac{2RT}{M}} = \sqrt{\frac{2\cdot 8{,}314\,\frac{J}{K\,mol}\cdot 298\,K}{0{,}040\ kg/mol}} = 352\,\frac{m}{s}$$

$$v_{ave} = \sqrt{\frac{8RT}{\pi M}} = \sqrt{\frac{8\cdot 8{,}314\,\frac{J}{K\,mol}\cdot 298\,K}{\pi\cdot 0{,}040\ kg/mol}} = 397\,\frac{m}{s}$$

$$v_{rms} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3\cdot 8{,}314\,\frac{J}{K\,mol}\cdot 298\,K}{0{,}040\ kg/mol}} = 431\,\frac{m}{s}$$

speed of sound in dry air: $346\,\frac{m}{s}$

" " a typical airliner: $500\,\frac{miles}{h} = 224\,\frac{m}{s}$



# Thermal Conduction

Transport of energy = heat against gradT

Transp. gas in a box with gradT

gradT only, no. density of particles $\tilde{N}(x)$ is everywhere the same in the box

→ Relaxation to equilibrium by transport of $E_{kin}$ from high T to low T

$E_{kin}$ transport by particle collisions, ~~also in~~ although in liquids and solids E transport also possible by radiation or by convection currents

differencesin density $\rho$ by gradT → convection currents: E transport still by collisions of particles in the currents

current → no random motion → different from normal collision transport (random motion)

convection transport and radiative transport are assumed to be negligible here

Thermodynamics: average energy of a monatomic gas particle: $\frac{3}{2}k_BT$ (3 dimensions)

polyatomic molecules: more energy possible in rotational and vibrational degrees of freedom

$E_{kin}$ is transported, when the flux plane is hit by particles. No mass transfere, because the particle density is the same everywhere.

→ no $E_{kin}$ transport by normal diffusion

statistical and kinetic theory viewpoints o
gas diffusion.

## 34.5 Thermal Conductio

**Thermal conduction** is the transport process in w gradient in temperature. Figure 34.7 depicts a cc which a gradient in temperature exists. Note that t ture only, and that the particle number densi Equilibrium is reached when the system has an id box. Because temperature and kinetic energy are will involve the transport of kinetic energy from the lower temperature side.

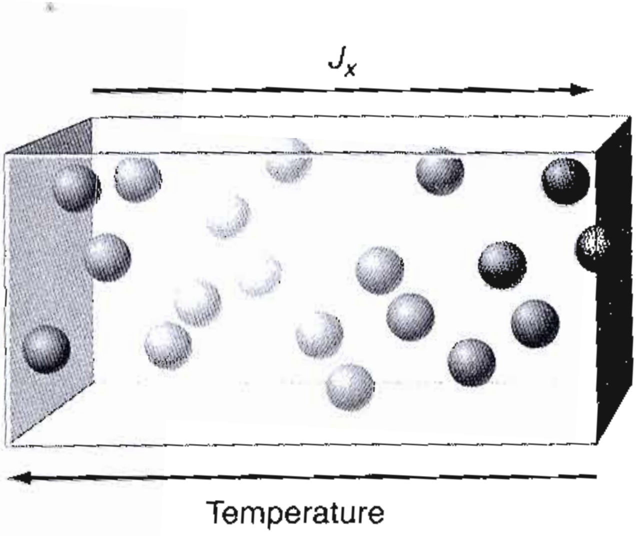


FIGURE 34.7
Temperature gradient in a collection of gas particles. Regions containing high kinetic energy particles are red and low kinetic energy regions are blue. The gradient in kinetic energy, and therefore temperature, is indicated, and the flux in energy in response to this gradient, $J_x$, is also shown.

Thermal conduction occurs through a vari phase of matter. In this derivation we assume th collisions and that equilibrium with the energy sion, thereby ensuring that the particles are at e collision. This collisional picture of energy trar ever, it can also be applied to liquids and sol translate freely, yet the molecular energy can nearby molecules, resulting in energy transfer. energy can also be transferred through convec differences in density resulting from the temp currents. Although energy is still transferred tl cles in the currents collide with other particle that transfer through convection is physically have defined it. In radiative transfer, matter is emitting and absorbing electromagnetic radi matter is absorbed by lower temperature matt vection and radiative transfer are assumed to from planes located ±λ from the flux plane:

$$J_{-\lambda,0} = \frac{1}{4}\nu_{ave}\widetilde{N}\varepsilon(-\lambda) \quad (34.31)$$

$$J_{\lambda,0} = \frac{1}{4}\nu_{ave}\widetilde{N}\varepsilon(\lambda) \quad (34.32)$$

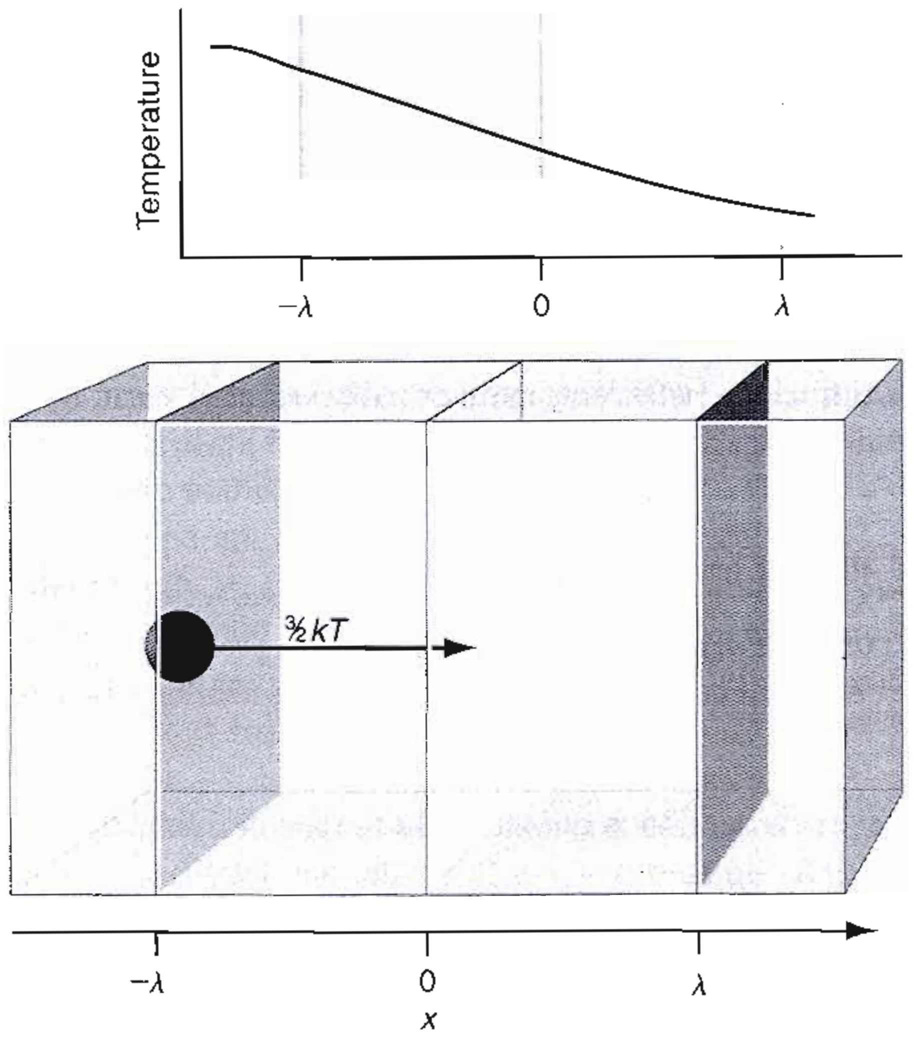


**FIGURE 34.8**
Model used to determine the thermal conductivity of a gas. The gradient in temperature will result in the transfer of kinetic energy from regions of high temperature (indicated by the red plane) to regions of lower temperature (indicated by the blue plane). The plane located at $x = 0$ is the location at which the flux o kinetic energy in response to the gradien is determined. Two planes, located one mean free path away (±λ) from the flux plane, are established, with particles trav eling from one of these planes to the flux plane. Energy is transferred via collision events at the flux plane.

energy at planes $\pm\lambda$ away from the flux plane $(x=0)$: (Transp.)

$$\varepsilon(-\lambda) = \varepsilon(0) - \lambda\left(\frac{dE}{dx}\right)_{x=0}$$

$$\varepsilon(+\lambda) = \varepsilon(0) + \lambda\left(\frac{dE}{dx}\right)_{x=0}$$

Maxwell distribution

as before: flux $\mathcal{J} = \tilde{N}\,\varepsilon(x)\int_0^\infty v_x\, f(v_x)\, dv_x$

$$= \frac{1}{4}\tilde{N}\,\varepsilon(x)\, v_{ave}$$

$\tilde{N}$ particle number density = const.

only grad $\varepsilon$ in above equations

$$\mathcal{J}_{-\lambda,0} = \frac{1}{4} v_{ave}\,\tilde{N}\,\varepsilon(-\lambda) \qquad \mathcal{J}_{+\lambda,0} = \frac{1}{4} v_{ave}\,\tilde{N}\,\varepsilon(\lambda)$$

total energy flux: difference of the two:

$$\mathcal{J}_t = \mathcal{J}_{-\lambda,0} - \mathcal{J}_{+\lambda,0} = \frac{1}{4} v_{ave}\,\tilde{N}\left[\varepsilon(-\lambda) - \varepsilon(+\lambda)\right]$$

$$\varepsilon(-\lambda) - \varepsilon(+\lambda) = \varepsilon(0) - \lambda\left(\frac{d\varepsilon}{dx}\right)_{x=0} - \left[\varepsilon(0) + \lambda\left(\frac{d\varepsilon}{dx}\right)_{x=0}\right]$$

$$= -2\lambda\left(\frac{d\varepsilon}{dx}\right)_{x=0}, \quad \varepsilon = \frac{3}{2}k_B T$$

$$\varepsilon(\lambda) - \varepsilon(+\lambda) = -2\lambda\left(\frac{d\,\frac{3}{2}k_B T}{dx}\right)_{x=0} = -3k_B\,\lambda\left(\frac{dT}{dx}\right)_{x=0}$$

$$\mathcal{J}_t = \frac{1}{4} v_{ave}\,\tilde{N}\left[\varepsilon(-\lambda) - \varepsilon(+\lambda)\right] = -\frac{3}{4}k_B\, v_{ave}\,\tilde{N}\,\lambda\left(\frac{dT}{dx}\right)_{x=0}$$

orientational averaging over particle ~~tar~~ trajectories

→ factor $\frac{2}{3}$

$$\rightarrow \mathcal{J}_t = -\frac{1}{2}k_B\, v_{ave}\,\tilde{N}\,\lambda\left(\frac{dT}{dx}\right)_{x=0}$$

= total energy flux for an ideal monatomic gas with energy transfer of $\frac{3}{2}k_B T$ in each collision the constant volume molar heat capacity

is $\frac{3}{2}R$

$$C_{V,m} = \frac{3}{2}R = \frac{3}{2}k_B N_A \qquad \frac{1}{N_A}C_{V,m} = \frac{3}{2}k_B$$

for ideal monatomic gases

→ flux in terms of $C_{V,m}$ which is not only ok for monatomic systems, _if_ the correct $C_{V,m}$ is used:

$$J_t = -\frac{1}{3}\frac{1}{N_A}C_{V,m}\,V_{ave}\,\tilde{N}\,\lambda\left(\frac{dT}{dx}\right)_{x=0}$$

in general: flux = - proportionality constant · gradient

here the proportionality constant is the _thermal conductivity_, called $\kappa$:

$$\kappa = \frac{1}{3}\,\frac{C_{V,m}}{N_A}\,V_{ave}\,\tilde{N}(x=0)\,\lambda$$

unit analysis → $[\kappa] = 1\,\frac{J}{K\,m\,s}$

every factor in $\kappa$ is known from thermodynamics or kinetic gas theory ⇒ calculation of $\kappa$ for ideal gases rather easy

for liquids $\kappa$ is still the proportionality constant between energy flux and T-gradient, however, for liquids no simple equation as for gases exists.

$\lambda$ in the equation for $\kappa$: similar to diffusion coeff.

The thermal conductivity can be used to obtain the hard-sphere radius of gases.

_Example_ $\kappa = 0.0177\,\frac{J}{K\,m\,s}$ for Ar at 300 K, 1 atm

What is the collisional cross section $\sigma$ for Ar, assuming it to be an ideal gas?

as above: $\lambda = \frac{RT}{PN_A} \cdot \frac{1}{\sqrt{2}\sigma}$

$$= \frac{V}{\tilde{N}} \frac{1}{\sqrt{2}\sigma} = \frac{1}{\tilde{N}\sqrt{2}\sigma}$$

→ $\lambda$ decreases when $P$ increases

in the equation for $\kappa$: $\tilde{N}\lambda = \frac{1}{\sqrt{2}\sigma}$

→ $\kappa$ seems to be independent of $P$

Transp. $\kappa$ vs $P$ for $N_2$, Ar at 300K

→ $\kappa$ is mostly independent of P up to 50 atm

at higher P intermolecular forces become important

→ hard-sphere model not good for $P > 50$ atm

→ kinetic gas theory cannot be used at $P > 50$ atm

after 50 atm, $\kappa$ shows a steep increase with P

low pressure (not shown), such that $\lambda >$ container

→ $E_{kin}$ in container transported by particle-wall collision

→ $\kappa$ increases with P also at low P

$\tilde{N}$ cancels in $\kappa$ with $\lambda$

→ T dependence mostly from $v_{ave}$ and $C_{v,m}$

monatomic gases: $C_{v,m}$ should not depenend much on T

$v_{ave}$ in $\kappa$ predicts a $T^{1/2}$ dependence of $\kappa$

same for diatomics and polyatomics

Transp. T dependence of $\kappa$ for $N_2$, Ar at 1 atm

lines show the $T^{1/2}$ dependence fit

$\kappa_{exp.}(300K) = \kappa_{calc.}(300K)$, from there $T^{1/2}$ dependence other terms needed to calculate $\lambda$ are

$.07 \times 10^{-23}\ \mathrm{J\ K^{-1}}$

$98\ \mathrm{m\ s^{-1}}$

$2.45 \times 10^{25}\mathrm{m^{-3}}$

$$\frac{\ ^{-1})}{\times 10^{25}\mathrm{m^{-3}})} = 2.63 \times 10^{-7}\mathrm{m}$$

ion 33.7), the collisional cross section is

$$\frac{1}{0^{25}\mathrm{m^{-3}})(2.63 \times 10^{-7}\mathrm{m})}$$

esponds to a particle diameter of
close to the 194 pm value provided by

lependent on $\nu_{ave}$, $\widetilde{N}$, and $\lambda$, quantities
re. Therefore, $\kappa$ will also demonstrate
ons regarding the dependence of $\kappa$ on $T$
approach used to describe the gas par-
oportional to $\widetilde{N}$ such that the mean-free

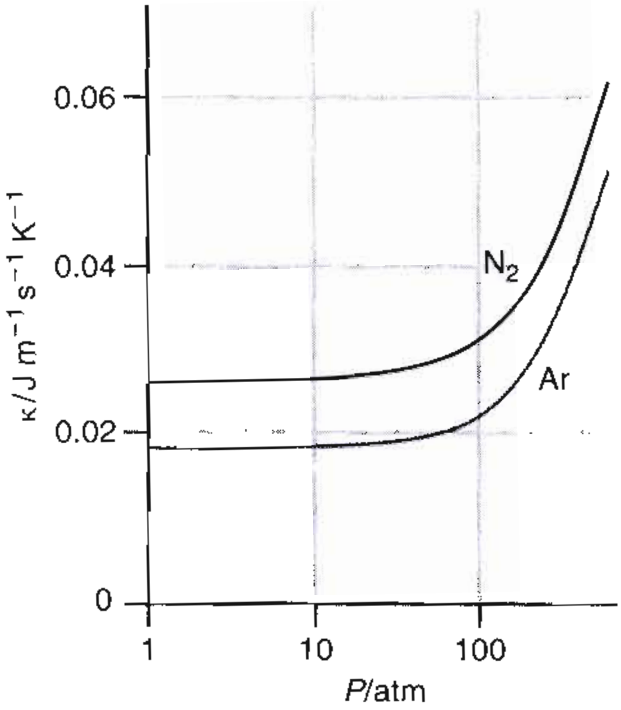


**FIGURE 34.9**
Thermal conductivity as a function of pressure for $N_2$ and Ar at 300 K. Note that the pressure scale is logarithmic. The figure demonstrates that $\kappa$ is roughly independent of pressure up to 50 atm.

Section 33.7), the collisional cross section is

$$\frac{1}{\times 10^{25}\mathrm{m}^{-3})(2.63 \times 10^{-7}\mathrm{m})}$$

corresponds to a particle diameter of
ably close to the 194 pm value provided by

l is dependent on $\nu_{ave}$, $\widetilde{N}$, and $\lambda$, quantities
ressure. Therefore, $\kappa$ will also demonstrate
dictions regarding the dependence of $\kappa$ on $T$
heory approach used to describe the gas par-
ely proportional to $\widetilde{N}$ such that the mean free

$$\left(\frac{V}{N}\right)\frac{1}{\sqrt{2}\sigma} = \frac{1}{\widetilde{N}\sqrt{2}\sigma}$$

results in the absence of $\widetilde{N}$ dependence in
result that $\kappa$ is predicted to be independent of
dependence of $\kappa$ for $N_2$ and Ar at 300 K. The
ally independent of pressure up to 50 atm! At
s between gas molecules become appreciable,
odel, and the expressions derived using gas
n is indicated by the dramatic rise in $\kappa$ at high
also observed at very low pressure, when the
ns of the container. In this case, the energy is
to the other by wall–particle collisions such
essure regime.

idence of $\kappa$, the cancellation of $\widetilde{N}$ with the
$_{m}$ carrying temperature dependence. For a
onstrate minimal temperature dependence.
36) predicts that $\kappa$ is proportional to $T^{1/2}$.
ic and polyatomic molecules in which the
al. Figure 34.10 presents the variation in $\kappa$
Also presented is the predicted $T^{1/2}$ depend-
e experimental and predicted temperature
s more rapidly with temperature than the
ence of intermolecular interactions that are
employed in gas kinetic theory. Notice that
erimental $\kappa$ are evident at low temperature

**FIGURE 34.9**
Thermal conductivity as a function of pressure for $N_2$ and Ar at 300 K. Note that the pressure scale is logarithmic. The figure demonstrates that $\kappa$ is roughly independent of pressure up to 50 atm.

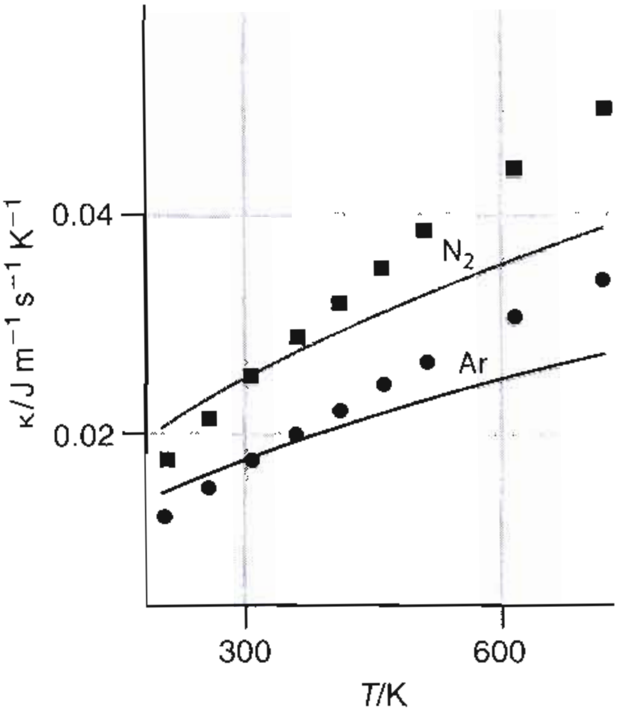


**FIGURE 34.10**
Variation of $\kappa$ with temperature for $N_2$ and Ar at 1 atm. Experimental data are indicated by the squares and circles, and the predicted $T^{1/2}$ dependence as the solid lines. The calculated $\kappa$ was set equal to the experimental value at 300 K, and then $T^{1/2}$ dependence was applied to generate the predicted variation in $\kappa$ with temperature.

κ increases faster with T than $T^{1/2}$ (39)-6

reason: intermolecular interactions which are neglected in the hard-sphere model and in kinetic gas theory

differences between $T^{1/2}$ and $\kappa_{exp}$ also at low T, while above at low P the agreement is quite well

- viscosity of gases
- viscosity measurement

## Linear momentum transport

when a gas flows through a pipe under pressure then some gases flow more easy than others.

Measuring the resistance against flow: viscosity $\eta$

Transp. cut of gas flow between two plates:

$x$: along the flow
$z$: perpendicular to flow direction

experiment: speed of flow fastest in the center between the plates and $v_x \to 0$ at the plates

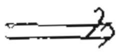
→ gradient in $v_x$ along $z$

grad$v_x$ along the coordinate perpendicular to the flow direction

linear momentum in x direction: $mv_x$

⇒ when grad$v_x$ exists also grad $p_x$ exists

assumption: flow slow enough to be laminar
(= no turbulences)



⇒ cut planes along the flow direction → layers of constant speed (average speed)

speed too high: flow gets turbulent
→ layers are intermixed → no more constant speed layers exist

discussion here: only laminar flow
exactly like before

as well, as opposed to the good agreeme
behavior of $\kappa$ with pressure evident in Figu

## 34.6 Viscosity of Ga

The third transport phenomenon considered
rience provides an intuitive guide with res
flow of a gas through a pipe under pressure.
ers, and the property that characterizes res
the symbol $\eta$ (lowercase Greek eta). W
momentum? Figure 34.11 provides a cut
plates. It can be shown experimentally tha
way between the plates and decreases as th
the fluid–plate boundary. Therefore, a grad
onal to the direction of flow ($z$ in Figure 34
direction is $mv_x$, a gradient in linear mome

We assume that the gas flow is **laminar**
into layers of constant speed as illustrated in
gases and some liquids provided the flow rate
of the chapter). At high flow rates, the **turb**
are intermixed such that a clear dissection o
cannot be performed. The discussion present

The analysis of linear momentum tran
and thermal conductivity. As illustrated in
exists in the $z$ direction; therefore, planes o
lel to the direction of fluid flow as illustr
momentum occurs by a particle from on
plane and thereby transferring its moment

To derive the relationship between flu
proceed in a fashion analogous to that use
mal conductivity (Section 34.5). First, the

$$p(-\lambda) = p(0$$

$$p(\lambda) = p(0$$

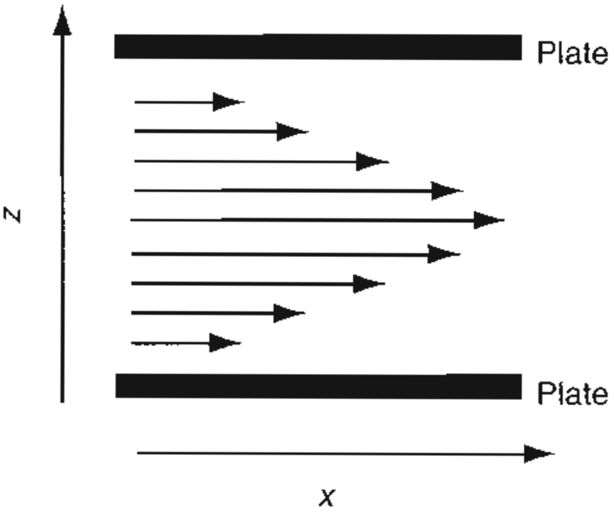


FIGURE 34.11
Cross section of a fluid flowing between two plates. The fluid is indicated by the green area between the plates, with arrow lengths representing the speed of the fluid.

transport of momentum by particles crossing from one constant momentum layer to another

collision with flux plane → transfer of momentum to the flux plane at $z=0$

$$p(\lambda) = p(0) + \lambda\left(\frac{dp}{dz}\right)_{z=0}$$

$$p(-\lambda) = p(0) - \lambda\left(\frac{dp}{dz}\right)_{z=0}$$

→ flux of momentum from planes $\pm\lambda$ away:

from before for energy:

$$J_{-\lambda,0} = \frac{1}{4} v_{ave} \tilde{N} p(-\lambda)$$

$$J_{+\lambda,0} = \frac{1}{4} v_{ave} \tilde{N} p(\lambda)$$

$\tilde{N}$ = const. again, only $p$ is different

the total flux is again the difference:

$$J_{-\lambda,0} - J_{+\lambda,0} = J_z \text{ (total)}$$

$$= \frac{1}{4} v_{ave} \tilde{N}\left[p(-\lambda) - p(+\lambda)\right] \quad p(0) \text{ cancels!}$$

$$= \frac{1}{4} v_{ave} \tilde{N}\left[-2\lambda\left(\frac{dp}{dz}\right)_{z=0}\right]$$

$$= -\frac{1}{2} v_{ave} \tilde{N} \lambda \left(\frac{d\, m v_x}{dz}\right)_{z=0}$$

$$= -\frac{1}{2} v_{ave} \tilde{N} \lambda m \left(\frac{dv_x}{dz}\right)_{z=0}$$

a factor of $\frac{2}{3}$ is again necessary for the orientational average of particle trajectories:

$$J_z = -\frac{1}{3} v_{ave} \tilde{N} \lambda m \left(\frac{dv_x}{dz}\right)_{z=0}$$

⇒ proportionality constant between flux and gradient is viscosity $\eta$:

$$\eta = \frac{1}{3} v_{ave} \tilde{N} \lambda m$$

$m$: mass of 1 particle

$$m = M/N_A$$

plane and thereby transferring its momentum to the adjacent layer.

To derive the relationship between flux and the gradient in linear momentum, w proceed in a fashion analogous to that used to derive diffusion (Section 34.2) and thermal conductivity (Section 34.5). First, the linear momentum $p$ at ±λ is given by

$$p(-\lambda) = p(0) - \lambda\left(\frac{dp}{dz}\right)_{z=0} \tag{34.37}$$

$$p(\lambda) = p(0) + \lambda\left(\frac{dp}{dz}\right)_{z=0} \tag{34.38}$$

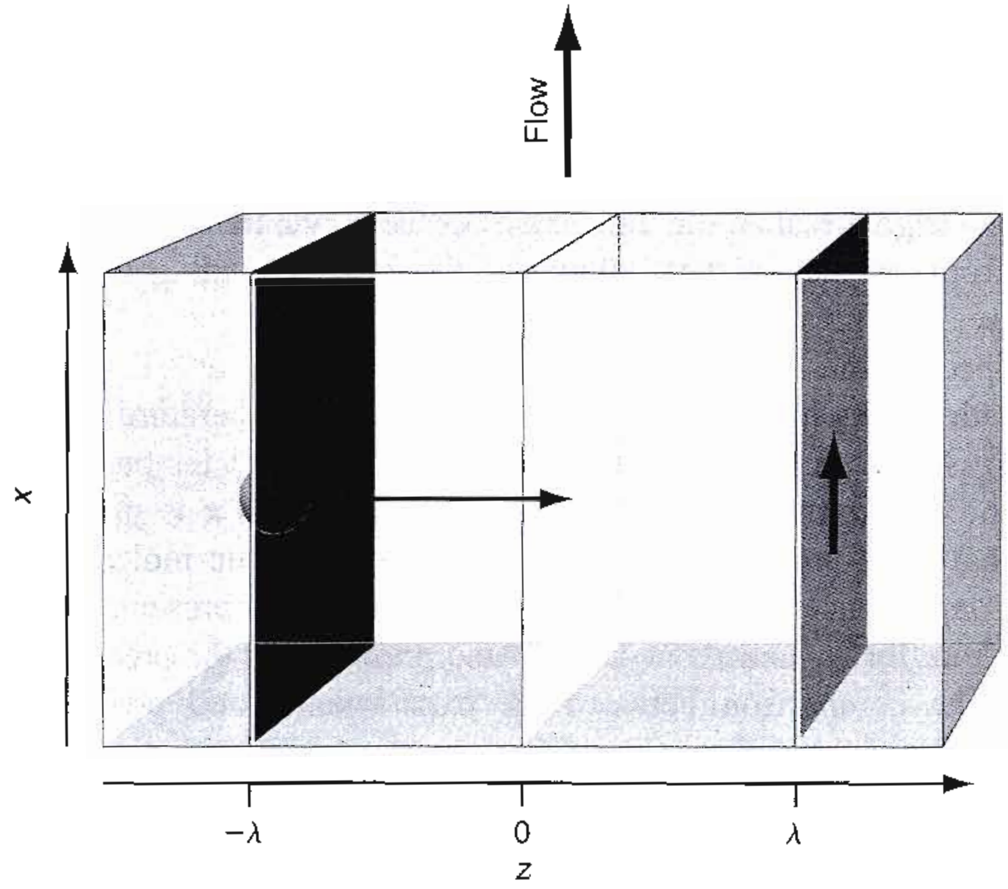


**FIGURE 34.12**
Parameterization of the box model used to derive viscosity. Planes of identical particle velocity ($v_x$) are given by the blue planes, with the magnitude of velocity given by the arrows. The gradient in linear momentum will result in momentum transfer from regions of high momentum (darker blue plane) to regions of lower momentum (indicated by the light blue plane). The plane located at $z = 0$ is the location at which the flux of linear momentum in response to the gradient is determined.

$\eta$: viscosity of a gas in terms of parameters from kinetic gas theory

unit of viscosity $[\eta] = 1\,P$ (poise) $= 0.1\,\frac{kg}{m\,s}$

usual is $\mu P$ for gas viscosity and $cP$ ($10^{-2}$) for liquid viscosity

Example: $\eta = 227\,\mu P$ for Ar at 300K, 1 atm collisional cross section of Ar assumed as ideal gas?

$\sigma$ from $\lambda$!

$$\lambda = \frac{3\eta}{v_{ave}\tilde{N} m} \qquad PV = nRT = \frac{N}{N_A} RT$$

$$\frac{N}{V} = \tilde{N} = \frac{PN_A}{RT}$$

$$v_{ave} = \sqrt{\frac{8RT}{\pi m}} = 398\,\frac{m}{s}$$

$$\tilde{N} = \frac{PN_A}{RT} = 2.45 \cdot 10^{25}\,m^{-3}$$

$$m = \frac{M}{N_A} = \frac{0.040\,kg/mol}{6.022 \cdot 10^{23}\,1/mol} = 6.64 \cdot 10^{-26}\,kg$$

$$\lambda = \frac{3\eta}{v_{ave}\tilde{N} m} = \frac{3 \cdot 227 \cdot 10^{-6}\,P}{398\,\frac{m}{s} \cdot 2.45 \cdot 10^{25}\,m^{-3} \cdot 6.64 \cdot 10^{-26}\,kg}$$

$$= \frac{3 \cdot 227 \cdot 10^{-7}\,\frac{kg}{m\,s}}{398\,\frac{m}{s} \cdot 2.45 \cdot 10^{25}\,m^{-3} \cdot 6.64 \cdot 10^{-26}\,kg} \quad \left(1\,P = 0.1\,\frac{kg}{m\,s} = 10^{-1}\,\frac{kg}{m\,s}\right)$$

$$= 1.28 \cdot 10^{-7}\,m$$

$$\sigma = \frac{1}{\sqrt{2}\tilde{N}\lambda} = \frac{1}{\sqrt{2} \cdot 2.45 \cdot 10^{25}\,m^{-3} \cdot \underset{1.28 \cdot 10^{-7}\,m}{\cancel{6.64 \cdot 10^{-26}\,kg}}}$$

$$= 2.25 \cdot 10^{-v}\,m^2$$

$\sigma$ from thermal conductivity was $\approx \frac{1}{2}$ this value

reason: intermolecular interactions are assumed to be well described by the hard-sphere model (ideal gas)

$d_K \approx$ tab. values

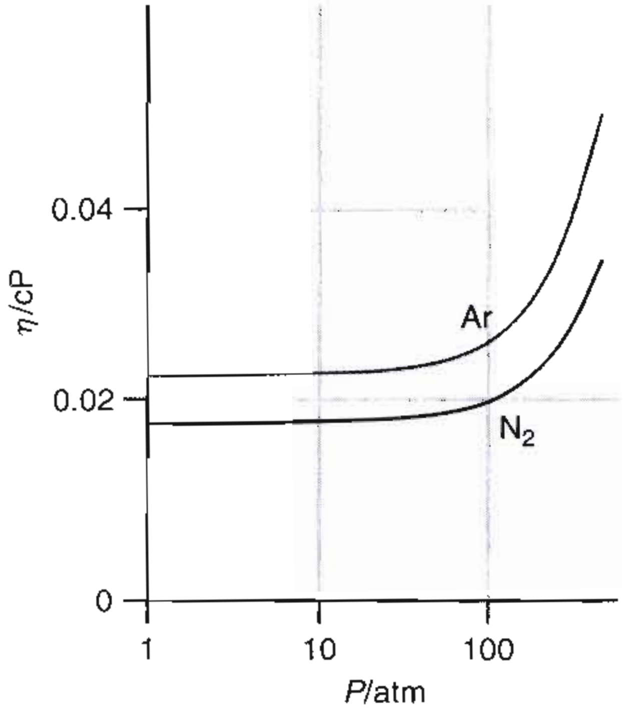


FIGURE 34.13
Pressure dependence of $\eta$ for gaseous $N_2$ and Ar at 300 K.

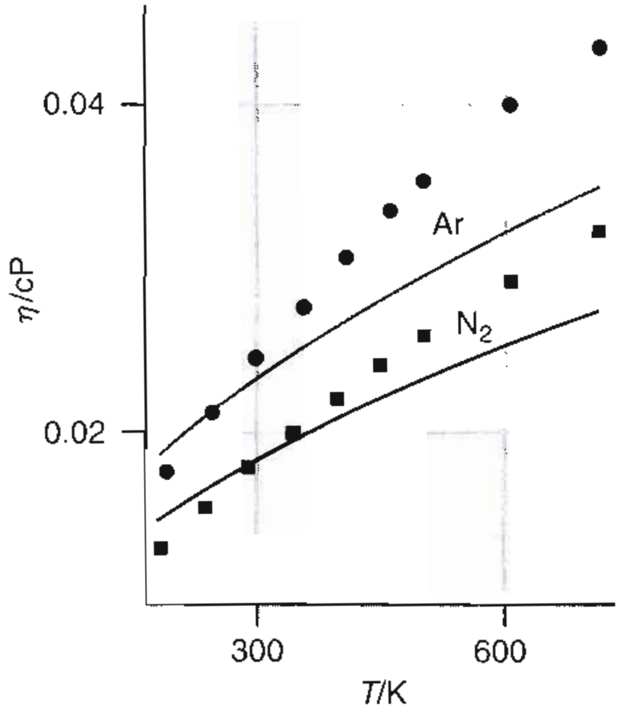


FIGURE 34.14
Temperature dependence of $\eta$ for $N_2$ and Ar at 1 atm. Experimental values are given by the squares and circles, and the predicted $T^{1/2}$ dependence is given as the

$$\lambda = \frac{3\eta}{\nu_{ave}\widetilde{N}_m} = \frac{3(2}{(398\ \mathrm{m\ s^{-1}})(2.45 \times}$$

$$= \frac{3(227 \times 10^{-7}\ \mathrm{kg\ m^{-}}}{(398\ \mathrm{m\ s^{-1}})(2.45 \times 10^{25}\ \mathrm{m^{-3}})(}$$

Note the conversion of poise to SI units in
mean free path, the collisional cross section c

$$\sigma = \frac{1}{\sqrt{2}\widetilde{N}\lambda} = \frac{1}{\sqrt{2}(2.45 \times 10^{25}\,\mathrm{m^{-3}})\ (}$$

In Example Problem 34.5, the thermal co
the collisional cross section that was roughly
collisional cross-section values determined usi
erties illustrates the approximate nature of the
have assumed that the intermolecular interacti
approximation. The difference in $\sigma$ suggests t
describing the interaction of particles during c

Similar to thermal conductivity, viscosity i
that are both temperature and pressure depen
dependence, but the product of $\widetilde{N}$ and $\lambda$ conta
predicted to be independent of pressure. Figur
of $\eta$ for $N_2$ and Ar at 300 K. The behavior is
mal conductivity (Figure 34.9), with $\eta$ demo
$P \sim 50$ atm. At elevated pressures, intermole
the increased interaction between particles gi
$P > 50$ atm, similar to the case for thermal c

With respect to the temperature dependenc
dictates that $\eta$ should increase as $T^{1/2}$, identic
mal conductivity (Figure 34.10). This result
demonstrate a decrease in $\eta$ with an increase
increase in $\eta$ with temperature for a gas is b
Figure 34.14 where the variation in $\eta$ with
presented. Also shown is the predicted $T^{1/2}$
viscosity with temperature is a remarkable con
comparison of the experimental and predicte
that $\eta$ increases more rapidly than predicted du
actions that are neglected in the hard-sphere
temperature dependence of $\kappa$ provided earlier.
gas is consistent with the increase in velocit

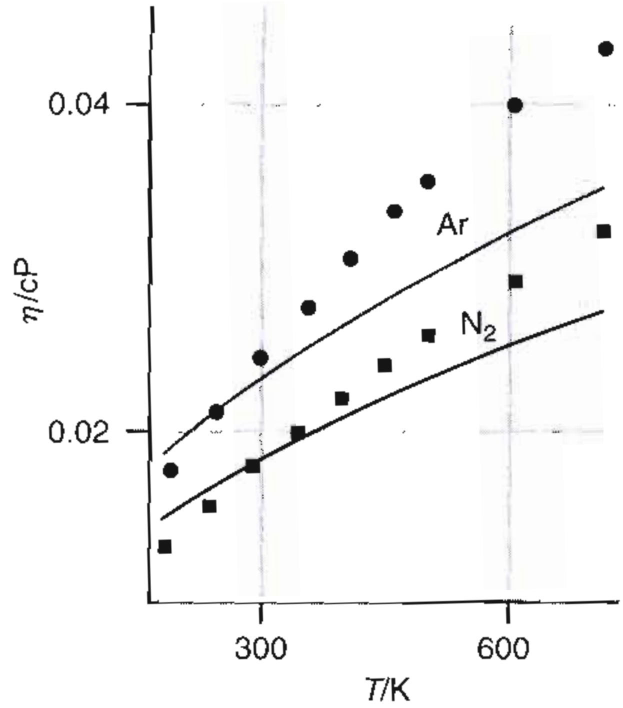


**FIGURE 34.14**
Temperature dependence of $\eta$ for $N_2$ and Ar at 1 atm. Experimental values are given by the squares and circles, and the predicted $T^{1/2}$ dependence is given as the solid line.

Similar to thermal conductivity, vi
that are both temperature and pressure
dependence, but the product of $\widetilde{N}$ and
predicted to be independent of pressur
of $\eta$ for $N_2$ and Ar at 300 K. The beha
mal conductivity (Figure 34.9), with
$P \sim 50$ atm. At elevated pressures, int
the increased interaction between parti
$P > 50$ atm, similar to the case for the

With respect to the temperature de
dictates that $\eta$ should increase as $T^{1/2}$,
mal conductivity (Figure 34.10). This
demonstrate a decrease in $\eta$ with an i
increase in $\eta$ with temperature for a g
Figure 34.14 where the variation in
presented. Also shown is the predicted
viscosity with temperature is a remarka
comparison of the experimental and p
that $\eta$ increases more rapidly than predi
actions that are neglected in the hard-
temperature dependence of $\kappa$ provided
gas is consistent with the increase in ve
corresponding increase in momentum fl

## 34.7 Measuring Vi

Viscosity is a measure of a fluid's resist
the viscosity of gases and liquids is mea
ured by monitoring the flow of a fluid th
greater the viscosity, the smaller the flow
derived by Poiseuille to describe flow of
of laminar flow:

$$\frac{\Delta V}{\Delta t} = \frac{\pi}{8}$$

there is a difference $\Delta\sigma$ between thermal conductivity and viscosity

$\Rightarrow$ intermolecular forces must be described better!

also as before for $\kappa$: $\eta = f(v_{ave}, \tilde{N}, \lambda)$, all $f(T,P)$

but $\tilde{N}\lambda$ is not P dependent ($\tilde{N}$ cancels out)

$$\lambda = \frac{1}{\sqrt{2}\,\tilde{N}\,\sigma} \Rightarrow \tilde{N}\cdot\lambda = \frac{1}{\sqrt{2}\,\sigma}$$

→ $\eta$ not P dependent

Transp. $\eta$ for $A \cdot N_2$, Ar vs P at 300K

almost identical to $\kappa$ vs P: little P dependence

up to 50 atm, then sharp rise of $\eta$ with P

high P: intermolecular forces get more important

Transp.: $\eta$ for $N_2$, Ar vs T at 1 atm

also identical to $\kappa$ vs T

$\ell$

$\eta = A e^{E_a/RT}$

liquids: $\eta$ decreases when T increases

gases: $\eta$ increases when T increases

$\eta$- increase is more rapid than the $T^{1/2}$ increase as predicted from ideal gas theory

sharper $\eta(T)$ increase: because of speed increases as T increases → increase in momentum flux

the intermolecular forces are not the only reason for that sharp $\eta$ increase

## Measurement of $\eta$

$\eta$ = fluid's resistance to flow

measuring the flow of a fluid through a tube:

the larger $\eta$, the smaller is the flow through the tube for the description of flow through a tube: Poisseuille equation (for laminar flow only):

$$\frac{\Delta V}{\Delta t} = \frac{\pi r^4}{8\eta}\,\frac{P_2 - P_1}{x_2 - x_1}$$

$\frac{\Delta V}{\Delta t}$ volume of fluid passing the tube in $\Delta t$

$\frac{P_2 - P_1}{x_2 - x_1}$: pressure gradient $\Delta P$ over tube length $L = x_2 - x_1$, $r$ tube radius

$\frac{\Delta V}{\Delta t} = f\left(\frac{V}{\eta}\right)$ the more viscous (higher $\eta$) the fluid the smaller is the flow rate.

<u>ideal gas</u>: $\frac{\Delta V}{\Delta t} = \frac{\pi r^4}{16\eta L P_0}(P_2^2 - P_1^2)$

pressures: $P_2$ at entry, $P_1$ at exit of the tube

$P_0$: pressure at place of $V$ measurement, usually at exit of tube $\Rightarrow$ usually $P_0 = P_1$

<u>Example</u> A $CO_2$ gas-cylinder has 50 lb (22.7 kg) of $CO_2$. How long can it be used in an experiment that needs $CO_2$ flow through a 1.00 m long tube (diameter 0.75 mm) at an input pressure of $\overset{1.05}{\cancel{1.00}}$ atm and an output pressure of 1.00 atm all at 293 K, for ~~$O_2$~~ $CO_2$, $\eta = 146\,\mu P$.

$$\frac{\Delta V}{\Delta t} = \frac{\pi r^4}{16\eta L P_0}(P_2^2 - P_1^2)$$

$$= \frac{\pi\,(0.375\cdot 10^{-3}\,m)^4}{16\cdot 1.46\cdot 10^{-5}\,\frac{kg}{ms}\cdot 1.00\,m\cdot 101{,}325\,Pa}\left((106391\,Pa)^2 - (101325\,Pa)^2\right)$$

$$= 2.76\cdot 10^{-6}\,\frac{m^3}{s}$$

$146\,\mu P = 146 \cdot 10^{-6}\,Pa = 1.46 \cdot 10^{-4}\,P = 1.46 \cdot 10^{-5}\,\frac{kg}{m\,s}$

$1\,P = 0.1\,\frac{kg}{ms}$

$1.00\,atm = 101\,325\,Pa$

$$n_{CO_2} = \frac{22.7\,kg\ CO_2\ (\text{in cylinder})}{0.044\,kg/mol\ (M_{CO_2})} = 516\,mol$$

$$V = \frac{nRT}{P} = 1.26 \cdot 10^4\,L \cdot \frac{10^{-3}\,m^3}{L} = 12.6\,m^3$$

$$\frac{nRT}{P} = \frac{561\,mol \cdot 8.314\,\frac{J}{K\,mol} \cdot 298\,K}{1.00\,atm \cdot 101\,325\,Pa/atm} = 12.6\,m^3 = 1.26 \cdot 10^{4}\,L \cdot \frac{10^{-3}\,m^3}{L}$$

$$\Delta t = \frac{V}{\Delta V/\Delta t} = \frac{12.6\,m^3}{2.76 \cdot 10^{-6}\,m^3/s}$$

$= 4.56 \cdot 10^6\,s$

$= 52.8\,d$ use of cylinder

## Ostwald viscosimeter for liquid $\eta$

Transp. Ostwald viscosimeter

measured: time it takes for the liquid to flow from upper to lower mark

flow is through a thin capillary ensuring laminar flow

the liquid is forced through the capillary by the pressure due to its weight: $\rho g h = \Delta P$

$$\frac{\Delta V}{\Delta t} = \frac{\pi r^4}{8\eta}\,\frac{\rho g h}{l}$$ $l$: capillary length

$$\rightarrow \eta = \left(\frac{\pi r^4}{8}\,\frac{gh}{l\,\Delta V}\right)\rho\,\Delta t = A\,\rho\,\Delta t$$

A: viscosimeter constant

weight of $CO_2$. A cylinder contains 50 lb
der be used in an experiment that requires
ugh a 1.00-m-long tube (diameter = 0.75 mm)
tput pressure of 1.00 atm? The flow is meas-

e $\Delta V/\Delta t$ is

$$)$$

$$\frac{.375 \times 10^{-3}\ \mathrm{m})^4}{\mathrm{m}^{-1}\ \mathrm{s}^{-1})(1.00\ \mathrm{m})(101{,}325\ \mathrm{Pa})}$$

$$-\ (101{,}325\ \mathrm{Pa})^2)$$

1

ylinder to the volume occupied at 298 K and

$$\frac{1}{\mathrm{kg\ mol}^{-1}}\Bigg) = 516\ \mathrm{mol}$$

$$10^4\ \mathrm{L}\left(\frac{10^{-3}\ \mathrm{m}^3}{\mathrm{L}}\right) = 12.4\ \mathrm{m}^3$$

tained in the cylinder, the duration over which

$$\frac{}{{}^3\ \mathrm{s}^{-1}} = 4.49 \times 10^6\ \mathrm{s}$$

s.

viscosity of liquids is an **Ostwald viscometer**
ty, one measures the time it takes for the liquid
to the “low” level mark, and the fluid flows
aminar flow. The pressure driving the liquid
the fluid density, $g$ is the acceleration due to
levels in the two sections of the viscometer, as
ight difference will evolve as the fluid flows,

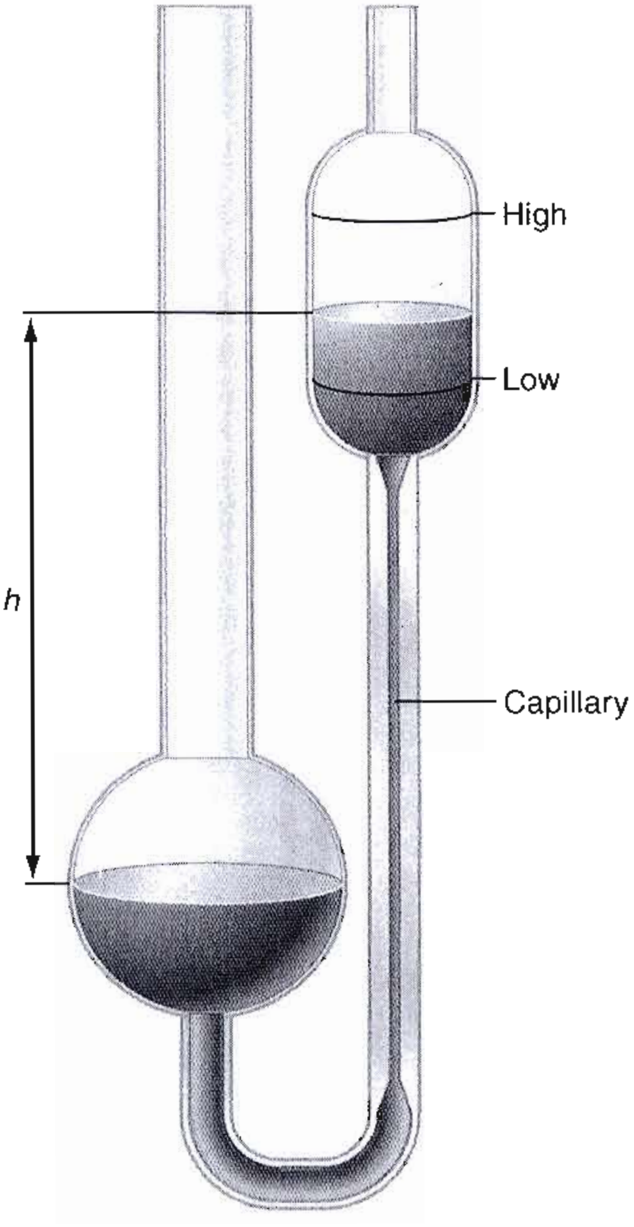


FIGURE 34.15
An Ostwald viscometer. The time for a volume of fluid ($\Delta V$) to flow from the “High” level mark to the “Low” level mark is measured and then used to determine the viscosity of the fluid by means of Equation (34.47).

dimensions of viscosimeter → A

normally is a comparison with a liquid where $\eta$ is well known

for example $H_2O$

$$\frac{\eta_{H_2O}}{\eta_x} = \frac{A \rho_{H_2O} \Delta t_{H_2O}}{A \rho_x \Delta t_x}$$

$$\eta_x = \eta_{H_2O} \frac{\Delta t_x}{\Delta t_{H_2O}} \cdot \frac{\rho_x}{\rho_{H_2O}}$$

- Diffusion of liquids
- viscosity of liquids
- Sedimentation and Centrifugation

found by R. Brown in a microscopy experiment: random motion that leads to particle diffusion

He used ≈ 5 $\mu m$ diameter pollen grains (seeds of plants) suspended in $H_2O$

Observation: the grains are moving

He designed experiments to prove that the motion is not from convection currents in the $H_2O$

⇒ The motion is due to the particles themselves

Brownian motion: random motion of relatively large particles (≈ 5 $\mu m$) in liquids with small molecules (small compared to the particles, e.g. $H_2O$)

= diffusion of large particles in solution

Transp. particle, mass $m$, in liquid with viscosity $\eta$

motion of particle from collisions with solvent molecules

→ Force, changing in time: $F(t)$

$F$ is decomposed in the directional components along the cartesian axes $(x, y, z)$

$x$ component: $F_x(t)$

if the particle makes a move in $x$ direction due to collisions with $H_2O$ molecules → because of the viscosity $\eta$ of $H_2O$ a frictional force $F_{fr,x}$ will act against the move which will provide a time-varying force, $F(t)$. We decompose $F(t)$ into its directional components and focus on the component in the $x$ direction, $F_x(t)$. Motion of the particle in the $x$ direction will result in a frictional force due to the liquid's viscosity:

$$F_{fr,x} = -f\mathrm{v}_x = -f\left(\frac{dx}{dt}\right) \tag{34.48}$$

The negative sign in Equation (34.48) indicates that the frictional force is in opposition to the direction of motion. In Equation (34.48), $f$ is referred to as the friction coefficient and is dependent on both the geometry of the particle and the viscosity of the fluid. The total force on the particle is simply the sum of the collisional and frictional forces:

$$F_{total,x} = F_x(t) + F_{fr,x}$$

$$m\left(\frac{d^2x}{dt^2}\right) = F_x(t) - f\left(\frac{dx}{dt}\right) \tag{34.49}$$

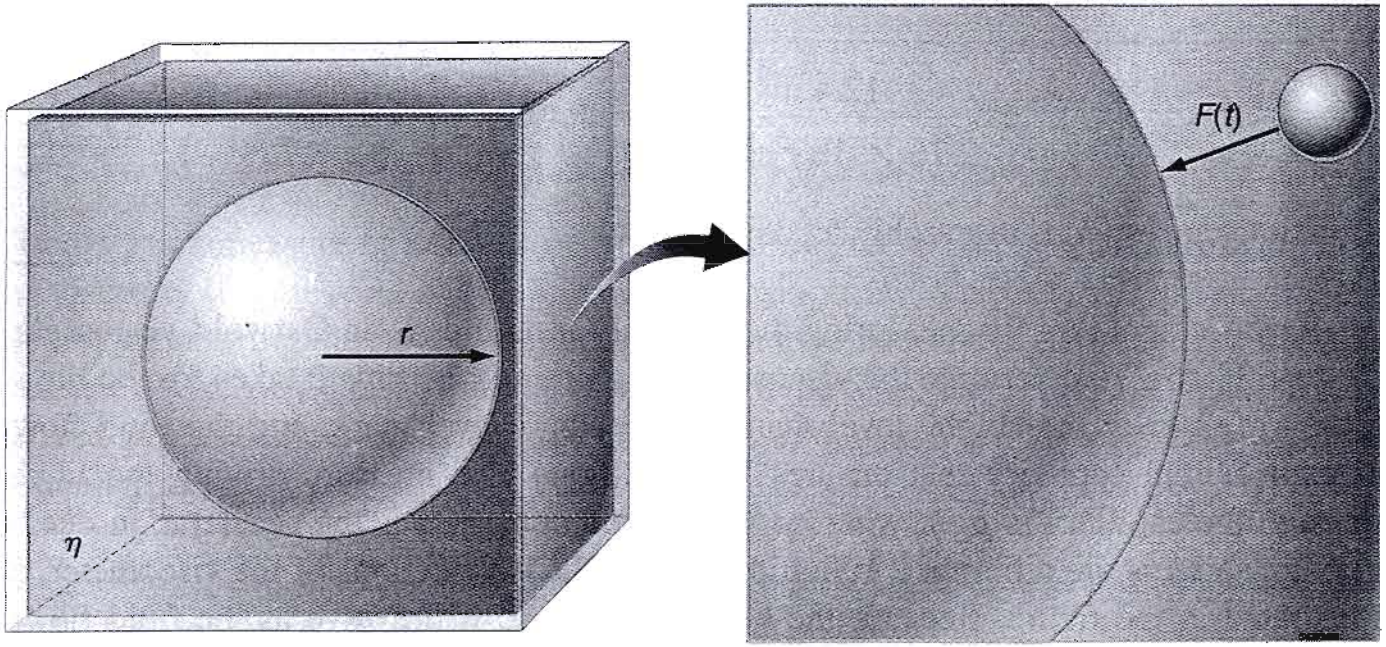


FIGURE 34.16
Illustration of Brownian motion. A spherical particle with radius $r$ is embedded in a liquid of viscosity $\eta$. The particle undergoes collisions with solvent molecules (the red dot in the right-hand figure) resulting in a time-varying force, $F(t)$, that initiates particle motion. Particle motion is opposed by a frictional force that is dependent on the solvent viscosity.

$$F_{fr,x} = -f v_x = -f \frac{dx}{dt}$$

⊖ because $F_{fr,x}$ is against the move with $v_x$

$f$, the frictional coefficient depends on the form of the large particle and on $\eta$ of the liquid ($H_2O$)

total force on the particle = coll. + frictional force

$$F_{t,x} = F_x(t) + F_{fr,x}$$

$$m\frac{d^2x}{dt^2} = F_x(t) - f\frac{dx}{dt}$$

differential equation, studied 1905 by Einstein:

average over liquid-molecule-particle collisions

→ average of the square displacement of the particle in time $t$: $\langle x^2 \rangle = \frac{2k_BTt}{f}$

if it is a spherical particle, $f = 6\pi\eta r$

$$\rightarrow \langle x^2 \rangle = 2\frac{k_BT}{6\pi\eta r}t$$

earlier found: $\langle x^2 \rangle = 2Dt$ D diffusion coefficient

$$\rightarrow D = \frac{k_BT}{6\pi\eta r}$$

Stokes-Einstein equation for the diffusion of spherical large particles in a liquid with small molecules

$$D = f[\eta(\text{solvent}), \text{particle size } r, T]$$

equation works well when the diffusing particle is much larger than the solvent molecules.

if particle size ≈ liquid molecule size

$$\rightarrow \quad D = \frac{k_B T}{4\pi \eta r}$$

also good for self-diffusion ≡ diffusion of a solvent molecule in the solvent itself

Hemoglobin: protein for $O_2$ transport in the body

$D = 6,90 \cdot 10^{-11} \frac{m^2}{s}$ in water ($\eta = 0,891\,cP = 0,891 \cdot 10^{-3} \frac{kg}{ms}$)

if the molecule is spherical, what is its radius?

$$r = \frac{k_B T}{6\pi \eta D} = \frac{1,38 \cdot 10^{-23}\ J/K \cdot 298K}{6\pi \cdot 0.891 \cdot 10^{-3} \frac{kg}{ms} \cdot 6.90 \cdot 10^{-11} \frac{m^2}{s}} = 3,55 \cdot 10^{-9}\,m$$
$$= 3,55\,nm$$

x-ray crystallography: hemoglobin is approximately a sphere of radius 2.75 nm

one reason for the differences in $H_2O$ hemoglobin has associated (hydration) water ⇒ increased size

$\eta = f(T)$ is easily explained for gases from kinetic gas theory but not for liquids.

reason: distances between particles in a liquid are very small → intermolecular forces are important

~~gre~~ general rule: the stronger the inter~~molecular~~ molecular forces are, the larger is $\eta$ of the liquid

$\eta$ (liquids) increases as T decreases

T decrease: particles have less kinetic energy which is needed to escape attractions of other particles.

general;

Arrhenius type law $\quad \eta = Ae^{E_{vis}/RT}$ $\quad E_{vis}$ is activation energy for viscous flow

# Sedimentation & Centrifugation

dimentation: large particle sinks in a liquid
can be used to measure molar masses

Transp: molecule, mass m, sediments in a liquid of density $\rho$ under earth's gravitational pull

hree forces act on the particles

, frictional force $F_{fr} = -f v_x$

x, ~~z~~ pointing ~~down~~ up, then $v_x$ points down

2) gravitational force $F_{gr} = m \cdot g$

3) buoyant force: $F_b = -m \bar{V} \rho g$

same direction as frictional force

$\bar{V}$: specific volume of solute

$\bar{V}$ = volume of the liquid displaced by the solute per gram of solute ($cm^3/g$)

t=0: particle on top of the liquid, then falls
initially the downward speed $v_x(t=0) = 0$
the acceleration happens (gravitational pull) and $v_x$ increases until a maximum (= largest), no more changing speed is reached: terminal velocity: equilibrium: frictional and buoyant forces balance the gravitational pull

$$F_t = ma = F_{fr} + F_{gr} + F_b = 0$$

is reduced, the kinetic energy of the particles is kinetic energy to overcome the potential energy resulting in the fluid being more resistant to flow.

SUPPLEMENTAL

## 34.9 Sedimentation a

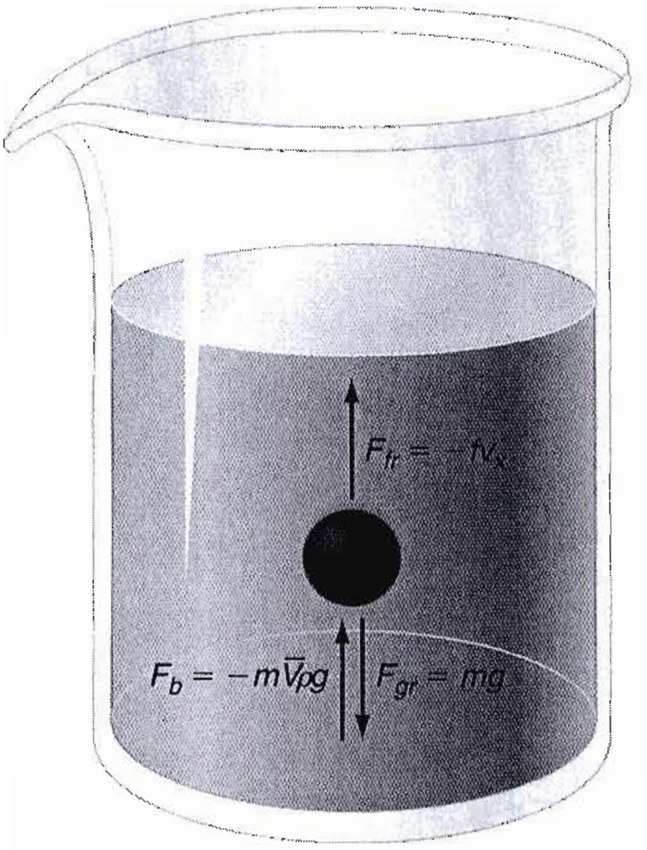


**FIGURE 34.17**
Illustration of the forces involved in sedimentation of a particle; $F_{fr}$ is the frictional force, $F_{gr}$ is the gravitational force, and $F_b$ is the buoyant force.

An important application of transport phe Sedimentation can be used with diffusion to de molecules. Figure 34.17 depicts a molecule wi liquid of density $\rho$ under the influence of E forces are acting on the particle:

1. The frictional force: $F_{fr} = -f\mathrm{v}_x$
2. The gravitational force: $F_{gr} = mg$
3. The buoyant force: $F_b = -m\overline{V}\rho g$

In the expression for the buoyant force, $\overline{V}$ is th the change in solution volume per mass of solu

Imagine placing the particle at the top c Initially, the downward velocity ($\mathrm{v}_x$) is zero, velocity will increase. Eventually, a particle v tional and buoyant forces are balanced by tl known as the terminal velocity, and when this tion is zero. Using Newton's second law,

$$F_{Total} = ma = F_{fr}$$

$$0 = -f\mathrm{v}_{x,ter} +$$

$$\mathrm{v}_{x,ter} = \frac{mg(1 - \overline{V}}{f}$$

$$\bar{\mathrm{s}} = \frac{\mathrm{v}_{x,ter}}{g} = \frac{m(}{}$$

The **sedimentation coefficient** $\bar{\mathrm{s}}$ is defined a acceleration due to gravity. Sedimentation co units of Svedbergs (S) with 1 S = $10^{-13}$ s; ho avoid confusion with other units in upcoming s

Sedimentation is generally not performed u Instead, acceleration of the particle is accompli

$\rightarrow 0 = -f v_{x,ter} + mg - m\bar{v}\rho g$

$$v_{x,ter} = \frac{mg(1-\bar{v}\rho)}{f}$$

sedimentation coefficient $\bar{s} = \frac{v_{x,ter}}{\text{gravitational acceleration}}$

$$\bar{s} = \frac{v_{x,ter}}{g} = \frac{m(1-\bar{v}\rho)}{f}$$

unit of $\bar{s}$, common is Svedberg: $1\,S = 10^{-13}\,s$

normally sedimentation is <u>not</u> studied in earth's gravitational pull, but in a centrifuge

$\rightarrow$ acceleration $\approx 10^5$ gravitational acceleration

angular velocity $\bar{\omega}$ $\left(\frac{rad}{s}\right)$

centrifugal acceleration: $\bar{\omega}^2 x$

x: distance of the particle from the rotation axis

also there is a terminal velocity

$$\bar{s} = \frac{v_{x,ter}}{\bar{\omega}^2 x} = \frac{m(1-\bar{v}\rho)}{f}$$

Lysozyme ($M = 14\,100\ g/mol$) has $\bar{s} = 1.91 \cdot 10^{-13}\,s = 1.91\,S$ and $\bar{v} = 0.703\ cm^3/g$ in water at 20°C

$\rho_{H_2O} = 0.998\ g/cm^3$, $\eta_{H_2O} = 1.002\ cP = 1.002 \cdot 10^{-3}\ \frac{kg}{ms}$

What is the radius of Lysozyme?

$$f = \frac{m(1-\bar{v}\rho)}{\bar{s}}$$

$$= \frac{\frac{14100\ g/mol}{6.022 \cdot 10^{23}\ mol^{-1}}\left[1 - 0.703\ \frac{mL}{g} \cdot 0.998\ \frac{g}{mL}\right]}{1.91 \cdot 10^{-13}\ s} = 3.66 \cdot 10^{-8}\ \frac{g}{s}$$

cular radius. Solving Equation (34.56)

$$1 - (0.703 \text{ mL g}^{-1})(0.998 \text{ g mL}^{-1})\Big)$$

$$1.91 \times 10^{-13} \text{ s}$$

r a spherical particle by Equation (34.51)

$$= 1.94 \times 10^{-9} \text{ m} = 1.94 \text{ nm}$$

lecular sedimentation coefficients is by this process, an initially homogeneous rifuge and spun. Sedimentation occurs, rom the axis of rotation experiencing an a corresponding reduction in concentra- of rotation. A boundary between these nd this boundary will move away from f we define the $x_b$ as the midpoint of the relationship exists between the location

$$= \frac{\frac{dx_b}{dt}}{\varpi^2 x_b}$$

$$\frac{dx_b}{x_b}$$

$$\frac{x_{b,t}}{b,t=0}\Big) \qquad \textbf{(34.57)}$$

$x_{b,\,t=0}$) versus time will yield a straight ation coefficient. The determination of trifugation is illustrated in Example

ermined by centrifugation at 55,000 rpm ed regarding the location of the bound-

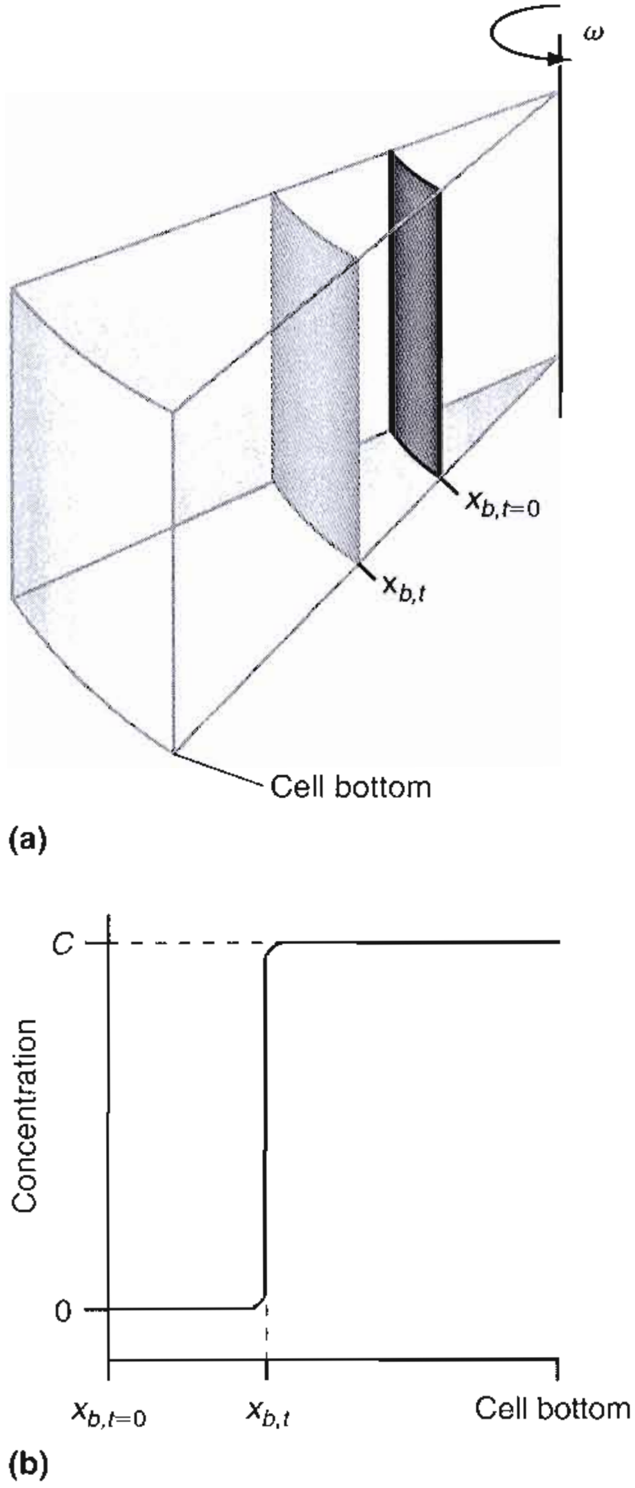


**FIGURE 34.18**
Determination of sedimentation coefficient by centrifugation. (**a**) Schematic drawing of the centrifuge cell, which is rotating with angular velocity $\varpi$. The blue plane at $x_{b,t=0}$ is the location of

olecular sedimentation coefficients is by In this process, an initially homogeneous ntrifuge and spun. Sedimentation occurs, from the axis of rotation experiencing an d a corresponding reduction in concentra- is of rotation. A boundary between these and this boundary will move away from . If we define the $x_b$ as the midpoint of the g relationship exists between the location :

$$\frac{{}_{,ter}}{{}^{2}x} = \frac{\frac{dx_b}{dt}}{\varpi^2 x_b}$$

$$\int \frac{{}_{b}}{x_b} \quad {}_{=0}$$

$$\left(\frac{x_{b,t}}{x_{b,t=0}}\right) \qquad \textbf{(34.57)}$$

$_b/x_{b,\,t=0})$ versus time will yield a straight entation coefficient. The determination of entrifugation is illustrated in Example

letermined by centrifugation at 55,000 rpm ained regarding the location of the bound-

| $x_b$ (cm) |
|---|
| 6.00 |
| 6.07 |
| 6.14 |
| 6.21 |
| 6.28 |
| 6.35 |

coefficient of lysozyme in water at 20°C.

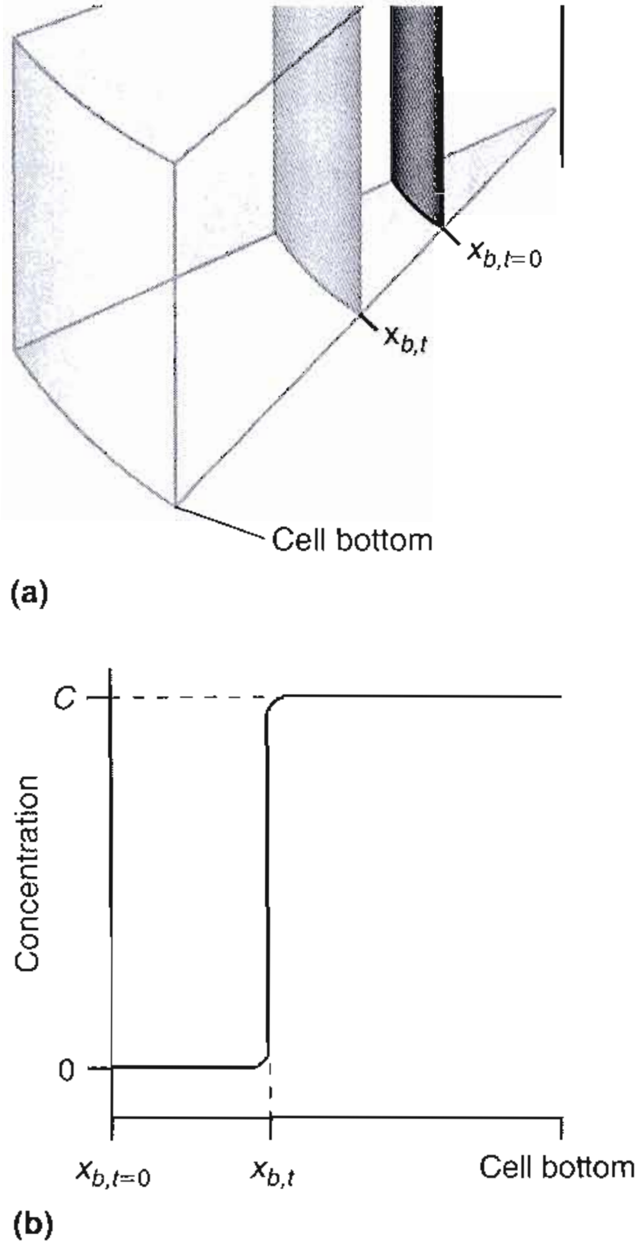


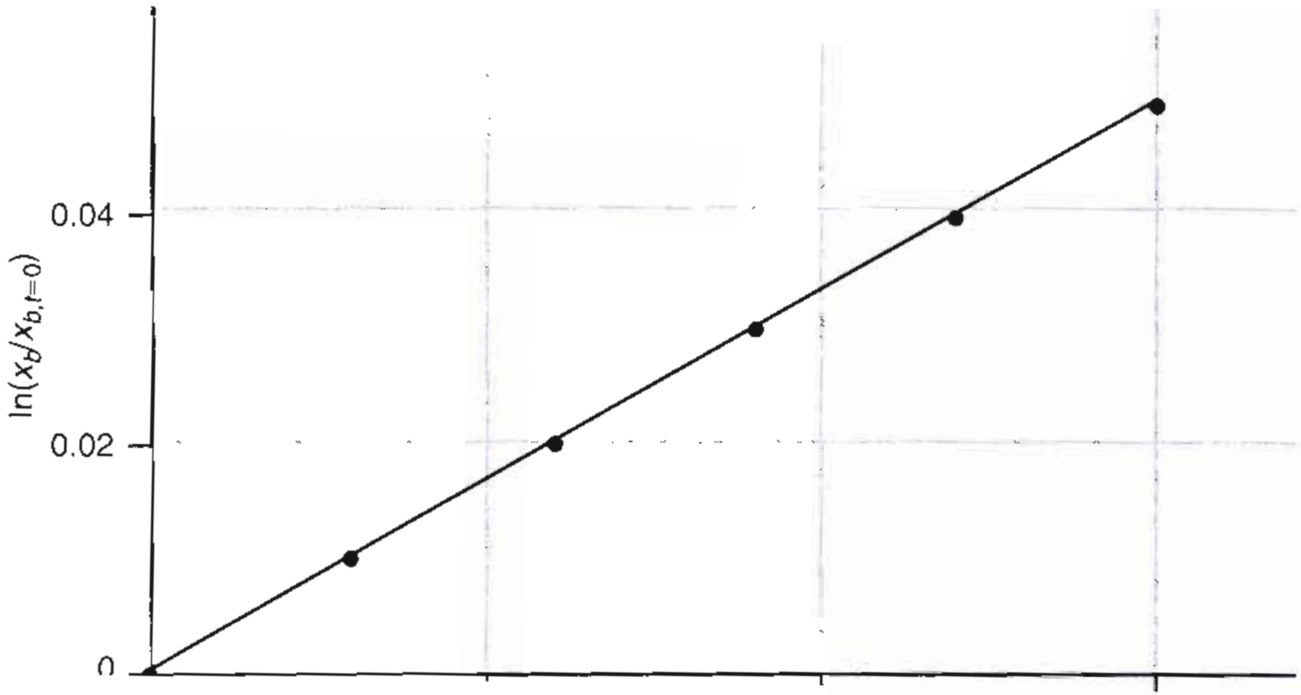
**FIGURE 34.18**
Determination of sedimentation coefficient by centrifugation. **(a)** Schematic drawing of the centrifuge cell, which is rotating with angular velocity $\varpi$. The blue plane at $x_{b,t=0}$ is the location of the solution meniscus before centrifugation. As the sample is centrifuged, a boundary between the solution with increased molecular concentration versus the solvent is produced. This boundary is represented by the yellow plane at $x_{b,t}$. **(b)** As centrifugation proceeds, the boundary layer will move toward the cell bottom. A plot of $\ln(x_{b,t}/x_{b,t=0})$ versus time will yield a straight line with slope equal to $\varpi^2$ times the sedimentation coefficient.

## Solution

First, we transform the data to determine $\ln(x_b/x_{b,t=0})$ as a function of time:

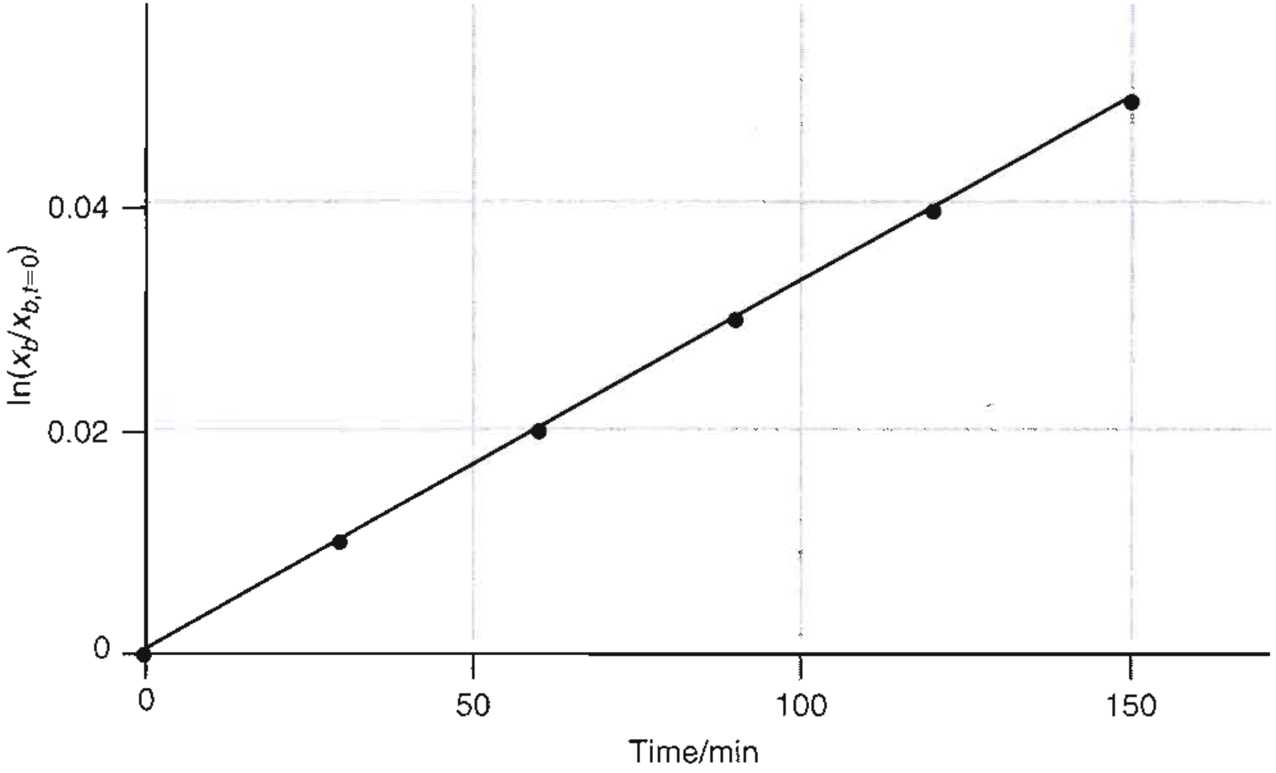
| **Time (min)** | $x_b$ **(cm)** | $(x_b/x_{b,t=0})$ | **ln** $(x_b/x_{b,t=0})$ |
|---|---|---|---|
| 0 | 6.00 | 1 | 0 |
| 30 | 6.07 | 1.01 | 0.00995 |
| 60 | 6.14 | 1.02 | 0.01980 |
| 90 | 6.21 | 1.03 | 0.02956 |
| 120 | 6.28 | 1.04 | 0.03922 |
| 150 | 6.35 | 1.05 | 0.04879 |

The plot of $\ln(x_b/x_{b,t=0})$ versus time is shown here:



| | | | |
|---|---|---|---|
| 150 | 6.35 | 1.05 | 0.04879 |

The plot of $\ln(x_b/x_{b,t=0})$ versus time is shown here:



The slope of the line in the preceding plot is $3.75 \times 10^{-4}\ \mathrm{min}^{-1}$, which is equal to $\varpi$ times the sedimentation coefficient:

$$3.75 \times 10^{-4}\ \mathrm{min}^{-1} = 6.25 \times 10^{-6}\ \mathrm{s}^{-1} = \varpi^2 \bar{s}$$

$$\bar{s} = \frac{6.25 \times 10^{-6}\ \mathrm{s}^{-1}}{\varpi^2} = \frac{6.25 \times 10^{-6}\ \mathrm{s}^{-1}}{((55{,}000\ \mathrm{rev\ min}^{-1})(2\pi\ \mathrm{rad\ rev}^{-1})(0.0167\ \mathrm{min\ s}^{-1}))^2}$$

$$\bar{s} = 1.88 \times 10^{-13}\ \mathrm{s}$$

Finally with knowledge of the sedimentation coefficient and diffusion coefficient the molecular weight of a macromolecule can be determined. Equation (34.56) can be sphericals: $f = 6\pi\eta r$

$$r = \frac{f}{6\pi\eta} = \frac{3{,}66\cdot10^{-8}\,g/s}{6\pi\cdot 1{,}002\ g/ms}$$

$$1{,}002\ cP = 1{,}002\cdot10^{-3}\,\frac{kg}{ms} = 1{,}002\,\frac{g}{ms}$$

Transp: measurement of $\bar{s}$ of macromolecules by centrifugation

initial: homogeneous solution of macromolecules

centrifugation → sedimentation

~~increa~~ increase of macromolecule concentration away from the rotation axis, decrease of it close to the axis

→ the boundary between these two regions will move away from the rotation axis

Transp: $x_b$ = midpoint of the boundary layer

$$\to \bar{s} = \frac{v_{x,ter}}{\bar{\omega}^2 x} = \frac{dx_b/dt}{\bar{\omega}^2 x_b}$$

$$\to \bar{\omega}^2\bar{s}\int_0^t dt = \int_{x_b(t=0)}^{x_b}\frac{dx_b}{x_b}, \quad \bar{\omega}^2\bar{s}\,t = \ln\frac{x_b}{x_b(t=0)}$$

plot $\ln\frac{x_b}{x_b(t=0)}$ vs $t$: ~~strig~~ straight line, slope $= \bar{\omega}^2 s$

$\bar{s}$ of lysozyme by centrifugation ~~at~~ with 55000 rpm (rounds per minute, 1 round = 360° = $2\pi$)

using the data given, what is $\bar{s}$ of lysozyme at 20°C?

Transp. data treatment

$$\text{slope} = 3{,}75 \cdot 10^{-4}\ \text{min}^{-1}$$

$$= \bar{\omega}^2\, \bar{s} = 6{,}25 \cdot 10^{-6}\ s^{-1}$$

$$\rightarrow \bar{s} = \frac{6{,}25 \cdot 10^{-6}\ s^{-1}}{\bar{\omega}^2} = \frac{6{,}25 \cdot 10^{-\cancel{6}}\ s^{-1}}{\left[55000\ \text{rpm} \cdot \frac{2\pi}{\text{[illegible]}} \cdot 0{,}0167\ \frac{\text{min}}{s}\right]^2}$$

$$= 1{,}88 \cdot 10^{-13}\ s$$

M of macromolecules?

frictional coefficient (earlier):

$$f = \frac{m(1-\bar{v}\rho)}{\bar{s}}$$

$\bar{s}$ sedimentation coefficient

$\rho$ density of the solvent

$\bar{v}$ specific volume = volume of solvent displaced by the solute per g of solute ($cm^3/g$)

also we saw $f = 6\pi\eta r$

$$D = \frac{k_B T}{6\pi\eta r} \quad \text{for spherical particles} \Rightarrow D = \frac{k_B T}{f}$$

$$\rightarrow f = \frac{k_B T}{D}$$

$$\rightarrow \frac{m(1-\bar{v}\rho)}{\bar{s}} = \frac{k_B T}{D}$$

$$\Rightarrow m = \frac{k_B T \bar{s}}{D(1-\bar{v}\rho)}$$

$$N_A m = \frac{N_A k_B T \bar{s}}{D(1-\bar{v}\rho)}$$

$N_A m = M$

$N_A k_B = R$

$$M = \frac{RT\bar{s}}{D(1-\bar{v}\rho)}$$

# Surface Tension (Chap. 8.8)

effects of the boundary surface between a l and a g phase or two immiscible liquids.

without gravitation a liquid droplet would have spherical form because in a sphere most possible liquid molecules are surrounded by other liquid molecules.

l: forces are attractive ⇒ smallest surface area (molecules only on one side) = lowest energy

molecules in surface have higher energy than those in bulk

Creation of more surface aerea, $d\sigma$, at $V, T = \text{const.}$: change in ~~Helt~~ Helmholtz energy (same use ~~as~~ as $dG$ at $P, T = \text{const.}$): $dA = \gamma \, d\sigma$

propoitionality constant $\gamma$ is surface tension

$$[\gamma] = 1 \, \frac{J}{m^2} = 1 \, \frac{N}{m}$$

Transp. radial inward forces due to $\gamma \neq 0$, because the forces tend to minimize the surface

also in a planar layer in a frame

expansion of the droplet radius from $r$ ~~to~~ to $r + dr$:

$$\sigma = 4\pi r^2 \text{ (aerea of a sphere)}$$

$$\rightarrow d\sigma = 4\pi (r + dr)^2 - 4\pi r^2$$

$$= 4\pi \left[ r^2 + 2r\,dr + (dr)^2 - r^2 \right) = 4\pi \left[ 2r\,dr + (dr)^2 \right)$$

$$= 8\pi r\,dr \text{ because } (dr)^2 \ll r\,dr$$

work needed for this is $dA$ (at $V, T = \text{const.}$)

$$w = dA = \gamma \, d\sigma = 8\pi \gamma r \, dr$$

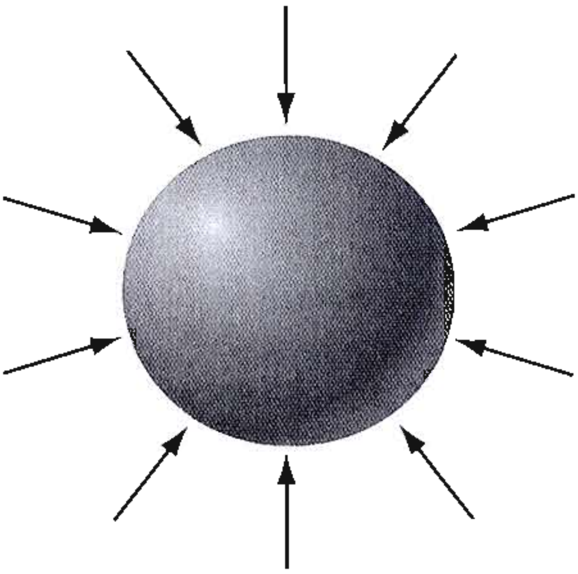


**FIGURE 8.17**
The forces acting on a spherical droplet that arise from surface tension.

area while keeping the volume constant. The w
additional surface area at constant $V$ and $T$ is

$$dA = \gamma d\sigma$$

where $A$ is the Helmholtz energy, $\gamma$ is the surface t
area. The **surface tension** has the units of energy/
N $m^{-1}$ (Newtons per meter). Equation (8.26) predic
film suspended in a wire frame will tend to minimi
for a spontaneous process at constant $V$ and $T$.

Consider the spherical droplet depicted in Figu
on the droplet in the radially inward direction f
shape. An expression for the force can be genera
droplet is increased from $r$ to $r + dr$, the area incr

$$\sigma = 4\pi r^2 \quad \text{so} \quad d\sigma =$$

From Equation (8.26), the work done in the expansio
which is normal to the surface of the droplet, is the w

$$F = 8\pi\gamma r$$

The net effect of this force is to generate a pressur
face. At equilibrium, there is a balance between th
The inward acting force is the sum of the force exe
force arising from the surface tension, whereas th
from the pressure in the liquid:

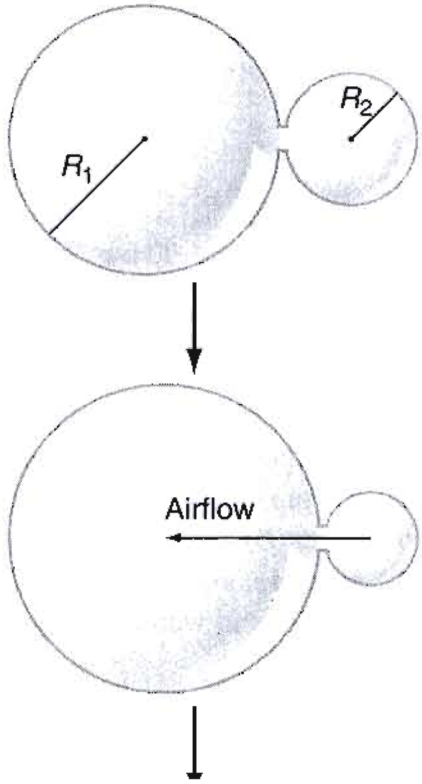
$$4\pi r^2 P_{outer} + 8\pi\gamma r = 4\pi$$

$$P_{inner} = P_{ou}$$

Note that $P_{inner} - P_{outer} \rightarrow 0$ as $r \rightarrow \infty$. There
only for a curved surface. From the geometry in
higher pressure is always on the concave side of t
tension for a number of liquids are listed in Table 8

Equation (8.29) has interesting implications f
with different curvatures $1/r$. Consider two air-
same surface tension $\gamma$, one with a large radius $R_1$
Assume there is a uniform pressure outside both
obtain the difference between the pressures $P_1$ an

$$P_1 - P_2 = \frac{2\gamma}{R_1} - \frac{2\gamma}{R_2} = 2\gamma$$



Now suppose the two bubbles come into contac
Because $R_1 > R_2$, from Equation (8.30) the press

→ force ⊥ surface = $\frac{\text{work}}{\text{distance } dr}$

$$F = 8\pi\gamma r$$

$V$ = const. is falfilled because $dr$ is infinitesimally small

→ pressure difference across the surface

equillibrium balance between inward and outward forces

inward force: external pressure + surface tension
outward forces: pressure in the liquid

force = pressure · aerea

$$4\pi r^2 P_{ext} + 8\pi\gamma r = 4\pi r^2 P_{int}$$

$$\rightarrow P_{int} = P_{ext} + \frac{2\gamma}{r}$$

$$\Delta P = P_{int} - P_{ext} \rightarrow 0 \text{ if } r \rightarrow \infty$$

no $\Delta P$ for infinite planar surfaces

- higher pressure always on concave side of surface

convex ( concave

Transp: 2 air filled bubbles in a liquid

$\gamma$, $R_1 > R_2$, $P_{ext}$ is uniform (air pressure)

$$\rightarrow P_1 - P_2 = \frac{2\gamma}{R_1} - \frac{2\gamma}{R_2} = 2\gamma\left(\frac{1}{R_1} - \frac{1}{R_2}\right)$$

bubbles in contact with $R_1 > R_2 \Rightarrow P_2 > P_1$

⇒ air flow from bubble 2 to bubble 1

The inward acting force is the sum of the force exerted b force arising from the surface tension, whereas the out from the pressure in the liquid:

$$4\pi r^2 P_{outer} + 8\pi\gamma r = 4\pi r^2 P_{in}$$

$$P_{inner} = P_{outer} +$$

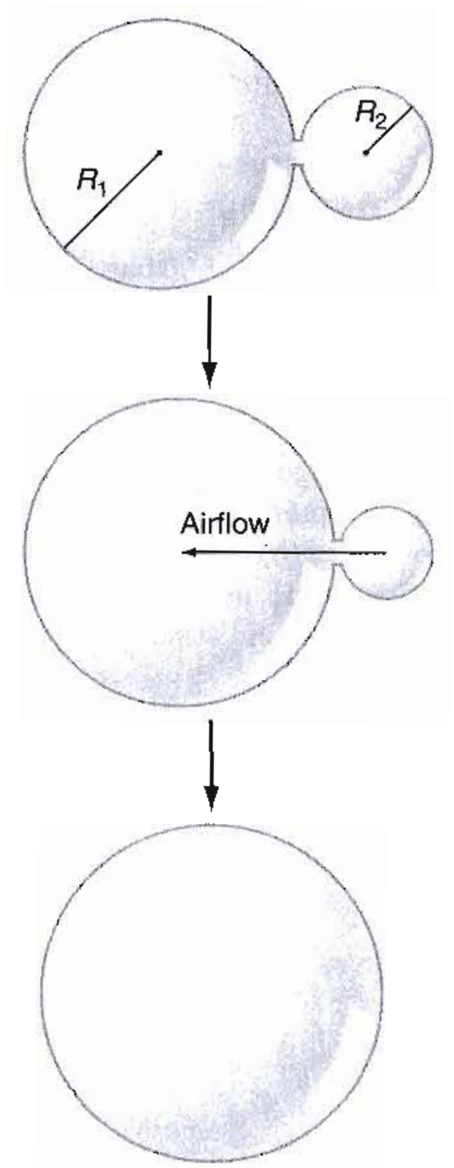


**FIGURE 8.18**
Two bubbles with unequal radii $R_1$ and $R_2$ make contact (top). Because the pressure within a bubble varies inversely with the bubble radius, air flows from the smaller into the larger bubble until a single large bubble remains (bottom).

Note that $P_{inner} - P_{outer} \rightarrow 0$ as $r \rightarrow \infty$. Therefore, only for a curved surface. From the geometry in Figu higher pressure is always on the concave side of the ir tension for a number of liquids are listed in Table 8.5.

Equation (8.29) has interesting implications for th with different curvatures $1/r$. Consider two air-filled same surface tension $\gamma$, one with a large radius $R_1$, an Assume there is a uniform pressure outside both bubb obtain the difference between the pressures $P_1$ and $P_2$

$$P_1 - P_2 = \frac{2\gamma}{R_1} - \frac{2\gamma}{R_2} = 2\gamma\left(\frac{1}{R_1}\right.$$

Now suppose the two bubbles come into contact as Because $R_1 > R_2$, from Equation (8.30) the pressure

**TABLE 8.5 Surface Tension of Selected Liquids a**

| Formula | Name | $\gamma$ (mN m$^{-1}$) | Fc |
|---|---|---|---|
| $Br_2$ | Bromine | 40.95 | C |
| $H_2O$ | Water | 71.99 | C |
| Hg | Mercury | 485.5 | C |
| $CCl_4$ | Carbon tetrachloride | 26.43 | C |
| $CH_3OH$ | Methanol | 22.07 | C |

*Source:* Data from Lide, D. R., ed. *Handbook of Chemistry a* FL: CRC Press, 2002.

[redacted]

until bubble 2 dissappears
($P_2$ gets larger when $R_2$ gets smaller)

leads to coarsening in foames (vanishing of bubbles)
Ostwald ripening of crystals (also bubble vanishing)
in lung tissue: <u>alveoli</u>: $H_2O$ surrounded air filled chambers

⇒ when 2 alveoli come in contact, larger one will expand, smaller one will disappear
⇒ after time: only 1 big alveolus, all others gone
≙ collapse of lung tissue due to $\gamma$ of water
in the alveoli there is phosphatidyl chloride as a surfactant which lowers $\gamma$ of the surrounding water = stabilizing lung tissue
in early born babies or smokers the surfactant is not there → destabilization of lung tissue by coarsening possible.

vapor pressure of a small drop = droplet: $p^*$
total pressure: $P_t = P_{ext} + p^*$

$$RT \ln \frac{p^{*} P_t}{p^{*}} = V_m^{\ell} (P_t - p^{*})$$

also $P_{int} = P_{ext} + \frac{2\gamma}{r}$

→ $H_2O$ droplet with $r = 10^{-7}\,m = 100\,nm$

$\Delta P^{*} \approx 1\%$ increase to planar surface

$r = 10^{-8}$ m $= 10$ nm : $\Delta P^* = 11\%$

$r = 10^{-9}$ m $= 1$ nm : $\Delta P^* = 270\%$

but ~~t~~ at 1 nm equation not good, because in a 1 nm droplet roughly only 1 $H_2O$ molecule fits

also fog condenses on larger droplet (formed on solid impurities : not spherical), while the smaller ones evaporate

## Capillary Effect

Happens in small tubes = capillaries, radius r and partially immersed in a liquid

when $\gamma$ of the liquid is larger than that of the glass → liquid will rise to wet the capillary = capillary rise (Transp.)

if $\gamma_{liquid} < \gamma_{glass}$ ⇒ liquid avoids the glass

→ capillary depression : Hg / glass

Curvature of surface = capillary radius

→ pressure difference across the curved surface is $\frac{2\gamma}{r}$ which must be balanced by the weight of the liquid column in the capillary

$$\frac{2\gamma}{r} = \rho g h \qquad \left[\frac{2\gamma}{r}\right] = 1\,\frac{N/m}{m} = 1\,\frac{N}{m^2}\,(Pa) = 1\,\frac{J}{m^3}$$

$$[\rho g h] = 1\,\frac{kg}{m^3}\,\frac{m}{s^2}\,m = 1\,\frac{kg\,m^2}{s^2}\cdot\frac{1}{m^3} = 1\,J/m^3$$

:) is greater than the pressure $P_1$ in bubble 1, so air e 1 until the smaller bubble disappears entirely as . In foams this process is called "coarsening" and in ing."

hat follows from Equations (8.29) and (8.30) is the e is composed of small water-lined, air-filled cham- Equation (8.29), the pressure difference across the cavity is proportional to the surface tension and us of the cavity. Therefore, if two air-filled alveoli, ii $r$ and $R$ and for which $r < R$ are interconnected, and the larger alveolus will expand because the pres- greater than the pressure within the larger alveolus. on of water that lines the alveoli, these cavities will se, leaving an ever diminishing number of alveoli of e alveoli according to Equations (8.29) will result ngs.

nt called phosphatidylcholine lowers the surface ten- li, thus stabilizing the lungs. But in persons lacking of their lungs, such as prematurely born infants and n of the water in the alveoli is not lowered, and as a ilized by coarsening.

pressure differential across a curved surface is that depends on its radius. By substituting numbers in tion (8.25) to calculate the vapor pressure, we find m water droplet is increased by 1%, that of a $10^{-8}$ and that of a $10^{-9}$ m droplet is increased by 270%. e application of Equation (8.29) is questionable l water molecule is comparable to the droplet diam- theory is needed to describe the forces within the in the formation of liquid droplets in a condensing evaporate more rapidly than large droplets, and the droplets, allowing them to grow at the expense of

**depression** are other consequences of the pressure ace. Assume that a capillary of radius $r$ is partially liquid comes in contact with a solid surface, there is a e energy of the system. If the surface tension of the solid, the liquid will wet the surface, as shown in urface tension of the liquid is higher than that of the rface, as shown in Figure 8.19b. In either case, there is llary across the gas–liquid interface because the inter- t the liquid–gas interface is tangent to the interior wall id interface, the radius of curvature of the interface is

re across the curved interface $2\gamma/r$ is balanced by the avitational field $\rho gh$. Therefore, $2\gamma/r = \rho gh$ and the ven by

$2\gamma$ (8.31)

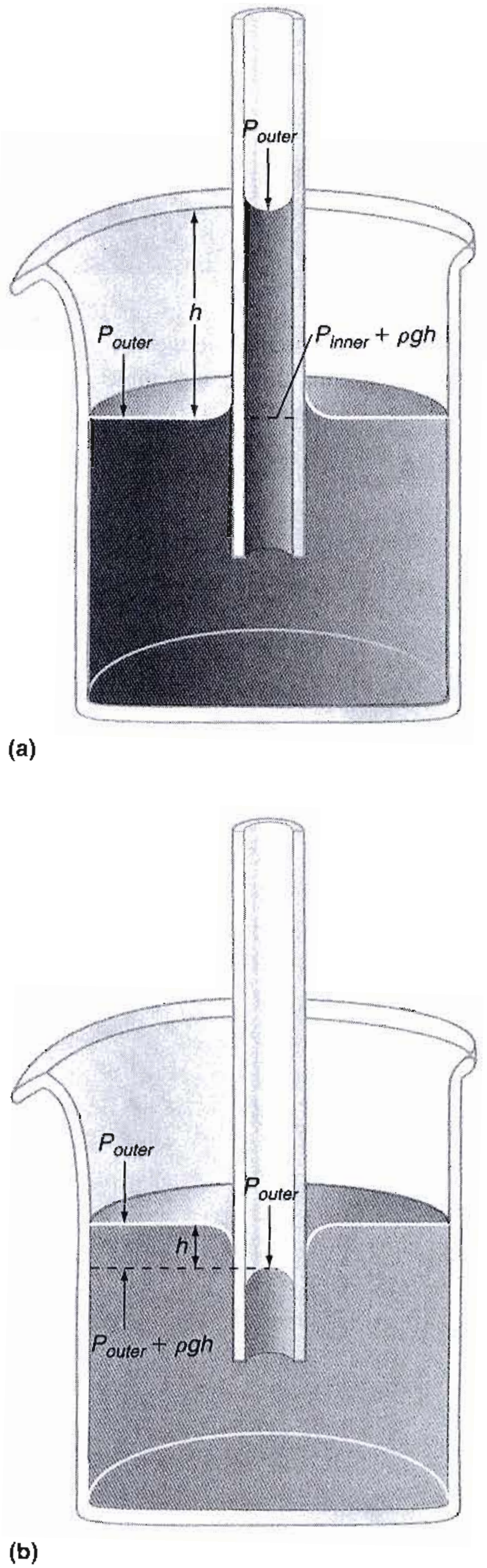


**FIGURE 8.19**
(a) If the liquid wets the interior wall of the capillary, a capillary rise is observed. The combination Pyrex–water exhibits this behavior. (b) If the liquid does not

of the cavity. Therefore, if two air filled alveoli, i $r$ and $R$ and for which $r < R$ are interconnected, nd the larger alveolus will expand because the pres- greater than the pressure within the larger alveolus. on of water that lines the alveoli, these cavities will se, leaving an ever diminishing number of alveoli of e alveoli according to Equations (8.29) will result ngs.

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across the curved interface $2\gamma/r$ is balanced by the ational field $\rho gh$. Therefore, $2\gamma/r = \rho gh$ and the by

$$h = \frac{2\gamma}{\rho g r} \tag{8.31}$$

as assumed that either (1) the liquid completely illary, in which case the liquid coats the capillary or (2) the liquid is completely nonwetting, in at the capillary walls but fills the core. In a more s intermediate between these two extremes. In haracterized by the **contact angle** $\theta$, as shown

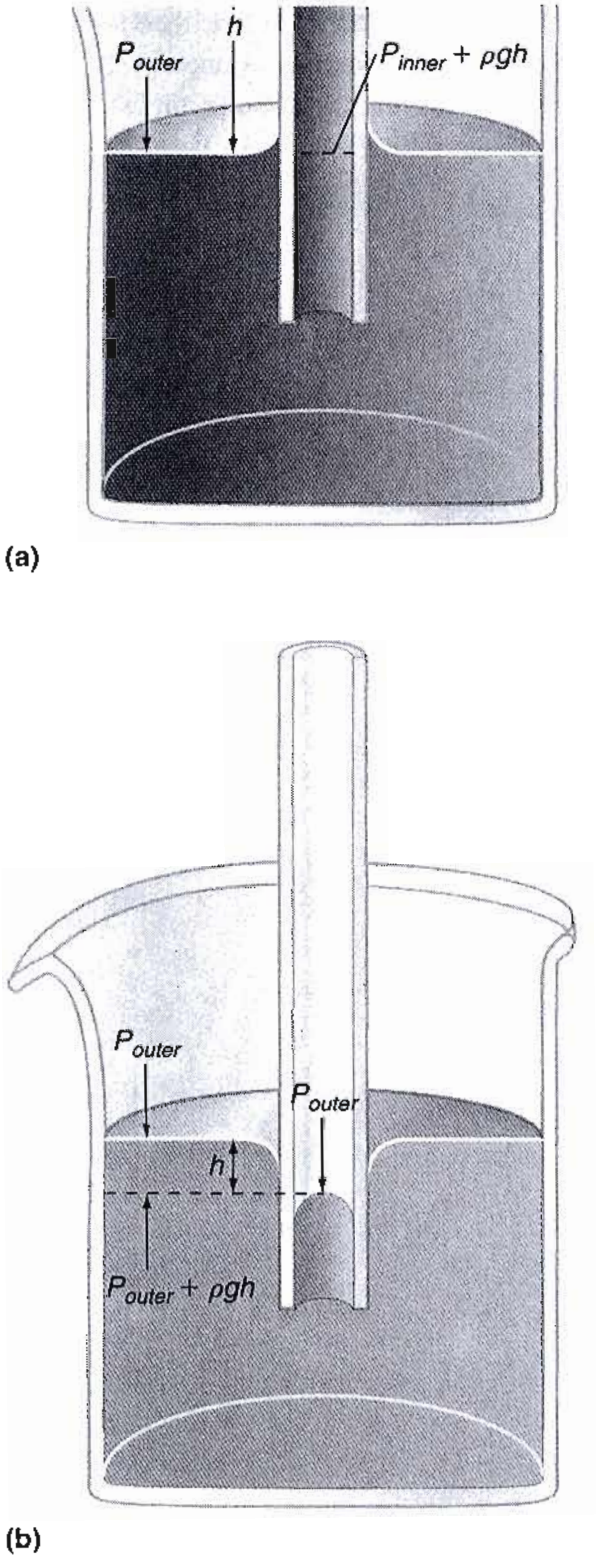


**FIGURE 8.19**
**(a)** If the liquid wets the interior wall of the capillary, a capillary rise is observed. The combination Pyrex–water exhibits this behavior. **(b)** If the liquid does not wet the capillary surface, a capillary depression is observed. The combination Pyrex–mercury exhibits this behavior.

mass of liquid column:

$$m = \rho h \cdot 4\pi r^2$$

→ gravitational force $F_g = \rho g h \, 4\pi r^2$ (m·g)

~~pers~~ presscure difference because of $\gamma$: $\Delta P = \frac{2\gamma}{r}$

$$\rightarrow F_\gamma = \frac{2\gamma}{r} 4\pi r^2$$ (aerea of column = $4\pi r^2$)

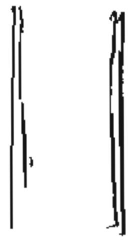
$$F_\gamma = F_g \Rightarrow \frac{2\gamma}{r} = \rho g h \rightarrow h = \frac{2\gamma}{\rho g r}$$

assumption so far: complete wetting: liquid does not fill the core of the capillary

= surface form ∪

no wetting: liquid fills the core

Transperancy contact angle $\theta$ between 0° (complete wetting) and 180° (no wetting)



complete wetting

no wetting all liquid inside capillary

measure h ⇒ $\Delta\gamma$ between solid and liquid

insect, supported on water by 4 legs. Each leg creates a depression in the $H_2O$ surface (hemisphere of radius $1.2 \cdot 10^{-4}$ m). ~~force on~~

lifting force on insect's legs when $\theta = 0°$

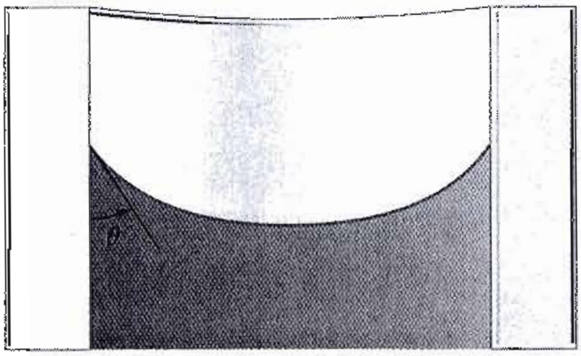


**FIGURE 8.20**
For cases intermediate between wetting and nonwetting, the contact angle $\theta$ lies in the range $0° < \theta < \ = 180°$.

Complete **wetting** corresponds to $\theta = 0°$, and to $\theta = 180°$. For intermediate cases,

$$P_{inner} = P_{outer} + \frac{2\gamma \cos\theta}{r} \quad \text{and}$$

The measurement of the contact angle is one of the measure the difference in surface tension at the soli

## EXAMPLE PROBLEM 8.3

The six-legged water strider supports itself on the s legs. Each of these legs causes a depression to be f that each depression can be approximated as a hemi and that $\theta$ (as in Figure 8.20) is 0°. Calculate the fo exerts on the pond.

**Solution**

$$\Delta P = \frac{2\gamma \cos\theta}{r} = \frac{2 \times 71.99 \times 10^{-3}\,\mathrm{N\,m^{-1}}}{1.2 \times 10^{-4}\,\mathrm{m}} = 1$$

$$F = PA = P \times \pi r^2 = 1.20 \times 10^3\,\mathrm{Pa} \times \pi(1.$$

## EXAMPLE PROBLEM 8.4

Water is transported upward in trees through channe Although the diameter of the xylem channels varies value is $2.0 \times 10^{-5}$ m. Is capillary rise sufficient to redwood tree that is 100 m high? Assume complete

**Solution**

From Equation (8.31),

$$h = \frac{2\gamma}{\rho g r \cos\theta} = \frac{2 \times 71.99 \times 10}{997\,\mathrm{kg\,m^{-3}} \times 9.81\,\mathrm{m\,s^{-2}} \times}$$

No, capillary rise is not sufficient to account for water

As Example Problem 8.4 shows, capillary rise transport to the leaves in all but the smallest plants.

$\Delta P = \frac{2\gamma}{r} \cos\theta$ $\quad \gamma_{H_2O} = 71{,}99 \frac{mN}{m}$ 298 K

$\cos 0° = 1$

$$\Delta P = \frac{2 \cdot 71{,}99 \cdot 10^{-3}\, N/m}{1{,}2 \cdot 10^{-4}\, m} = 1{,}20 \cdot 10^{3} \frac{N}{m^2} = 1{,}20\ kPa$$

$F = \Delta P \cdot A = \Delta P \cdot \pi r^2 = 1{,}20 \cdot 10^{3}\, Pa\ \pi (1{,}2 \cdot 10^{-4} m)^2 = 5{,}4 \cdot 10^{-5}\, N$

<u>in trees</u> $H_2O$ is transported upwards from roots to leaves through xylems: channels with a diameter of $2 \cdot 10^{-5}\, m$

– is capillary rise ~~enoy~~ enough for water transport to the top of a 100 m Redwood tree?

$\rho_{H_2O} = 997 \frac{kg}{m^3}$

$$h = \frac{2\gamma}{\rho g r} = \frac{2 \cdot 71{,}99 \cdot 10^{-3} \frac{N}{m}}{997 \frac{kg}{m^3} \cdot 9{,}81 \frac{m}{s^2} \cdot 1 \cdot 10^{-5}\, m} = \overset{1{,}47\ m}{\cancel{0{,}24\ m}}$$

⇒ capillary rise cannot bring $H_2O$ to the top of a 100 m tree alone

Consider a cylinder, filled with water and with a piston on top. Pulling of the piston ⇒ negative pressure on top

How high can the piston pulled without breaking the water column?

depends on cavitation = formation (nucleation) of bubbles in the water

bubble pressure $P_{int}, P_{ext} = P_{vap}(H_2O)$

water: high tensile strength: Large pulling without cavitation possible

→ with this effect $h \leq 9.7m$

in xylems: cavitation is suppressed (absent) without cavitation a negative pressure of more than - 1000 atm can be created at tree top (negtive, because piston lifting causes tension not compression)

In cappilaries of xylem radius negative pressures of more than -50 atm on top were observed

make a cut into the base of a Redwood tree → sap just drops out and is not spurting out fast ⇒ pressure at the base of a xylem must be ≈ 1atm (outside atmospheric pressure) when only slow dropping out

while at the base of a 100 m tall $H_2O$ ~~cto~~ column the pressure must be much higher

reason when a Redwood tree is just a small seedling (baby) the capillary rise can fill its xylems up to the top (not more than 1m then)

Then when the tree grows the water is pulled up the rising xylems (because of the high tensile strength of water no cavitation occurs).

From the leaves $H_2O$ evaporates and ㊷ -8
is replenished from the roots by $\Delta P$ in the xylems

If growth of 100 m then 1atm at the base
$\Longrightarrow \approx -9$ atm at the top from $\Delta P = \rho g h$

$\Rightarrow$ If $H_2O$ would not have its high tensile strength (due to hydrogen bonds), cavitation would ~~occur~~ occur and the water columns in the xylems would break

$\rightarrow$ no tall trees would exist!

㊸ Quiz

㊹㊺ free because 2 night time Exams

old Final will be solved, copies given, no attendance taken