Chapter 20 Molecules in Motion

Transport properties of a substance

1. Diffusion: the migration of matter down a concentration gradient
2. Thermal conduction: the migration of energy down a temperature gradient
3. Electric conduction: the migration of electric charge along a potential gradient
4. Viscosity: the migration of linear momentum down a velocity gradient

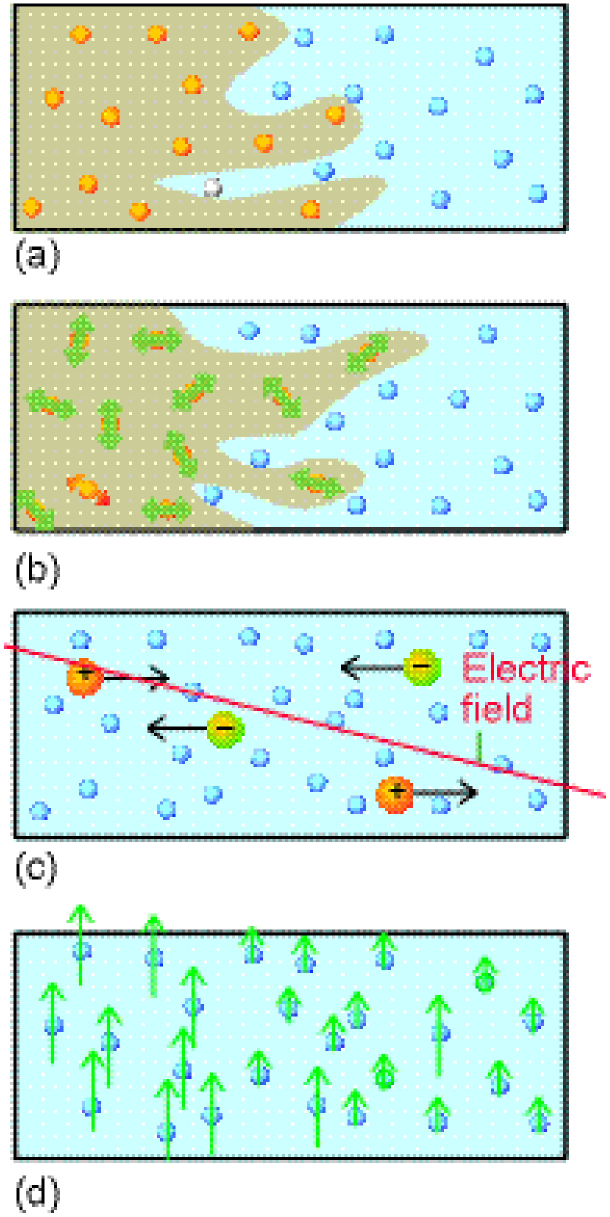


Figure 20.1

Four types of transport properties: (a) diffusion, the spreading of one species into another ; (b) thermal conduction, when molecules with different energies of thermal motion (represented by the arrows) spread into each other’s region; (c) electrical conduction, when ions migrate under the influence of an electric field; (d) viscosity, when molecules with different linear momenta (represented by the arrows) migrate.

The Kinetic Model of Gases

Three assumptions

1. The gas consists of molecules of mass *m* in ceaseless random motion.
2. The size of the molecules is negligible, in the sense that their diameters are much smaller than the average distance traveled between collisions.
3. The molecules do not interact except that they make perfectly elastic collisions when they are in contact.

An elastic collision means that the total translational kinetic energy of a colliding pair is the same before and after the collision: no energy is left in one of the colliding particles as rotational energy or vibrational energy, etc.

The collision frequency, z: the number of collisions made by a single particle

The mean free path, λ: the average distance each particle travels between collisions

The pressure exerted by a gas

When a molecule of mass m collides with the wall perpendicular to the x-axis, its component of momentum along the x-axis changes from mv_x to $-mv_x$. The total change of momentum on each collision is of magnitude $|2mv_x|$.

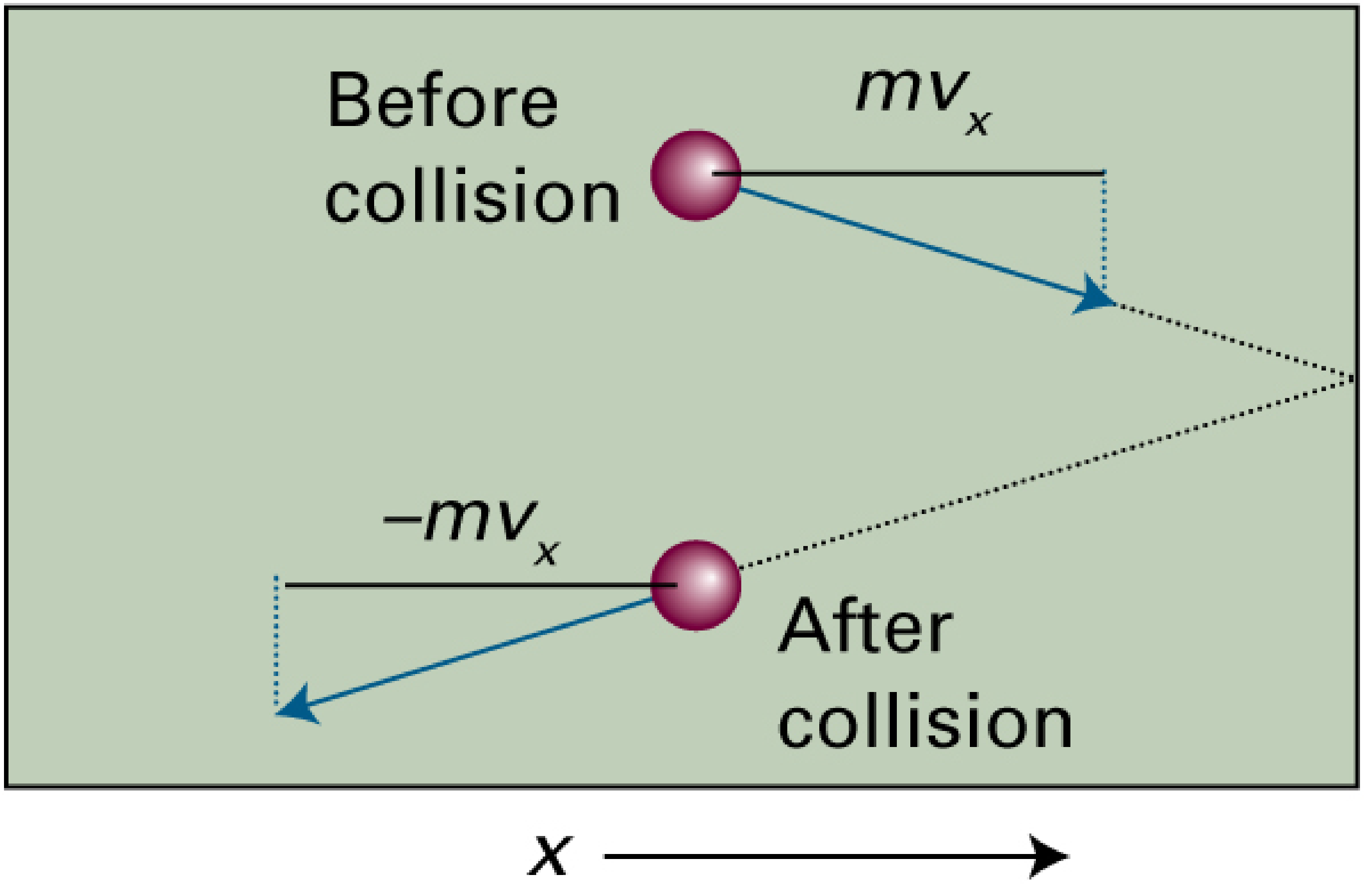


Figure 20.2
The pressure of a gas arises from the impact of its molecules on the walls. In an elastic collision of a molecule with a wall perpendicular to the *x*-axis, the *x*-component of velocity is reversed but the *y*- and *z*-components are unchanged.

The number of collisions in a time interval Δt $\cong$ the number of molecules able to reach in that time

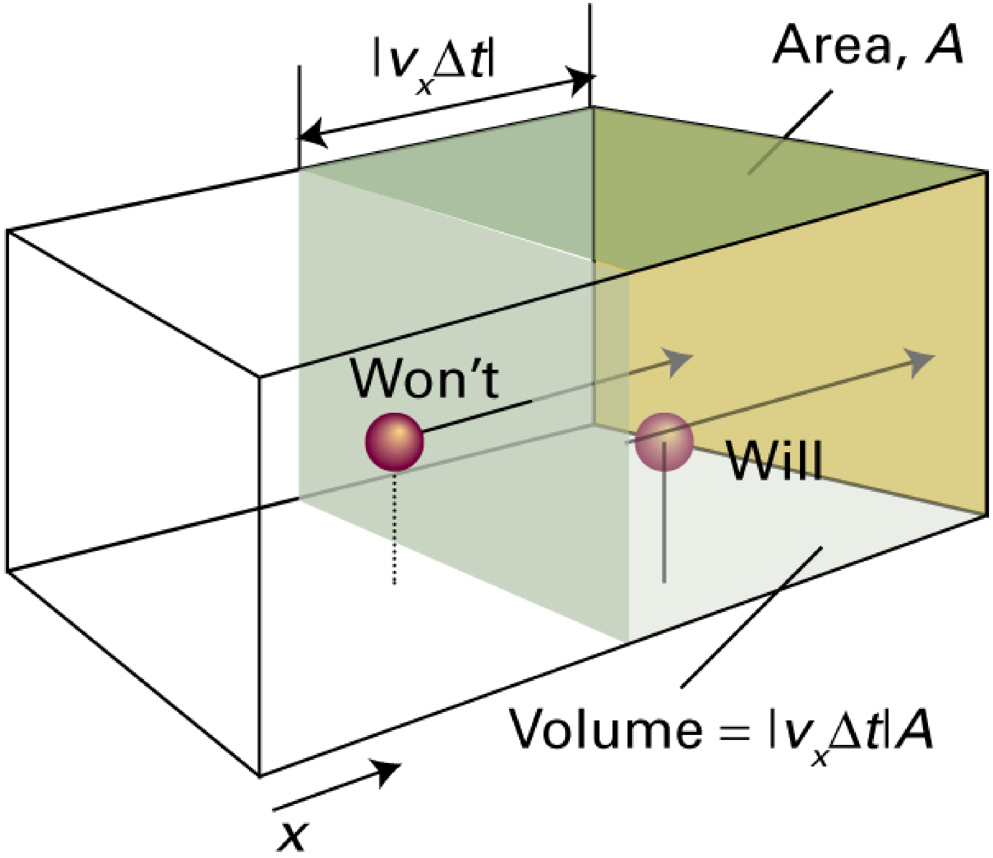


Figure 20.3
A molecule will reach the wall on the right within an interval Δt if it is within a distance $v_x\Delta t$ of the wall and traveling to the right.

The distance a molecule of velocity v_x can travel in a time $\Delta x = |v_x| \Delta t$, so all molecules lying within a distance $|v_x| \Delta t$ of the wall will strike it if they are traveling towards it.

A : the cross-section of the container

$\dfrac{nN_A}{V}$: the number of molecules per unit volume

All molecules lying in a volume $A|v_x|\Delta t$ will reach the wall.

$\therefore \dfrac{nN_A A|v_x|\Delta t}{V}$: the number of molecules in the volume of interest

On the average, half of these are moving to the right, and half to the left, and so the average number of collisions in the interval Δt is $\frac{1}{2} nN_A A|v_x|\Delta t/V$.

$\therefore$ the total momentum change

$$= \frac{nN_A A v_x \Delta t}{2V} \times 2mv_x = \frac{nmN_A A v_x{}^2 \Delta t}{V} = \frac{nMAv_x{}^2 \Delta t}{V}, \quad \text{where } M = mN_A$$

The rate of change of momentum = force = $\dfrac{nMAv_x{}^2}{V}$

The pressure = $\dfrac{nMv_x{}^2}{V}$

Not all molecules travel with the same velocity, and so the detected pressure is the average quantity just calculated.

$$p = \frac{nM\left\langle {v_x}^2 \right\rangle}{V}$$

Since the motion of the molecules is random,

$$\left\langle {v_x}^2 \right\rangle = \left\langle {v_y}^2 \right\rangle = \left\langle {v_z}^2 \right\rangle$$

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

$$\left\langle v^2 \right\rangle = \left\langle {v_x}^2 \right\rangle + \left\langle {v_y}^2 \right\rangle + \left\langle {v_z}^2 \right\rangle = 3\left\langle {v_x}^2 \right\rangle, \ \left\langle {v_x}^2 \right\rangle = \frac{1}{3}\left\langle v^2 \right\rangle$$

Let $c^2 = \left\langle v^2 \right\rangle$: the mean square speed of the molecules

$c = \sqrt{\left\langle v^2 \right\rangle}$: the root mean square (rms) speed

$$\therefore p = \frac{nM\left\langle {v_x}^2 \right\rangle}{V} = \frac{nM\left\langle v^2 \right\rangle}{3V} = \frac{nMc^2}{3V}$$

$$\therefore pV = \frac{1}{3}nMc^2$$

Molecular speeds

$$pV = nRT = \frac{1}{3}nMc^2$$

$$\therefore c = \left(\frac{3RT}{M}\right)^{\frac{1}{2}}$$

The above equation is an expression for the root mean square speed of molecules. However, in an actual gas the speeds of individual molecules span a wide range, and the collisions in the gas continually redistribute the speeds among the molecules.

The probability that a molecule has a velocity with components in the range v_x to $v_x + dv_x$, v_y to $v_y + dv_y$ and $v_z + dv_z = f\left(v_x, v_y, v_z\right)dv_x dv_y dv_z$

Fraction in the range v_1 to $v_2 = \int_{v_1}^{v_2} f(v)dv$

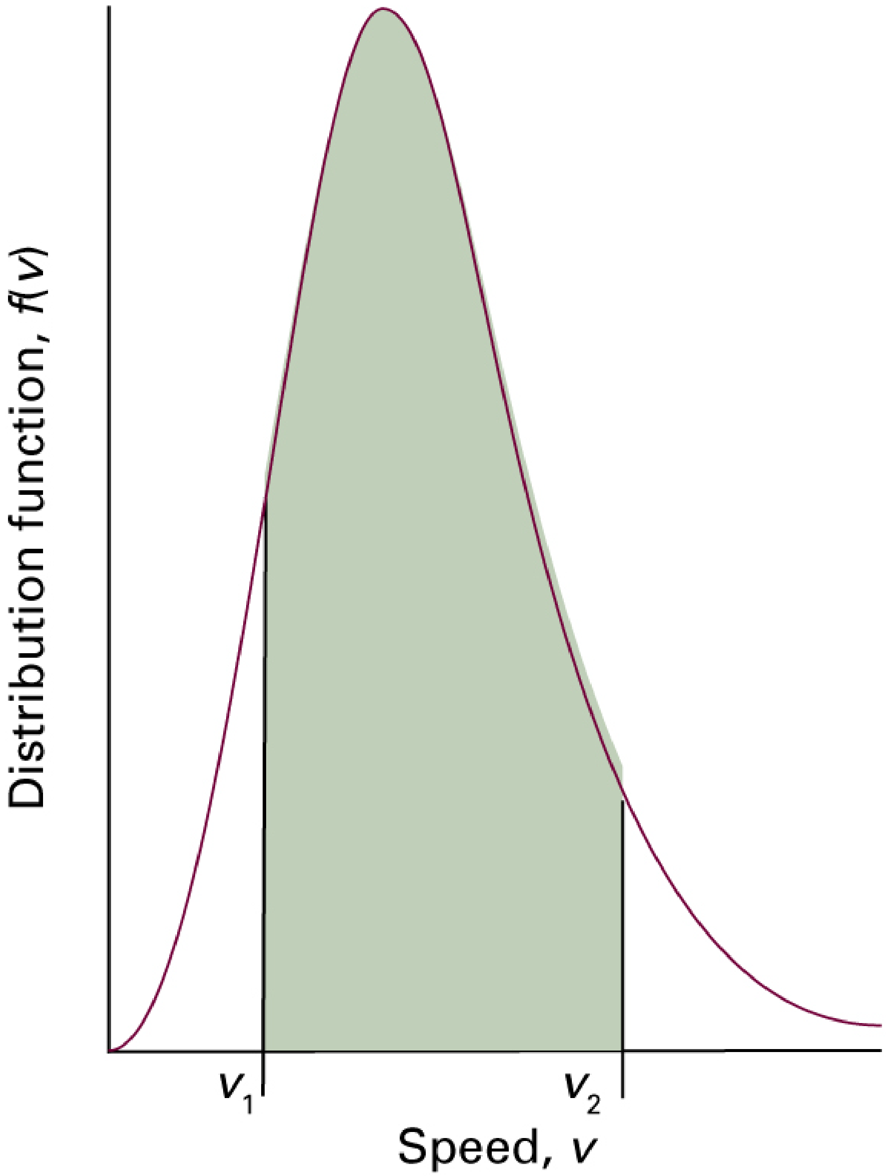


Figure 20.4
To calculate the probability that a molecule will have a speed in the range v_1 to v_2, we integrate the distribution between those two limits; the integral is equal to the area of the curve between the limits, as shown shaded here.

The distribution $f\left(v_x, v_y, v_z\right)$ can depend only on the speed v, where $v^2 = {v_x}^2 + {v_y}^2 + {v_z}^2$, can not depend on the individual components.

$$f\left(v_x, v_y, v_z\right) dv_x dv_y dv_z = f\left(v_x\right) f\left(v_y\right) f\left(v_z\right) dv_x dv_y dv_z$$

$$f\left(v_x\right) = f\left({v_x}^2\right), \quad f\left(v_y\right) = f\left({v_y}^2\right), \quad f\left(v_z\right) = f\left({v_z}^2\right)$$

$$\therefore f\left(v\right) = f\left(v^2\right) = f\left({v_x}^2 + {v_y}^2 + {v_z}^2\right) = f\left({v_x}^2\right) f\left({v_y}^2\right) f\left({v_z}^2\right)$$

Only an exponential function satisfies this equation $\left(e^{a+b+c} = e^a e^b e^c\right)$.

$$\therefore f(v_x) = Ke^{\pm\varsigma v_x^2}$$

$$f(v_x) f(v_y) f(v_z) = K^3 e^{\pm\varsigma(v_x^2 + v_y^2 + v_z^2)}$$

The evaluation of *K* and ς

$$\int_{-\infty}^{\infty} f\left(v_x\right) dv_x = 1$$

$$\int_{-\infty}^{\infty} f\left(v_x\right) dv_x = K \int_{-\infty}^{\infty} e^{-\varsigma {v_x}^2} dv_x = K\left(\frac{\pi}{\varsigma}\right)^{\frac{1}{2}} = 1$$

$$\therefore K = \left(\frac{\varsigma}{\pi}\right)^{\frac{1}{2}}$$

$$\left\langle {v_x}^2 \right\rangle = \int_{-\infty}^{\infty} {v_x}^2 f(v_x) dv_x = \left(\frac{\zeta}{\pi}\right)^{\frac{1}{2}} \int_{-\infty}^{\infty} {v_x}^2 e^{-\zeta {v_x}^2} dv_x = \left(\frac{\zeta}{\pi}\right)^{\frac{1}{2}} \frac{1}{2}\left(\frac{\pi}{\zeta^3}\right)^{\frac{1}{2}} = \frac{1}{2\zeta}$$

$$c^2 = \left\langle v^2 \right\rangle = \left\langle {v_x}^2 \right\rangle + \left\langle {v_y}^2 \right\rangle + \left\langle {v_z}^2 \right\rangle = \frac{3}{2\zeta}$$

$$c = \left(\frac{3RT}{M}\right)^{\frac{1}{2}} \qquad \therefore \frac{3RT}{M} = \frac{3}{2\zeta}$$

$$\therefore \zeta = \frac{M}{2RT}$$

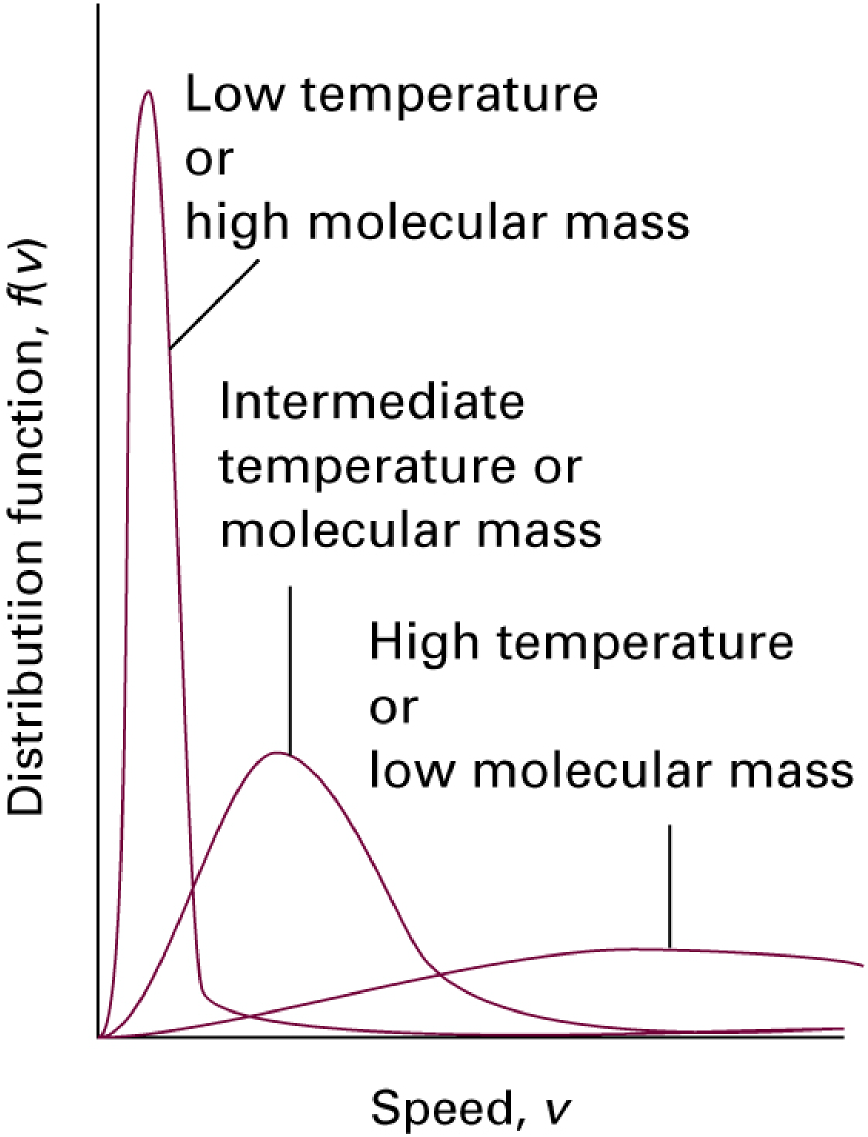
$$\boxed{\therefore f(v_x) = \left(\frac{M}{2\pi RT}\right)^{\frac{1}{2}} e^{-\frac{M{v_x}^2}{2RT}}}$$

Maxwell-Boltzmann distribution of molecular velocities

For three-dimensional case, the Maxwell-Boltzmann distribution

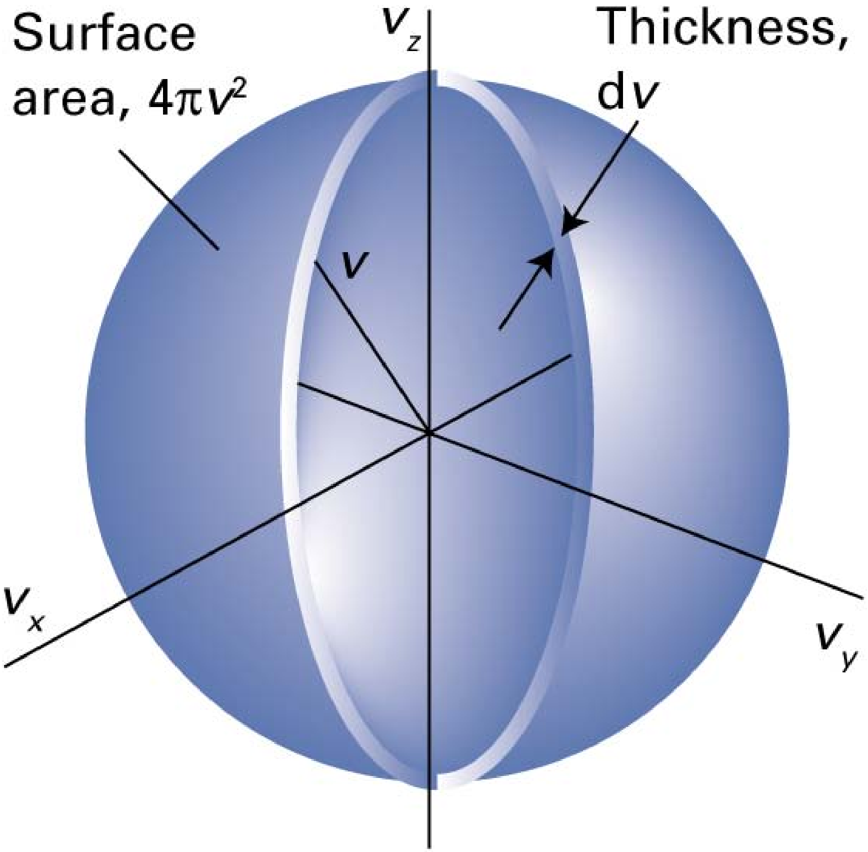
$$f(v_x, v_y, v_z) dv_x dv_y dv_z = f(v_x) f(v_y) f(v_z) dv_x dv_y dv_z$$

$$= \left(\frac{M}{2\pi RT}\right)^{\frac{3}{2}} e^{-\frac{Mv^2}{2RT}} dv_x dv_y dv_z$$



$$c = \left(\frac{3RT}{M}\right)^{\frac{1}{2}}$$

Figure 20.5
The distribution of molecular speeds with temperature and molar mass. Note that the most probable speed (corresponding to the peak of the distribution) increases with temperature and with decreasing molar mass and, simultaneously, the distribution becomes broader.



The volume of spherical shell $= 4\pi v^2 dv$

The probability that the speed lies in the range v to $v+dv$ irrespective of direction of motion:

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

$$\therefore f(v) = 4\pi\left(\frac{M}{2\pi RT}\right)^{\frac{3}{2}} v^2 e^{-\frac{Mv^2}{2RT}}$$

Figure 20.6
The probability $f(v)dv$ that the molecule has a speed in the range $v\left(=\sqrt{v_x^2+v_y^2+v_z^2}\right)$ to $v+dv$ is the sum of the probabilities that it lies in any way of the volume elements $dv_x dv_y dv_z$ in a spherical shell of radius v.

(1) The root mean square speed c is the square root of the average value of v^2.

$$c^2 = \frac{3}{2\zeta}, \qquad \zeta = \frac{M}{2RT} \qquad \therefore c = \left(\frac{3RT}{M}\right)^{\frac{1}{2}}$$

(2) The mean speed $\bar{c}$ is the mean of the speeds calculated using the Maxwell distribution.

$$\bar{c} = \langle v \rangle = \int_0^\infty v f(v) dv = \left(\frac{8RT}{\pi M}\right)^{\frac{1}{2}}$$

(3) The most probable speed c^* is the speed at which the Maxwell distribution passes through a maximum.

$$c^* = \left(\frac{2RT}{M}\right)^{\frac{1}{2}}$$

(4) The relative mean speed $\bar{c}_{\text{rel}} = \sqrt{2}\bar{c}$

For two dissimilar molecules of masses m_{A} and m_{B},

$$\bar{c}_{\text{rel}} = \left(\frac{8kT}{\pi\mu}\right)^{\frac{1}{2}}, \text{ where } \mu = \frac{m_A m_B}{m_A + m_B}$$

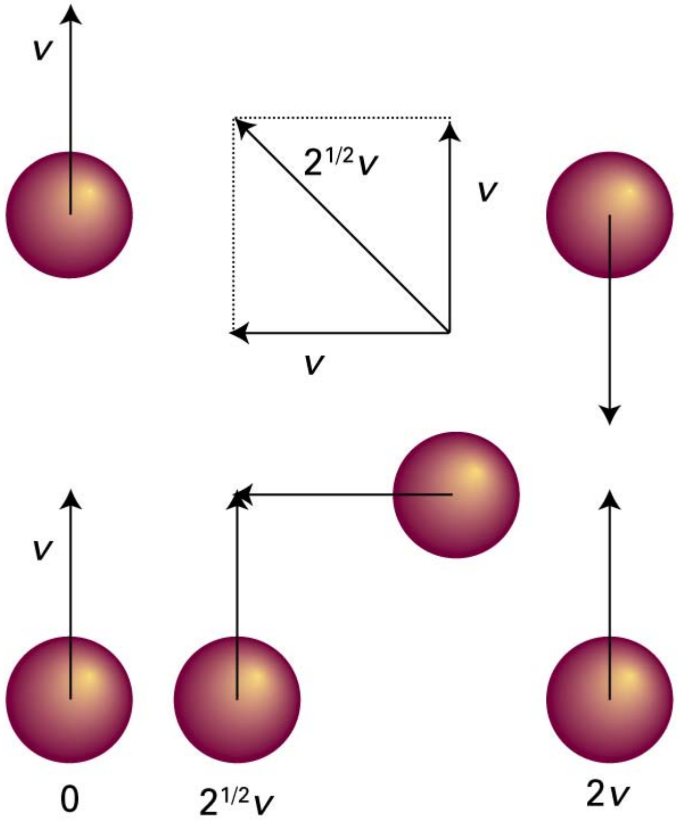


Figure 20.8

A simplified version of the argument to show that the mean relative speed of molecules in a gas is related to the mean speed. When the molecules are moving in the same direction, the mean relative speed is zero; it is $2v$ when the molecules are approaching each other. A typical mean direction of approach is from the side, and the mean speed of approach is then $\sqrt{2}v$. The last direction of approach is the most characteristic, so the mean speed of approach can be expected to be about $\sqrt{2}v$. This value is confirmed by more detailed calculation.

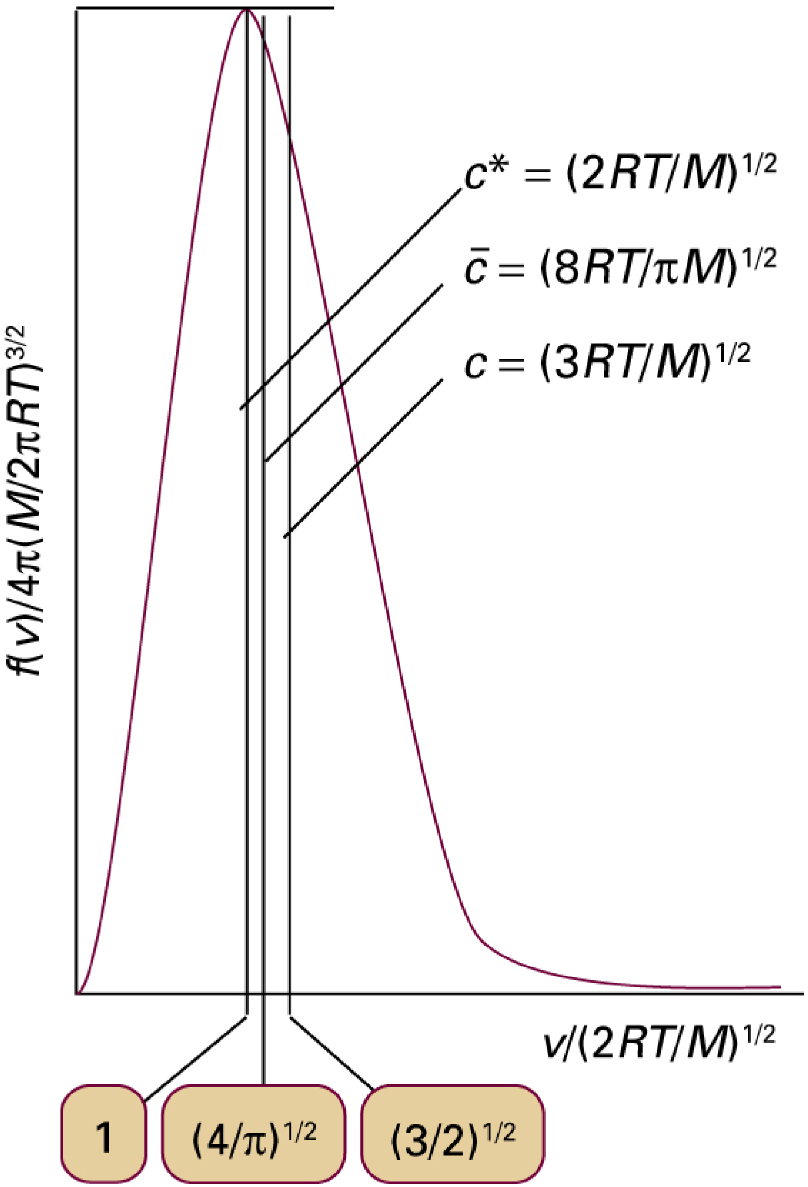


Figure 20.7
A summary of the conclusions that can be deduced from the Maxwell distribution for molecules of molar mass M at a temperature T: c^* is the most probable speed, $\bar{c}$ is the mean speed, and c is the root mean square speed.

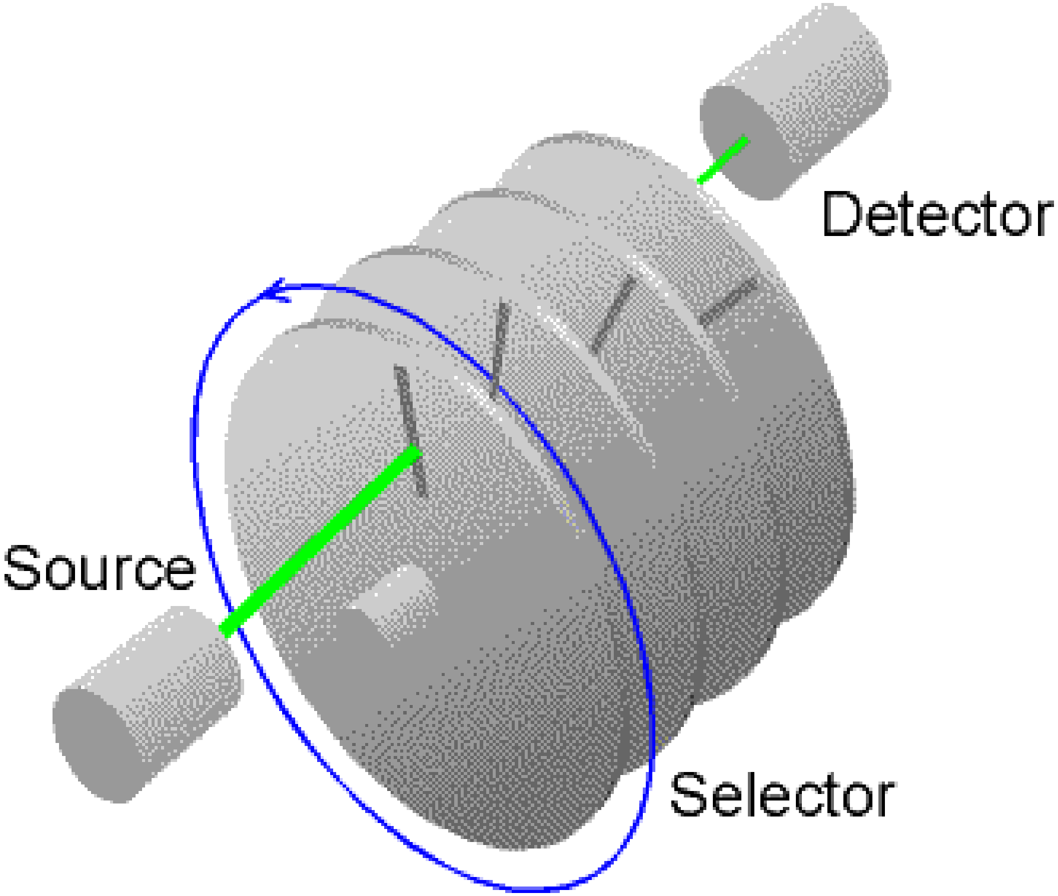


Figure 20.9 A velocity selector. The molecules are produced in the source (which may be an oven with a small hole in one wall), and travel in a beam towards the rotating disks. Only if the speed of a molecule is such as to carry it through each slot that rotates into its path will it reach the detector. Thus, the number of slow molecules can be counted by rotating the disks slowly, and the number of fast molecules counted by rotating the disks rapidly.

the collision frequency $(z) = \sigma \overline{c}_{\text{rel}} \tilde{N}$

$\sigma = \pi d^2, \; \tilde{N} = \dfrac{N}{V}$

$$z = \sigma \overline{c}_{\text{rel}} \tilde{N} = \sigma \overline{c}_{\text{rel}} \frac{N}{V} = \frac{\sigma \overline{c}_{\text{rel}} p}{kT}$$

the mean path $\lambda = \dfrac{\overline{c}}{z} = \dfrac{kT}{\sqrt{2}\sigma p}$

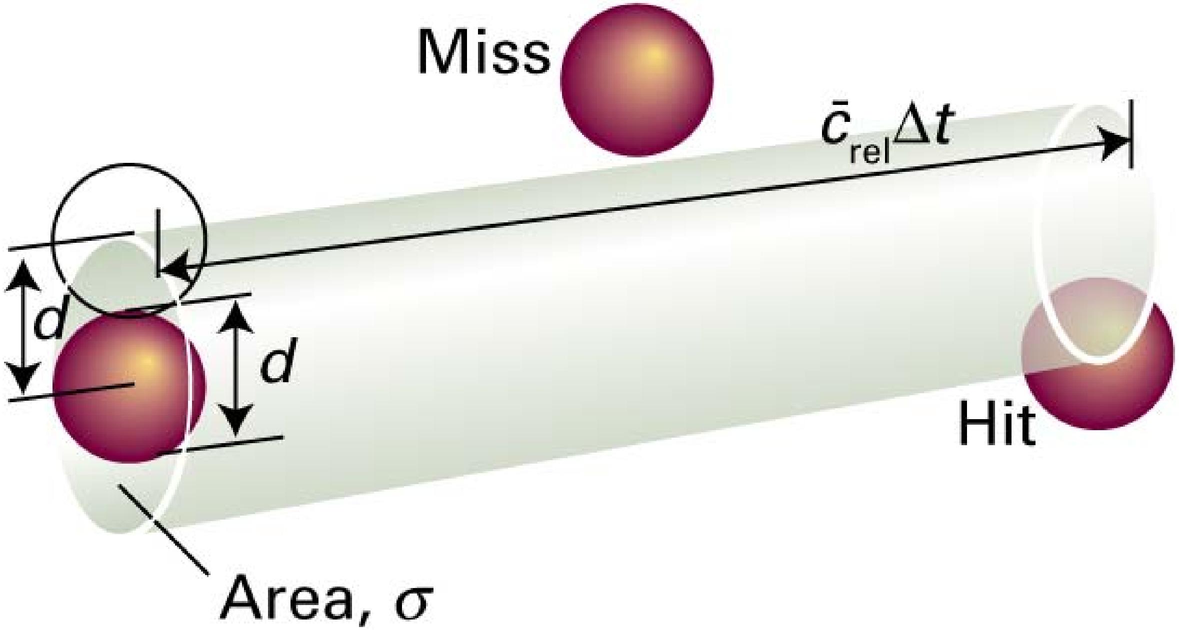


Figure 20.10

In an interval Δt, a molecule of diameter d sweeps out a tube of diameter $2d$ and length $\overline{c}_{\text{rel}}\Delta t$. As it does so it encounters other molecules with centers that lie within the tube, and each such encounter counts as one collision. In practice, the tube is not straight, but changes direction at each collision. Nevertheless, the volume swept out is the same, and this straightened version of the tube can be used as a basis of the calculation.

The mean free path λ,

$$\lambda = \frac{\overline{c}}{z} = \frac{1}{\sqrt{2}\sigma\left(\frac{N}{V}\right)} \qquad z = \sqrt{2}\overline{c}\sigma\left(\frac{N}{V}\right)$$

For a perfect gas,

$$\lambda = \frac{1}{\sqrt{2}\sigma\left(\frac{p}{kT}\right)} = \left(\frac{1}{\sqrt{2}\sigma}\right)\left(\frac{kT}{p}\right)$$

The mean free path is inversely proportional to the pressure.

Collisions with walls and surfaces

A : area of a wall perpendicular to the *x*-axis

$\tilde{N}$: the number density $\left(=\dfrac{N}{V}\right)$

If a molecule has a velocity v_x lying between 0 and $+\infty$, it will strike the wall in a time Δt if it lies within a distance $v_x\ \Delta t$ of it. Therefore all molecules in the volume $Av_x\Delta t$, with velocities in the right direction, will strike the wall in the interval Δt.

The total number of collision $=\tilde{N}A\Delta t\langle v_x\rangle = \tilde{N}A\Delta t\int_0^\infty v_x f(v_x)dv_x = \tilde{N}A\Delta t\left(\dfrac{kT}{2\pi m}\right)^{\frac{1}{2}}$

$$\langle v_x\rangle = \int_0^\infty v_x f(v_x)dv_x = \left(\frac{m}{2\pi kT}\right)^{\frac{1}{2}}\int_0^\infty v_x \exp\left(-\frac{mv_x{}^2}{2kT}\right)dv_x = \left(\frac{kT}{2\pi m}\right)^{\frac{1}{2}}$$

where $f(v_x) = \left(\dfrac{m}{2\pi kT}\right)^{\frac{1}{2}}\exp\left(-\dfrac{mv_x{}^2}{2kT}\right)$ is the Maxwell-Boltzmann distribution.

∴ The number of collisions per unit time per unit area

$$Z_W = \tilde{N}\left(\frac{kT}{2\pi m}\right)^{\frac{1}{2}} = \left(\frac{N}{V}\right)\left(\frac{kT}{2\pi m}\right)^{\frac{1}{2}} = \frac{p}{kT}\left(\frac{kT}{2\pi m}\right)^{\frac{1}{2}}$$

$$= \frac{p}{(2\pi mkT)^{\frac{1}{2}}}$$

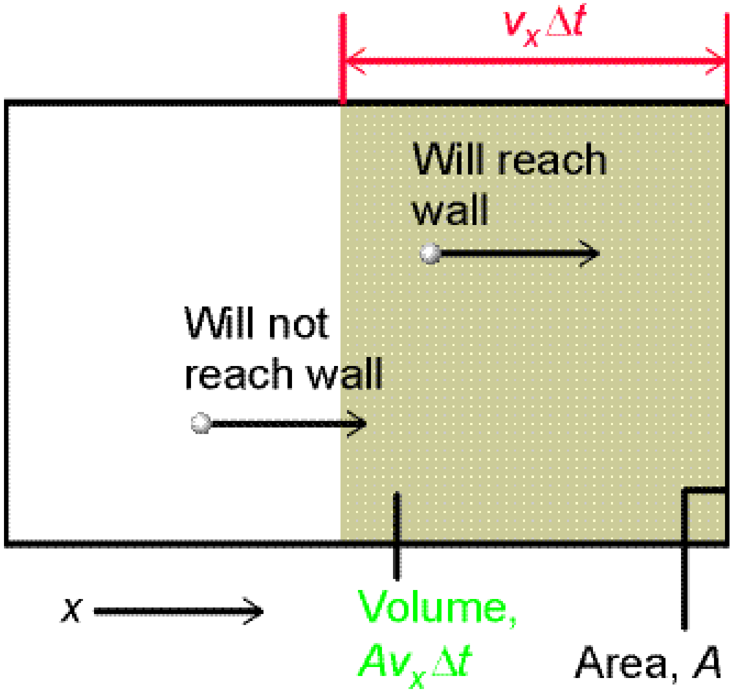


Figure 20.11
Only molecules within a distance $v_x\Delta t$ with $v_x>0$ can reach the wall on the right in an interval Δt.

The rate of effusion

When a gas at pressure p and temperature T is separated from a vacuum by a small hole, the rate of escape of its molecules is equal to the rate at which they strike the area constituting the hole.

$$Z_{\mathrm{W}} = \frac{p}{(2\pi mkT)^{\frac{1}{2}}}$$

: the number of collisions per unit time and unit area

If the area of the hole is A_0, the number of molecules that escape per unit time is

$$Z_{\mathrm{W}} A_0 = \frac{pA_0}{(2\pi mkT)^{\frac{1}{2}}}$$

Graham's law of effusion:
The rate of effusion is inversely proportional to the square-root of the molar mass.

* The calculation of the rate of effusion relies upon the hole being much shorter than mean free path of the gas molecule.

Example:

Derive an expression that shows how the pressure of an effusing perfect gas varies with time.

Example:

the diameter of hole = 0.50 *mm*

Δm = 385 mg (mass loss) for Δt =100 sec.

Calculate the vapour pressure of liquid cesium (Cs) at 500 °C.

Transport properties

– effusion

– diffusion

– thermal conductivity

– electrical conductivity

– viscosity

Flux, *J*: – a measure of the rate of the flow

– the amount of the property passing through unit area in unit time

Usually the flux of a property is proportional to the gradient of a related property of a system.

e. g., $J_z(\text{matter}) \propto \dfrac{d\tilde{N}}{dz}$ (mass transport)

$J_z(\text{energy}) \propto \dfrac{dT}{dz}$ (energy transport)

$\downarrow$

z-direction

Fick’s First Law of Diffusion

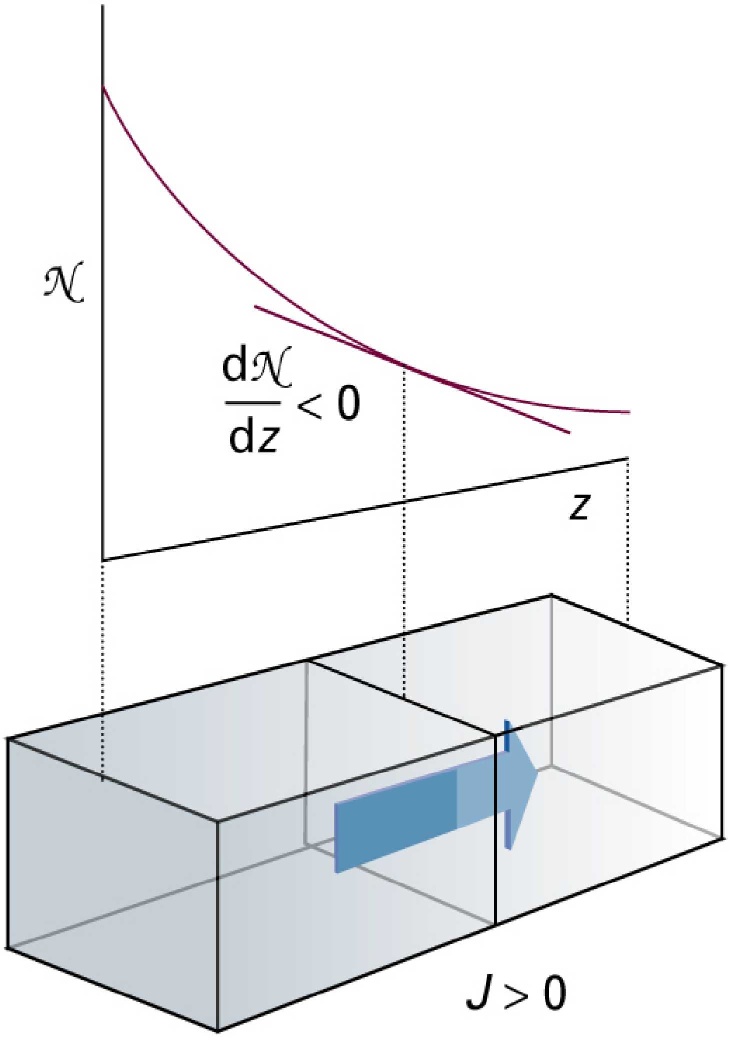
$$J_z(\text{matter}) = -D\left(\frac{d\tilde{N}}{dz}\right)$$

diffusion coefficient

The mass flow occurs down a concentration gradient.

$$J_z(\text{energy}) = -\kappa\left(\frac{dT}{dz}\right)$$

the coefficient of thermal conductivity



The connection between the flux of momentum and viscosity

Particles are continuously moving between the laminas, and bringing with them the *x*-component of momentum. A lamina is retarded by particles arriving from the left, because they have a low momentum in the *x*-direction, and is accelerated by particles arriving from the right. As a result, the laminas tend towards a uniform velocity, and we interpret the retarding effect of the slow layers on the fast ones as the fluid's viscosity.

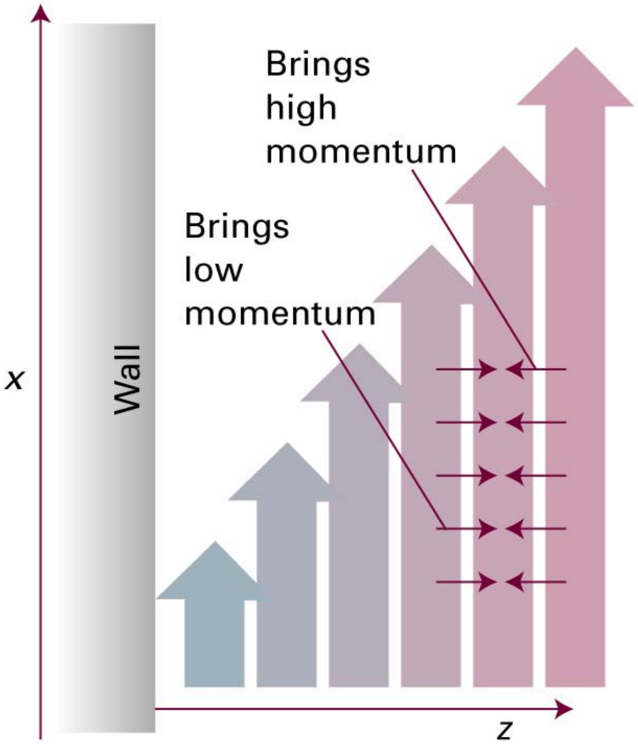


Figure 20.13
The viscosity of a gas arises from the transport of linear momentum. In this illustration the fluid is undergoing laminar flow, and particles bring their initial momentum when they enter a new layer. If they arrive with high *x*-component of momentum they accelerate the layer; if with low *x*-component of momentum they retard it.

Note, however, that the effect depends on the transfer of *x*-momentum into the lamina of interest, and so the viscosity depends on the flux of *x*-momentum in the *z*-direction. Furthermore, this flux depends on the gradient of the *x*-component of velocity of the fluid and so we write

$$\boldsymbol{J_z\,(\text{momentum along } x) \propto \left(\frac{dv_x}{dz}\right)}$$

or

$$\boldsymbol{\underset{\substack{\downarrow \\ \text{the (cofficient of) viscosity}}}{J_z = -\eta}\left(\frac{dv_x}{dz}\right)}$$

The rate of diffusion

The flux of particles is proportional to the gradient of their concentration.

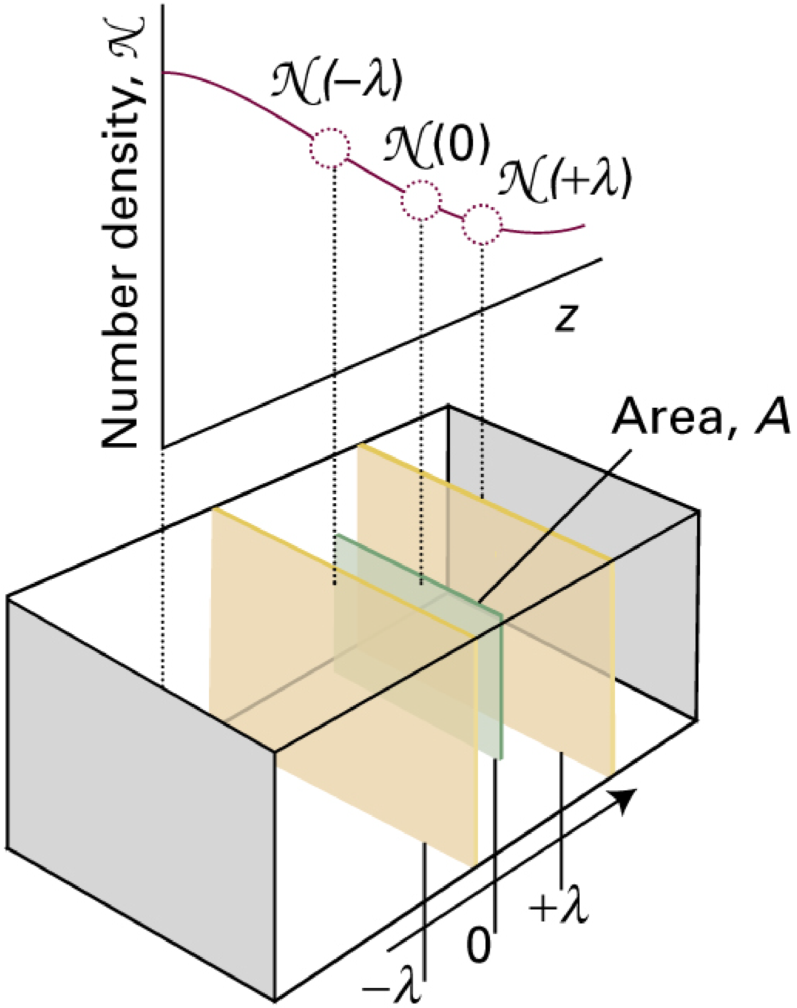


Figure 20.14 The calculation of the rate of diffusion of a gas considers the net flux of molecules through a plane of area A as a result of arrivals from on average a distance λ away in each direction, where λ is the mean free path.

A molecule can be identified as originating from some point where the density of particles is $\tilde{N}(z)$ only if the point z is no farther away from the window than some mean free path distance.

$$\tilde{N}(-\lambda) \cong \tilde{N}(0) - \lambda \left(\frac{d\tilde{N}}{dz} \right)_0$$

$$\downarrow$$

the gradient evaluated at the window (z =0)

Since the number of impacts on the window (area A) from the left in an interval Δt is on the average $\frac{1}{4}\tilde{N}(-\lambda)\bar{c}A\Delta t$,

$$J(\mathrm{L} \rightarrow \mathrm{R}) \approx \frac{1}{4}\tilde{N}(-\lambda)\bar{c}$$

$$J(\mathrm{R} \rightarrow \mathrm{L}) \approx \frac{1}{4}\tilde{N}(\lambda)\bar{c}$$

$$\tilde{N}(\lambda) \approx \tilde{N}(0) + \lambda \left(\frac{d\tilde{N}}{dz} \right)_0$$

$$Z_{\mathrm{W}} = \tilde{N}\left(\frac{kT}{2\pi m}\right)^{\frac{1}{2}} = \frac{1}{4}\bar{c}\tilde{N}$$

$$\bar{c} = \left(\frac{8kT}{\pi m}\right)^{\frac{1}{2}}$$

The net flux

$$J_z = \frac{1}{4}\left\{\left[\tilde{N}(0) - \lambda\left(\frac{d\tilde{N}}{dz}\right)_0\right] - \left[\tilde{N}(0) + \lambda\left(\frac{d\tilde{N}}{dz}\right)_0\right]\right\}\bar{c}$$

$$= -\frac{1}{2}\lambda\bar{c}\left(\frac{d\tilde{N}}{dz}\right)_0$$

The net flux is proportional to the gradient of the concentration.

Fick's Law

$$J_z = -D\left(\frac{d\tilde{N}}{dz}\right)_0$$

$$\therefore \boldsymbol{D = \frac{1}{2}\lambda\bar{c}}$$

Although a molecule may have begun its journey very close to the window, it could have a long-path before it penetrated. Since the path is long, it stands a high probability of colliding before passing through the window. As might be imagined, taking account of this effect introduces considerable labour into the calculation, but the net result turns out to be that the result we have derived is modified only to the extent of a factor 2/3 , representing the lower flux because of the collisions suffered by the longer travelling particles.

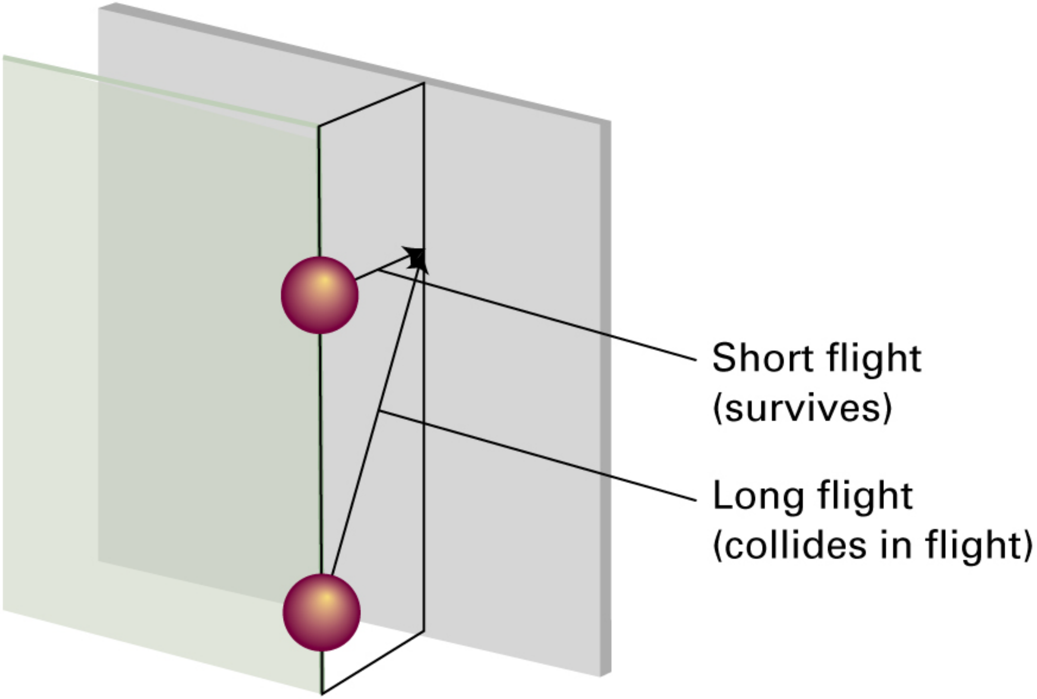


Figure 20.15
Some molecules travel further in order to cross a plane.

The result of this modification

$$\boldsymbol{J_z = -\frac{1}{3}\lambda\bar{c}\left(\frac{d\tilde{N}}{dz}\right)_0} \quad \text{with } \boldsymbol{J_z = -D\left(\frac{d\tilde{N}}{dz}\right)_0}$$

$$\therefore\ D = \frac{1}{3}\lambda\bar{c}$$

$$= \frac{1}{3}\left(\frac{1}{\sqrt{2}\sigma}\right)\left(\frac{kT}{p}\right)\left(\frac{8kT}{\pi m}\right)^{\frac{1}{2}}$$

$$= \frac{2}{3}\left(\frac{1}{\sigma p}\right)\left(\frac{k^3T^3}{\pi m}\right)^{\frac{1}{2}}$$

where $\sigma = \pi d^2$

$$\bar{c} = \left(\frac{8kT}{\pi m}\right)^{\frac{1}{2}}$$

$$\lambda = \left(\frac{1}{\sqrt{2}\sigma}\right)\left(\frac{kT}{p}\right)$$

Thermal conductivity

$\varepsilon = \nu kT$ where *v* is a number of the order of 1.

For monatomic particles, $\nu = 3/2$.

$$J\left(\mathrm{L}\rightarrow\mathrm{R}\right)=\frac{1}{4}\overline{c}\tilde{N}\varepsilon\left(-\lambda\right) \qquad \varepsilon\left(-\lambda\right)=\nu k\left\{T-\lambda\left(\frac{\partial T}{\partial z}\right)_0\right\}$$

$$J\left(\mathrm{R}\rightarrow\mathrm{L}\right)=\frac{1}{4}\overline{c}\tilde{N}\varepsilon\left(\lambda\right) \qquad \varepsilon\left(\lambda\right)=\nu k\left\{T+\lambda\left(\frac{\partial T}{\partial z}\right)_0\right\}$$

The net flux

$$J_z = J\left(\mathrm{L}\rightarrow\mathrm{R}\right)+J\left(\mathrm{R}\rightarrow\mathrm{L}\right)=-\frac{1}{2}\nu k\lambda\overline{c}\tilde{N}\left(\frac{\partial T}{\partial z}\right)_0$$

Correction

$$J_z = -\frac{1}{3}\nu k\lambda\overline{c}\tilde{N}\left(\frac{\partial T}{\partial z}\right)_0$$

$$J_z(\text{energy}) = -\kappa\left(\frac{dT}{dz}\right)$$

$$J_z = -\frac{1}{3}\nu k\lambda\bar{c}\tilde{N}\left(\frac{dT}{dz}\right)_0$$

$$\therefore \kappa = \frac{1}{3}\nu k\lambda\bar{c}\tilde{N}$$

Since $\tilde{N} = \frac{N}{V} = \frac{nN_A}{V} = N_A\left(\frac{n}{V}\right) = N_A[A]$ and $C_{V,m} = \nu k N_A$,

$$\boldsymbol{\kappa = \frac{1}{3}\lambda\bar{c}C_{V,m}[A]}$$

Thermal conductivity

Suppose every molecule carries an amount of energy ε.
When one molecule passes through the imaginary window, it transports that amount of energy.

$$J_z(\text{heat}) = \varepsilon J_z(\text{matter})$$

$$= -\frac{1}{3}\lambda\bar{c}\,\varepsilon\left(\frac{d\tilde{N}}{dz}\right)_0$$

$$= -\frac{1}{3}\lambda\bar{c}\left(\frac{d\mathrm{E}}{dz}\right)_0$$

$$J_z(\text{matter}) = -\frac{1}{3}\lambda\bar{c}\left(\frac{d\tilde{N}}{dz}\right)_0$$

where $\mathbf{E} = \varepsilon\tilde{N} = \varepsilon\left(\frac{N}{V}\right)$: the energy density
(the amount of energy per unit volume)

The energy gradient can be related to the temperature gradient by means of the heat capacity of the sample.

$$\left(\frac{d\mathrm{E}}{dz}\right)_0 = \left(\frac{d(U/V)}{dz}\right)_0 = \frac{1}{V}\left(\frac{dU}{dz}\right)_0 = \left(\frac{n}{V}\right)C_{V,m}\left(\frac{dT}{dz}\right)_0$$

$$\therefore\ J_z(\text{energy}) = -\frac{1}{3}\lambda\bar{c}\left(\frac{n}{V}\right)C_{V,m}\left(\frac{dT}{dz}\right)_0$$

$$\therefore\ \kappa = \frac{1}{3}\lambda\bar{c}\,C_{V,m}\left(\frac{n}{V}\right)$$

$$= \frac{1}{3}\frac{1}{\sqrt{2}\sigma\left(\frac{N}{\cancel{V}}\right)}\bar{c}\,C_{V,m}\left(\frac{n}{\cancel{V}}\right) = \frac{1}{3}\bar{c}\,C_{V,m}\Big/\sqrt{2}\sigma N_A$$

$$\left(\frac{dU}{dz}\right)_V = \left(\frac{dT}{dz}\right)\left(\frac{dU}{dT}\right)_V$$

$$= C_V\left(\frac{dT}{dz}\right)$$

$$J_z = -\kappa\left(\frac{dT}{dz}\right)$$

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

This shows that *k* is independent of pressure.

The physical reason for this pressure independence is that the thermal conductivity is large when many molecules are available to transport the energy but the pressure of many molecules limits the mean free paths and so the molecules are unable to carry the energy even great distances: these two effects balance.

The viscosity of gases

We have already seen that the coefficient of viscosity is determined by the rate at which momentum is transported.

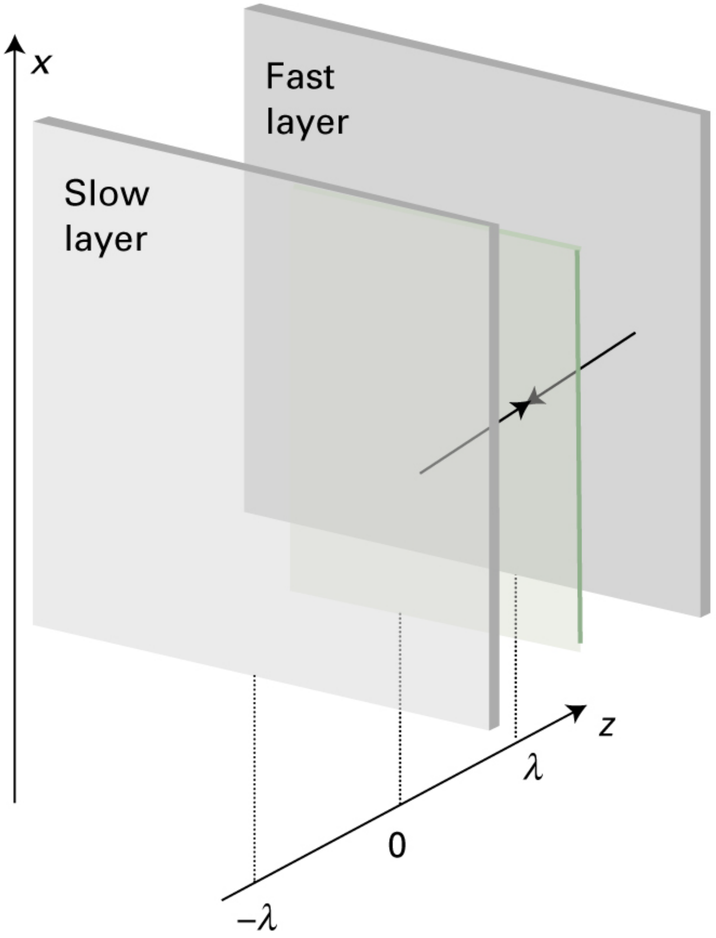


Figure 20.16 The calculation of the viscosity of a gas examines the net *x*-component of momentum brought to a plane from faster and slower layers on average a mean free path away in each direction.

The number of impacts on the imaginary window is $\frac{1}{4}\tilde{N}\overline{c}$ per unit area per unit time.

$$mv_x(\lambda) = mv_x(0) + \lambda m\left(\frac{dv_x}{dz}\right)_0 \quad \Leftarrow \quad v_x(\lambda) = v_x(0) + \lambda\left(\frac{dv_x}{dz}\right)_0$$

$$mv_x(-\lambda) = mv_x(0) - \lambda m\left(\frac{dv_x}{dz}\right)_0 \quad \Leftarrow \quad v_x(-\lambda) = v_x(0) - \lambda\left(\frac{dv_x}{dz}\right)_0$$

$\therefore$ the net flux of *x*- momentum in the *z*- direction

$$J_z\,(\text{momentum along } x) = \frac{1}{4}\tilde{N}\overline{c}\left\{\left[mv_x(0) - m\lambda\left(\frac{dv_x}{dz}\right)_0\right] - \left[mv_x(0) + m\lambda\left(\frac{dv_x}{dz}\right)_0\right]\right\}$$

$$= -\frac{1}{2}m\tilde{N}\lambda\overline{c}\left(\frac{dv_x}{dz}\right)_0$$

$$J_z = -\eta\left(\frac{dv_x}{dz}\right)$$

$$\therefore \eta = \frac{1}{2} m\lambda \tilde{N}\bar{c}$$

Modification of path length

$$\therefore \eta = \frac{1}{3} m\lambda \tilde{N}\bar{c} = \frac{1}{3} m\lambda \bar{c} N_A \left(\frac{n}{V}\right)$$

↓

due to correction of long path

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

$$\eta = \frac{1}{3} m\bar{c} N_A \left(\frac{n}{V}\right) \Big/ \sqrt{2}\,\sigma N_A \left(\frac{n}{V}\right) = \frac{1}{3}\left(\frac{1}{2}\right)^{\frac{1}{2}} m\bar{c} \Big/ \sigma$$

The viscosity increases with temperature because $\bar{c} \propto T^{\frac{1}{2}}$. The peculiar result arises because at higher temperatures the particles travel more quickly and thus the flux of momentum is greater.

This viscosity behavior is quite different from that shown by liquids, which flow more easily as temperature is increased. This difference stems from the fact that a liquid's viscosity is dominated by intermolecular forces: in order to flow, molecules need energy to escape from their neighbors, and this is more freely available at high temperatures than at low.

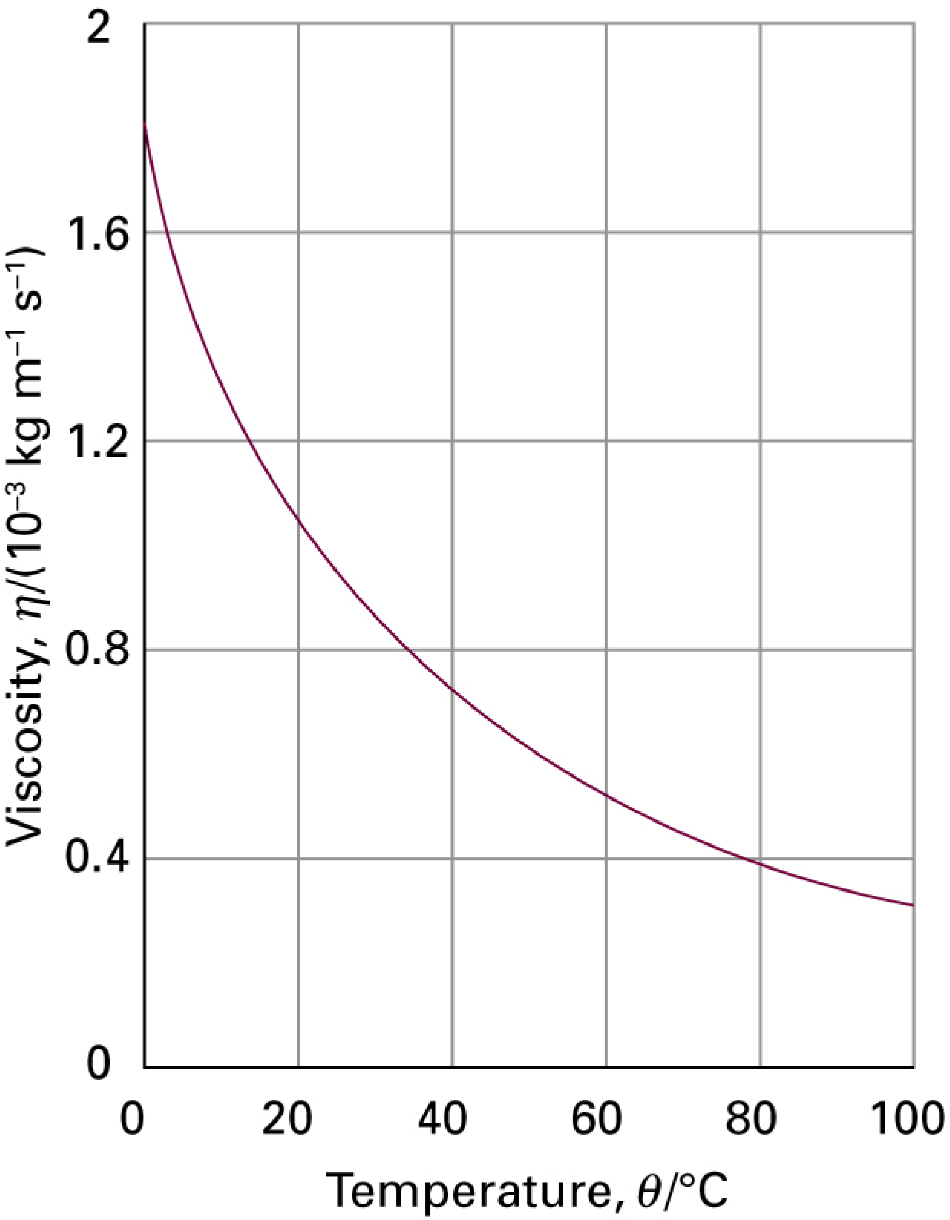


Figure 20.17 The experimental temperature dependence of the viscosity of water. As the temperature is increased, more molecules are able to escape from the potential wells provided by their neighbors, and so the liquid becomes more fluid. A plot of $\ln \eta$ against $1/T$ is a straight line with positive slope.

One method for determination of viscosity

Poiseuille’s formula for the flow of fluid through a tube of radius *r*

$$\frac{dV}{dt} = \frac{\left(p_1^2 - p_2^2\right)\pi r^4}{16 l \eta p_0}$$

V: the volume flowing

p_1, p_2: the pressures at each end of the tube of length l

p_0: the pressure at which the volume is measured

In order to determine the viscosity, the rate of flow under a known pressure difference is monitored and interpreted using this equation.

The conductivities of electrolyte solutions

The most direct evidence for the existence of ions in solutions is the observation that the solution can conduct an electric current.

Ion motion: the empirical facts

The simplest way of studying the motion of ions in solution is through their conductivity, their ability to conduct electricity.

$$R \propto \frac{l}{A}$$

R : resistance

$$R = \rho \frac{l}{A}$$

ρ : the resistivity or specific resistance

The conductivity κ is the inverse of the resistivity ρ,

$$R = \frac{1}{\kappa}\frac{l}{A} \qquad \therefore \kappa = \frac{l}{RA} \ (\Omega^{-1}m^{-1} \text{ or } \Omega^{-1}cm^{-1})$$

Ω^{-1}: reciprocal ohm, is sometimes called mho, and sometimes the siemens:

$$1\,S = 1\,\Omega^{-1}$$

Once the resistance of the sample has been measured, the conductivity can be calculated from a knowledge of the cell dimensions.

R^{*}: the resistance of a standard solution (usu., KCl in water)

κ^{*}: the known conductivity of the standard sample

$$\kappa = \left(\frac{R^{*}}{R}\right)\kappa^{*}$$

The conductivity depends on the number of charged ions present, and so it is normal to express the conductivity as a molar quantity.

$$\Lambda_m = \frac{\kappa}{c}$$

Λ_m : the molar conductivity

Two types of electrolytes

(1) strong electrolytes

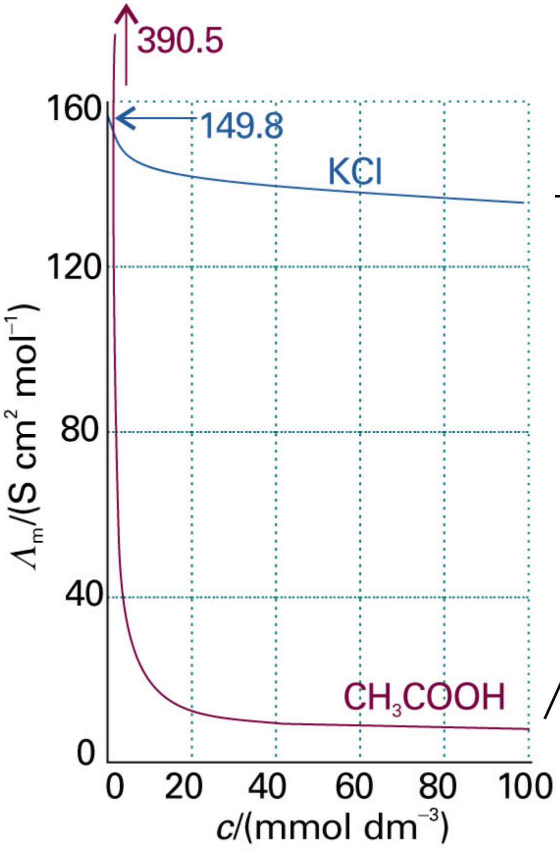
- Substances of one class have conductivities that depend only weakly on the concentration of the solute.
- The molar conductivity rises slightly so the concentration falls. As the concentration of solute decreases, the molar conductivity rises to a limit which is called the molar conductivity at infinite dilution, Λ_m^0 .

Kohlrausch’s law

$$\Lambda_m(c) = \Lambda_m^0 - \mathcal{K}c^{\frac{1}{2}}$$

Λ_m^0: the limiting molar conductivity

$\mathcal{K}$: the coefficient which depends more on the nature of the salt than its specific identity



→ strong electrolyte (ionophores)

weak electrolyte (ionogenes)

Figure 20.18
The concentration dependence of molar conductivities.

$$\Lambda_m^0 = \nu_+\lambda_+^0 + \nu_-\lambda_-^0$$

ν_+, ν_- : the number of cations and anions needed to form one molecule of the salt (e.g. $\nu_+ = \nu_- = 1$ for NaCl, $CuSO_4$; $\nu_+ = 1,\ \nu_- = 2$ for $MgCl_2$).

λ_+^0, λ_-^0: the molar conductivity at infinite dilution

(2) weak electrolytes

– Substances that have molar conductivities that depend markedly on the concentration.

– $MA \rightleftharpoons M^+ + A^-$: the existence of an equilibrium

The conductivity reflects the number of ions in the solution, and this depends on the equilibrium constant for the dissociation.

$$K = \frac{c_{M^+} c_{A^-}}{c_{MA}} = \frac{(\alpha c)(\alpha c)}{(1-\alpha)c} = \left(\frac{\alpha^2}{1-\alpha} \right) c$$

c : the concentration of added electrolytes

α : the degree of ionization

$$\Lambda_m = \alpha \Lambda_m^0$$

Λ_m : the measured molar conductance

Λ_m^0 : the molar conductance of the fully ionized solution

Oswald's Dilution Law

$$K=\left\{\frac{\left(\frac{\Lambda_m}{\Lambda_m^0}\right)^2}{1-\left(\frac{\Lambda_m}{\Lambda_m^0}\right)}\right\}c$$

$$K=\left(\frac{\alpha^2}{1-\alpha}\right)c$$

$$\Lambda_m=\alpha\Lambda_m^0\Rightarrow\alpha=\frac{\Lambda_m}{\Lambda_m^0}$$

The expression can be used to determine the dissociation equilibrium constant by measuring Λ_m and estimating Λ_m^0 from $\Lambda_m^0=\nu_+\lambda_+^0+\nu_-\lambda_-^0$:

$$\Lambda_m=\frac{1}{2}\left(\frac{K}{c}\right)\left\{\left(1+\frac{4c}{K}\right)^{\frac{1}{2}}-1\right\}\Lambda_m^0$$

the explicit dependence of the molar conductivity on the concentration

The mobility of ions

l : distance of electrode

$\Delta\phi$: potential

$\Delta\phi\,/l$: the potential gradient

The magnitude of the force is proportional to the potential gradient.

$\boldsymbol{F = ze\mathcal{E}}$

F : force

ze: the charge on an ion (where z is positive for cations and negative for anions)

$\mathcal{E}$: elective field $\left(= \dfrac{\Delta\phi}{l} \right)$

$$\therefore F = ze\Delta\phi / l$$

The force acting on an ion accelerates it, but as it rubs through the solvent, a frictional force retards it. It is therefore accelerated only to some limiting velocity which depends on the strength of the applied field and the viscosity of the solvent. This terminal velocity is called the drift speed of the ion in solution, and is denoted $\boldsymbol{s}$.

Stokes formula

the frictional force = $\mathbf{6\pi a\eta\, s}$

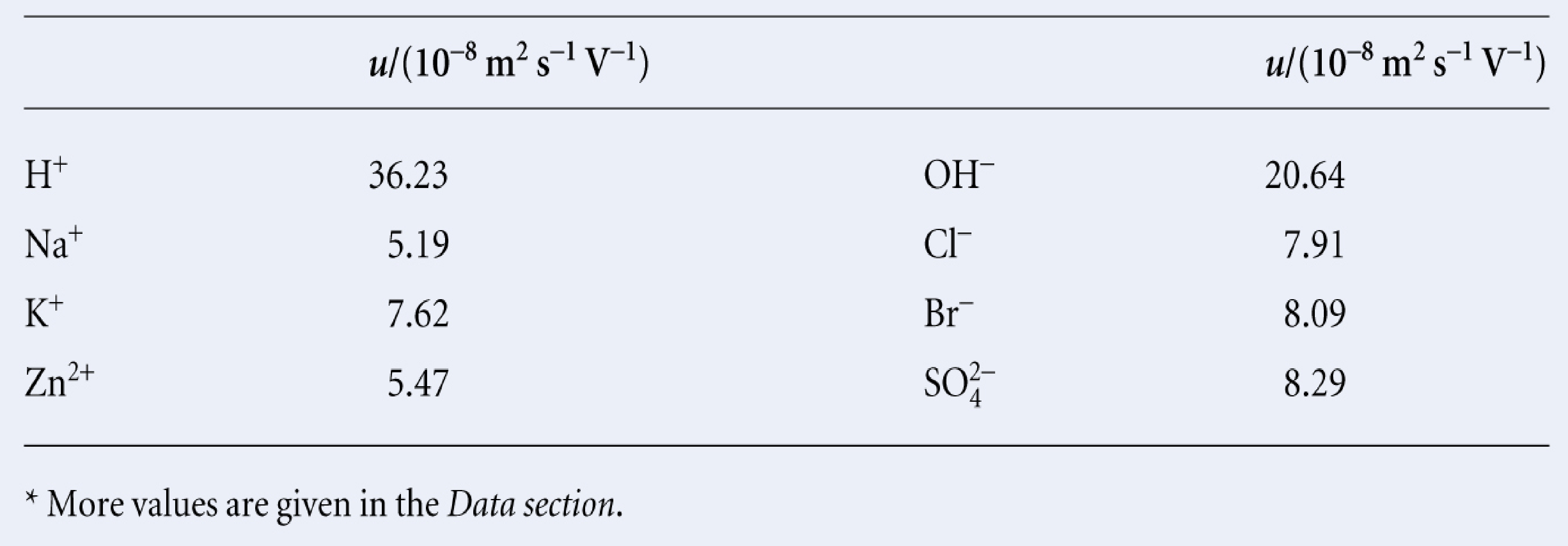
a: the radius of a spherical object

η: the viscosity of a medium

$$\mathbf{6\pi a\eta s \cong ze\mathcal{E}}$$

$$\therefore \mathbf{s \cong \frac{ze\mathcal{E}}{6\pi a\eta}}$$

Table 20.1 Ionic mobilities in water at 298 °K



	$u/(10^{-8}\ \mathrm{m^2\ s^{-1}\ V^{-1}})$		$u/(10^{-8}\ \mathrm{m^2\ s^{-1}\ V^{-1}})$
H^+	36.23	OH^-	20.64
Na^+	5.19	Cl^-	7.91
K^+	7.62	Br^-	8.09
Zn^{2+}	5.47	SO_4^{2-}	8.29

* More values are given in the *Data section*.

Since the drift speed governs the rate at which current may be conducted, it follows that we should expect the conductivity to decrease with increasing solution viscosity and increasing the size.

Experimental results confirm the first of these predictions, but not the second. For example, the molar conductivities of the alkali metal ions increase on going from Li^+ to Cs^+ even though the ion size are known to increase markedly.

Solvation effect

The solvent molecules cluster around the ion increase its effective size (hydrodynamic radius). Small ions are the source of stronger electric fields than large ions (this is a result of electrostatic theory, which shows that the electric field at the surface of a sphere of radius r is proportional to ze/r^2) and so the solvation is more extensive in the case of small ions. They have larger hydrodynamic radii than larger ions, lower drift velocities, and therefore lower conductivities.

The mobility of ions

The drift velocity of an ion is a quantity with direction as well as magnitude. We shall call its magnitude the drift speed $s_\pm$, so that $s_\pm = |\mathbf{v}_\pm|$.

$s_\pm \propto \mathcal{E}$ $\mathcal{E}$: electric field applied

$s_\pm = u_\pm \mathcal{E}$ $u_\pm$: – the mobility of the ion

– the speed of the ion in a field of unit length

directly related to the conductivity

The relation between mobility and conductivity

Consider a solution of a salt $M_{\nu_+}X_{\nu_-}$ of concentration c (molar concentration in moles per unit volume) so that it contains $\nu_+ cN_A$ cations and $\nu_- cN_A$ anions per unit volume. The cations have charge z_+e and the anions z_-e.

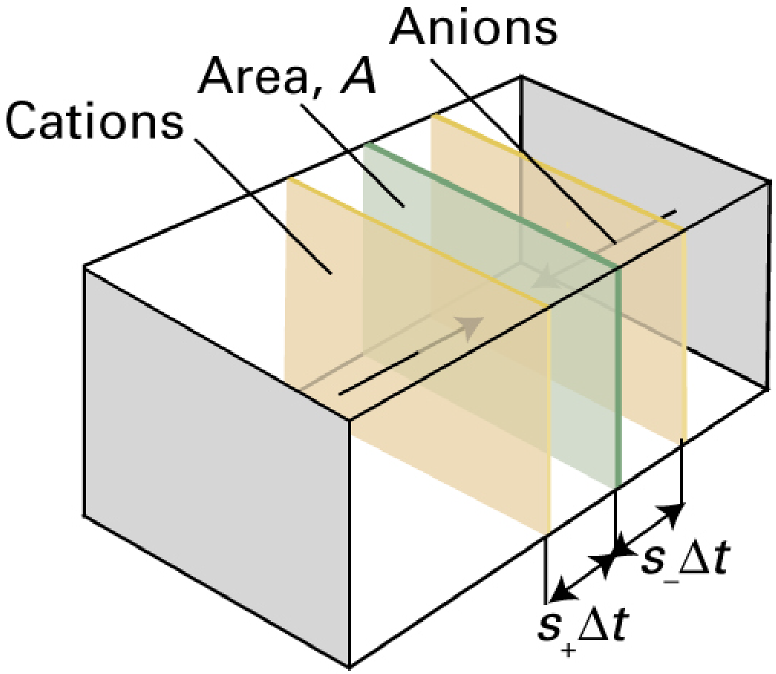


Figure 20.19
Calculating the charge flux.

volume: $s_+\Delta tA$

the number that pass through: $(s_+\Delta tA)\nu_+ cN_A$

Each ion carries a charge z_+e, and so the flux of positive charge, the number of charge passing through per unit area per unit time, is

$$J_{(+\text{charge})} = \left(s_+ \Delta t A\right) v_+ c N_A z_+ e \Big/ A \Delta t = v_+ s_+ z_+ c e N_A$$

Current is also transported by the anions; they move in the opposite direction but carry the opposite charge. The total flux is therefore

$$\begin{aligned} J_{(\text{charge})} &= v_+ s_+ z_+ c e N_A + v_- s_- \left|z_-\right| c e N_A \\ &= (u_+ v_+ z_+ + u_- v_- \left|z_-\right|) c F \mathcal{E} \end{aligned}$$

where $F = eN_A$ (the Faraday constant $= 9.65 \times 10^4\, C / mol$)

$$s_\pm = u_\pm\, \mathcal{E}$$

Since the current $I = JA$ and $E = \dfrac{\left|\Delta\phi\right|}{l}$,

$$I = \frac{\left(u_+ v_+ z_+ + u_- v_- \left|z_-\right|\right) c F A \left|\Delta\phi\right|}{l}$$

Ohm’s law

$$I = \frac{|\Delta\phi|}{R} = \frac{\kappa|\Delta\phi|A}{l} \qquad \left(\leftarrow R = \frac{1}{\kappa}\frac{l}{A}\right)$$

Comparison of these two expressions

$$\kappa = \left(v_+ u_+ z_+ + v_- u_- |z_-|\right)cF$$

the molar conductivity

$$\Lambda_m = \left(v_+ u_+ z_+ + v_- u_- |z_-|\right)F$$

For a 1:1 salt with $|z_+|=|z_-|=z$,

$$\boldsymbol{\Lambda_m = z\left(u_+ + u_-\right)F}$$

the individual conductivities of cation and anion

$$\boldsymbol{\lambda_\pm = u_\pm |z_\pm| F}$$

By measuring the conductivities we can find the mobilities through last two equations.

the transport number: the fraction of the total current carried by each type of ion

For 1:1 salt,

$$t_+ = \frac{u_+}{u_+ + u_-}\ ,\quad t_- = \frac{u_-}{u_+ + u_-}$$

$$t_\pm = \frac{\lambda_\pm}{\lambda_+ + \lambda_-} = \lambda_\pm / \Lambda_m \quad \text{or} \quad \lambda_\pm = \Lambda_m t_\pm$$

Therefore, if we have an independent way of measuring transport numbers, the individual ion conductivities, and then the mobilities, may be established.

Conductivities and ionic interactions

Examination of eq $\Lambda_m(c)=\Lambda_m^0-\mathcal{K}c^{\frac{1}{2}}$

(1) relaxation effect

An ion tends to gather into its vicinity a cluster of ions of opposite charge. The charge cloud is called the ionic atmosphere, and on the average it is spherically symmetrical.

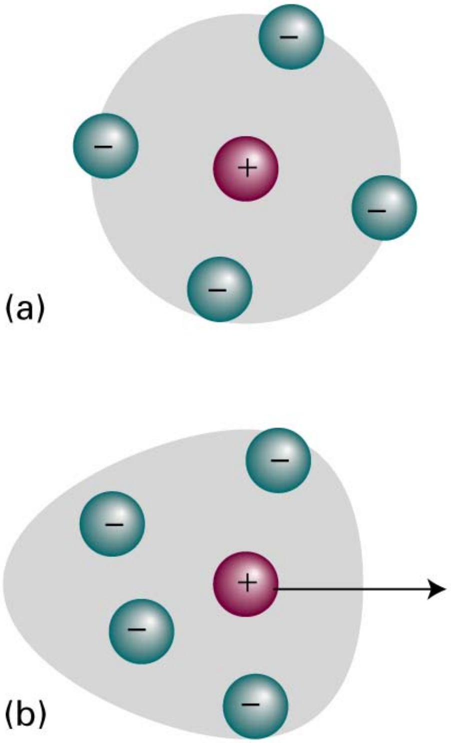


Figure 20.19
(a) The ionic atmosphere when the ions have no net motion and (b) the distortion arising from motion.

An external electric field induces a distortion of ionic atmosphere so that the overall effect displace the center of charge of the atmosphere a short distance behind the moving ion. As the charge of the ion and atmosphere are opposite, the result is to retard the motion of the moving ion. This is called the relaxation effect, because the formation and decay of the atmosphere is a kind of relaxation into an equilibrium distribution of the ions.

(2) electrophoretic effect

When the ions are not infinitely far apart, the viscous drag effect is enhanced because ions of opposite charge, each with their cluster of solvent molecules, are rubbing past each other. This enhances the viscous drag, which is called the electrophoretic effect, and lowers the drift velocity and therefore the conductivity.

Debye-Hückel-Onsager equation for molar conductivities

$$\Lambda_m = \Lambda_m^0 - (A + B\Lambda_m^0)c^{\frac{1}{2}}$$

$$A = \frac{zeF}{3\pi\eta}\left(\frac{2z^2e^2N_A}{\varepsilon kT}\right)^{\frac{1}{2}}, \quad B = \frac{e^2z^2q}{24\pi\varepsilon kT}\left(\frac{2z^2e^2N_A}{\pi\varepsilon kT}\right)^{\frac{1}{2}}$$

where ε : the electric permittivity of the medium

$q \sim$ 0.586 for a (1,1)-electrolyte

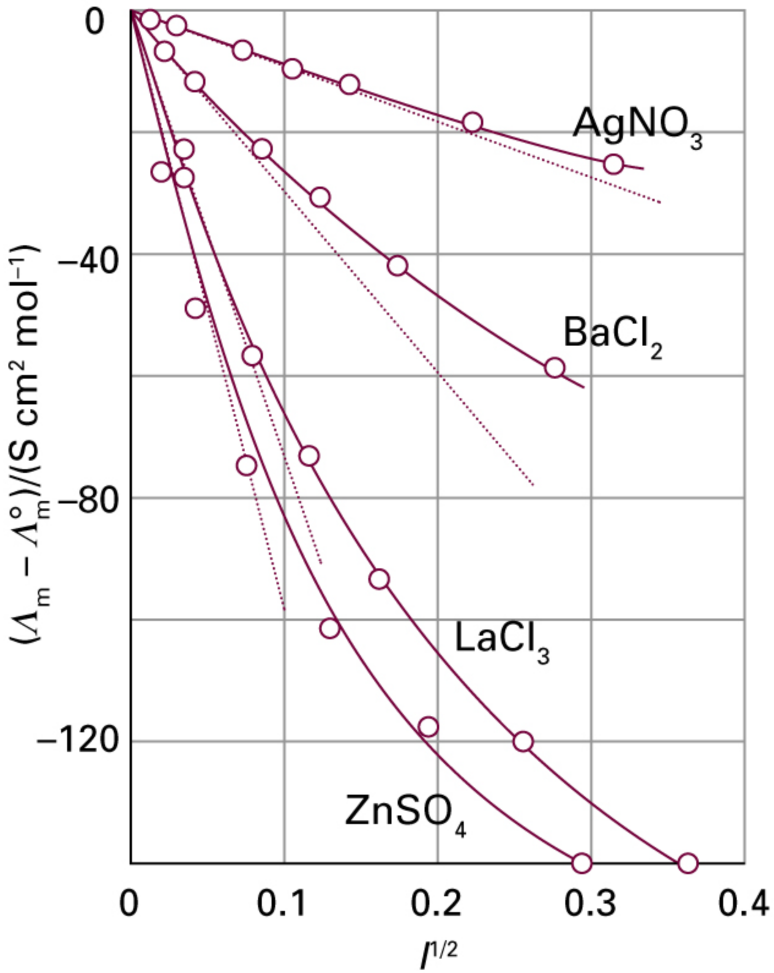


Figure 20.20
The dependence of molar conductivities on the square root of the ionic strength, and comparison (dotted line) with the dependence predicted by the Debye-Huckel-Onsager theory.

The slopes of the curves are predicted to depend on the valence type (*z* appears in the constants *A* and *B*).

The success of the Debye–Huckel–Onsager equation suggests that the model of ion-ion interactions is substantially correct.

Fundamental aspects of molecular transport

Diffusion: the thermodynamic view

When unit amount of solute is moved from a region where its chemical potential is $\mu(1)$ to one where it is $\mu(2)$, the work required is $w = \mu(2) - \mu(1)$.

$\therefore$ the work involved in transferring unit amount of material from *x* to *x* + *dx* is

$$dw = \mu(x+dx) - \mu(x) = \left[\cancel{\mu(x)} + \left(\frac{d\mu}{dx} \right) dx \right] - \cancel{\mu(x)}$$

$$= \left(\frac{d\mu}{dx} \right) dx$$

In classical mechanics

$dw = -Fdx$ F: force

By comparing the last two equations we see that the gradient of the chemical potential acts like a force.

$$F = -\left(\frac{d\mu}{dx}\right): \quad \text{thermodynamic force}$$

In an ideal solution where the concentration is *c*,

$$\mu = \mu^{o} + RT\ln\left(c/mol\cdot dm^{-3}\right)$$

If the concentration depends on position, the thermodynamic force acting is

$$\mathbf{F} = -\frac{d}{dx}\left(\mu^{o} + RT\ln c\right) = -\left(\frac{RT}{c}\right)\left(\frac{dc}{dx}\right)$$

Example:

Suppose that the concentration of a solute decays exponentially along the length of a container. Calculate the thermodynamic force on the solute at 25 ^{o}C when the concentration decreases to half its value in every 10 cm.

From the exponential form of the concentration it follows that

$$\frac{dc}{dx} = -\frac{c}{\lambda}$$

$$\mathrm{F} = -\frac{RT}{c}\left(\frac{\partial c}{\partial x}\right)_{p,T} \qquad \mathrm{F} = -\frac{d}{dx}\left(\mu^{\circ} + RT\ln c\right) = -\left(\frac{RT}{c}\right)\left(\frac{dc}{dx}\right)$$

$$\therefore \mathrm{F} = \frac{RT}{\lambda}$$

$$= \frac{8.31 JK^{-1}mol^{-1} \times 298K}{14.4 \times 10^{-2} m} = 17\, kN / mol$$

Fick’s first law of diffusion

The flux of diffusing particles is motion in response to a thermodynamic force arising from a concentration gradient. The particles reach a steady drift speed *s* when the thermodynamic force F is matched by the viscous drag.

$$s \propto \mathrm{F}$$

The particle flux *J* is proportional to the drift speed, and the thermodynamic force is proportional to the concentration gradient *dc*/*dx*. Since $J \propto s,\ s \propto \mathrm{F}$ and $\mathrm{F} \propto dc/dx$,

$$\therefore J \propto \frac{dc}{dx} \quad \text{==>} \quad \text{Fick's 1st law, } J_x(\text{matter}) = -D\frac{d\tilde{N}}{dx}$$

$$J = s\tilde{N} = scN_A$$

$$scN_A = -D\left(\frac{d\tilde{N}}{dx}\right) = -DN_A\left(\frac{dc}{dx}\right)$$

$$\therefore s = -\left(\frac{D}{c}\right)\left(\frac{dc}{dx}\right) = \left(\frac{D}{RT}\right)\mathrm{F} \quad \Leftarrow \left(\mathrm{F} = -\left(\frac{RT}{c}\right)\left(\frac{dc}{dx}\right)\right)$$

Therefore, once we know the effective force and D, we can calculate the drift speed of the particles (and vice versa), and this will be true whatever the origin of the force.

We know, however, that the mobility of an ion is related to the electrical force on it. Since the mobility is defined through $s = uE$, and since the electrical force is ezE, so that the force per mole zFE,

$$s = uE = \left(\frac{u}{zF}\right)(zFE) = \underbrace{\left(\frac{u}{zF}\right)}_{\text{the drift speed under the influence of unit force}}\mathrm{F}$$

The nature of the force is irrelevant; therefore the two drift speed (*D*/*RT*)F and (*u*/*zF*)F may be identified:

$$\therefore \frac{u}{zF} = \frac{D}{RT}$$

$$\therefore \boldsymbol{D = \frac{uRT}{zF} = \frac{ukT}{ze}}$$ Einstein relation

The above equation can be developed in two directions:

(1) The relation between the molar conductivity and the diffusion constant of the ions, D_+ and D_- for 1:1 salts

$$\Lambda_m = zF(u_+ + u_-) = \frac{z^2F^2}{RT}(D_+ + D_-)$$

$$\boldsymbol{\Lambda_m = \left(\frac{z^2F^2}{RT}\right)(D_+ + D_-)}$$ Nernst-Einstein relation

(2) The relation between the mobility and the viscosity

$$s = \frac{ezE}{6\pi\eta a} \qquad s = uE$$

By equating two equations,

$$u = \frac{ez}{6\pi\eta a}$$

Since the Einstein relation is $u = \frac{ezD}{kT}$, the two may be equated and combined into the Stokes-Einstein relation.

$$\boldsymbol{D = \frac{kT}{6\pi\eta a}}$$

An important feature of this result is that it is independent of the charge of the diffusing species, and therefore it also applies in the limit of vanishingly small charge or neutral molecules.

Example:

Evaluate the diffusion coefficient, limiting molar conductivity, and effective hydrodynamic radius of SO_4^{2-} in water at 298 *K*.

$$\eta(\text{water}) = 0.891\times10^{-3}\, kg/m\cdot s$$

$$u(\text{SO}_4{}^{2-}) = 8.29\times10^{-4}\, cm^2/sV$$

The Diffusion Equation

Let the concentration at *x* be *c* at the time *t*. The number of particles that enter the slab per unit time is *JA*, and so the increase in concentration inside the slab on the account of the flux from the left is (see Figure 20.21)

$$\frac{\partial c}{\partial t} = \frac{JA}{Al} = \frac{J}{l}$$

The outflow flux through the window is *J'*

$$\frac{\partial c}{\partial t} = \frac{-J'A}{Al} = \frac{-J'}{l}$$

The net rate of change of concentration is therefore

$$\frac{\partial c}{\partial t} = \frac{J - J'}{l}$$

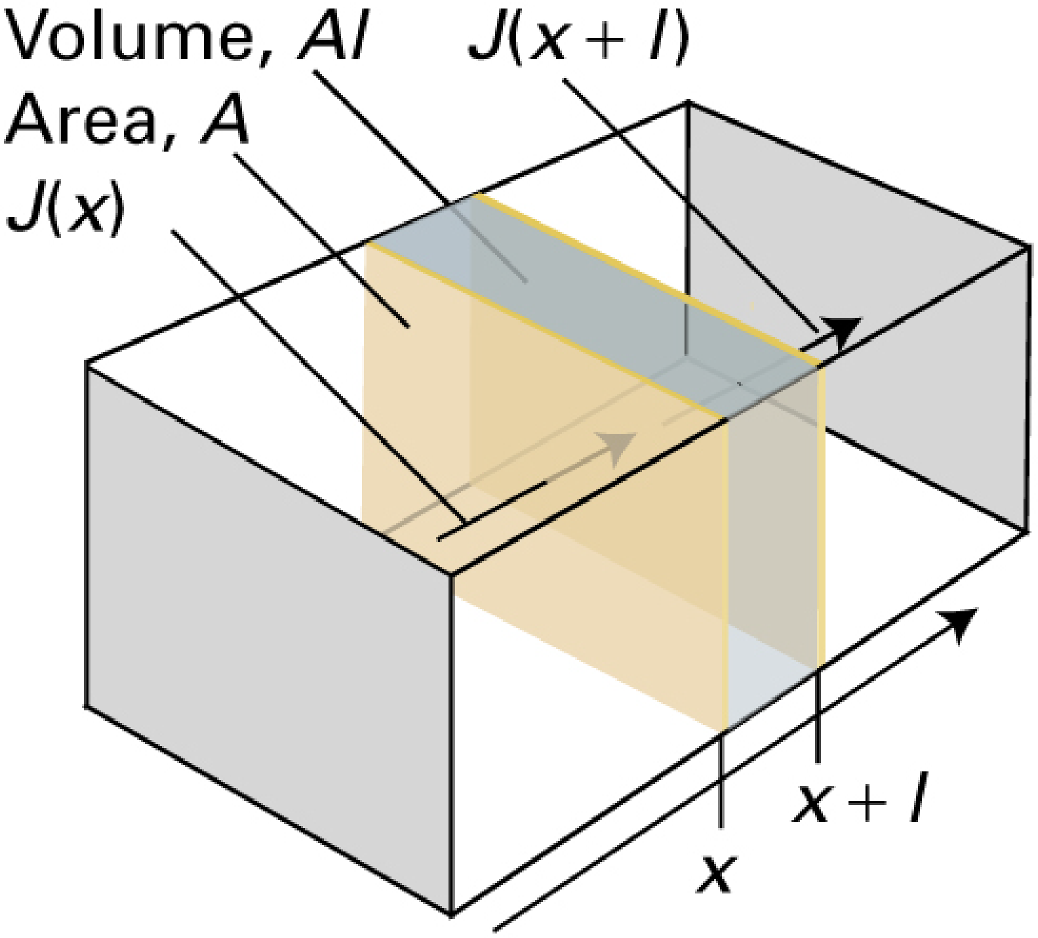


Figure 20.21

The net flux in a region is the difference between the flux entering from the region of high concentration (on the left) and the flux leaving to the region of low concentration (on the right).

$$J - J' = -D\frac{dc}{dx} + D\frac{dc'}{dx}$$

$$= -D\frac{\partial c}{\partial x} + D\frac{\partial}{\partial x}\left\{c + \left(\frac{\partial c}{\partial x}\right)l\right\}$$

$$= Dl\frac{\partial^2 c}{\partial x^2}$$

$$\frac{\partial c}{\partial t} = \frac{J - J'}{l}$$

$$\therefore \frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2}$$ Fick's 2nd law of diffusion

The rate of change of concentration is proportional to the curvature (the 2nd derivative) of the concentration dependence on the distance.

Diffusion with convection

Convection : the transport of particles arising from the motion
of a streaming fluid

If for the moment we ignore diffusion, the flux of particles through an area *A* in an interval Δt when the fluid is flowing at a velocity *v* can be calculated in the same way as before.

$$J = \frac{cAv\Delta t}{A\Delta t} = cv$$

J: the convection flux

The rate of change of concentration in a slab of thickness *l* and area *A* is, by the same argument as before, assuming that the velocity does not depend upon the position,

$$\frac{\partial c}{\partial t} = \frac{J - J'}{l} = \left\{ c - \left[c + \left(\frac{\partial c}{\partial x} \right) l \right] \right\} \frac{v}{l}$$

$$= -v \frac{\partial c}{\partial x}$$

When both diffusion and convection are of similar importance, the total change of concentration in a region is the sum of the two effects, and the generalized diffusion equation is

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2} - v\frac{\partial c}{\partial x}$$

The diffusion equation is a second-order differential equation in space and first-order in time, and therefore in order to arrive at a solution we have to specify two boundary conditions for the spatial dependence and a single initial condition for the time dependence.

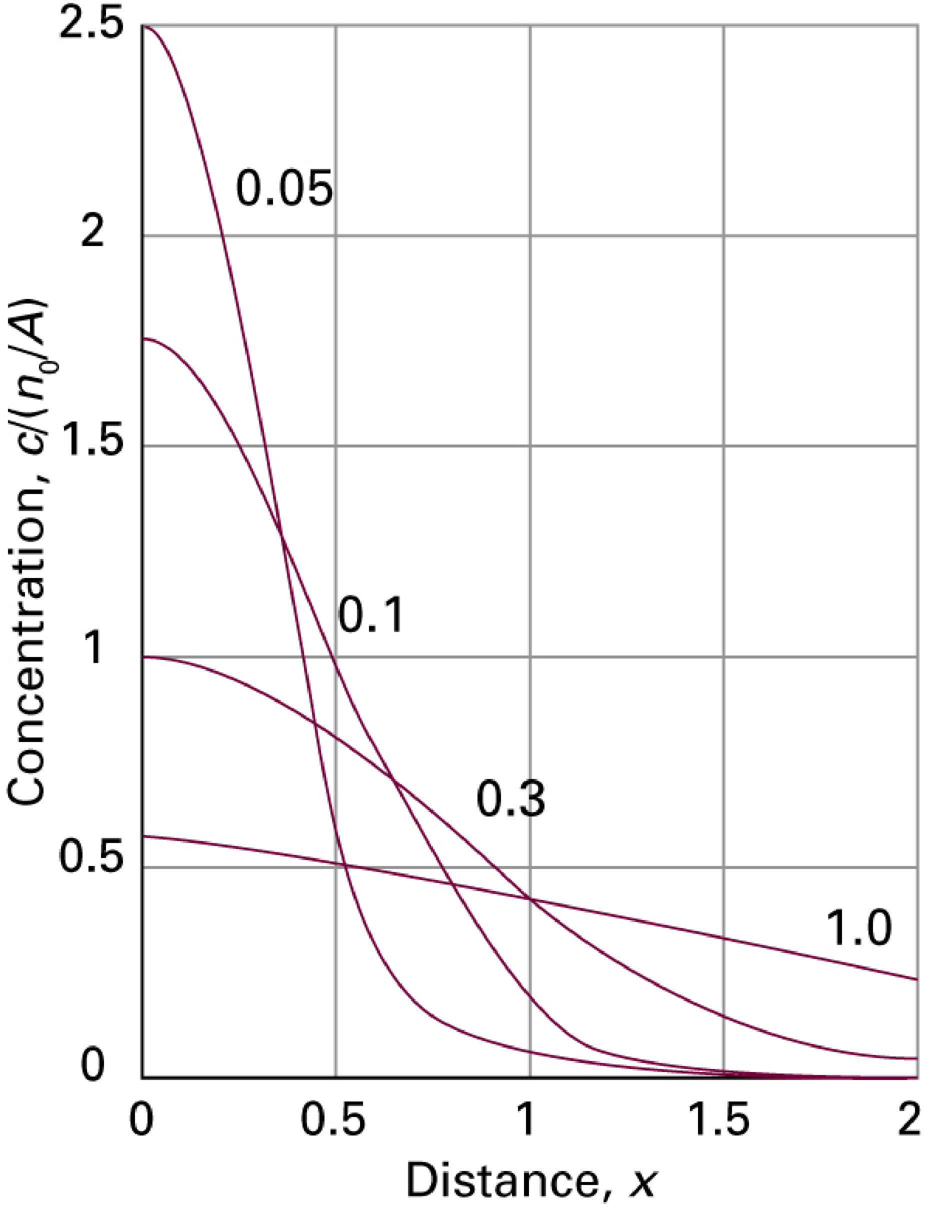
Consider the specific example of a solvent in which the solute is coated on one surface. At time goes, the initial condition is that all the N_o solute particles are concentrated on the y–z plane at x=0. The two boundary conditions are that (1) the concentration must be everywhere finite, and (2) the total amount of particles (number of moles) present must be n_o (with $n_o = N_o / N_A$) at all times.

The solution of the diffusion equation

$$c(x,t) = \frac{n_0}{A\sqrt{\pi D t}} e^{-\frac{x^2}{4Dt}}$$

Another useful solution is for the case of a localized concentration of solute in a three-dimensional solvent (a sugar lump suspended in a large flask of water). The concentration of diffused solute is spherically symmetrical, and at a radius r is

$$c(r,t) = \frac{n_0 e^{-\frac{r^2}{4Dt}}}{8(\pi D t)^{\frac{3}{2}}}$$



$$c(x,t)=\frac{n_0}{A\sqrt{\pi Dt}}e^{-\frac{x^2}{4Dt}}$$

Figure 20.22 The concentration profiles above a plane from which a solute is diffusing. The curves are plots of diffusion equation and are labelled with different values of *Dt*. The units of *Dt* and *x* are arbitrary, but are related so that Dt/x^2 is dimensionless.

The mean distance through which the solute has spread after a time *t*

The number of particles in a slab of thickness *dx* and area *A* at *x*, where the molar concentration is *c*

$$= cAN_A dx$$

The probability that any of the N_o molecules is there

$$= \frac{cAN_A dx}{N_o}$$

If the molecule is there, it has traveled a distance *x* from the origin: therefore, the mean distance traveled is

$$\langle x \rangle = \int_0^\infty \frac{xcAN_A dx}{N_o} = \frac{1}{\sqrt{\pi Dt}} \int_0^\infty x e^{-\frac{x^2}{4Dt}} dx = 2\left(\frac{Dt}{\pi}\right)^{\frac{1}{2}} \qquad c = \frac{n_0}{A\sqrt{\pi Dt}} e^{-\frac{x^2}{4Dt}}$$

The average distance varies as the square root of the time lapses.

By combining Stokes-Einstein relation and the above equation

$$\langle x\rangle = 2\left(\frac{kTt}{6\pi^2\eta a}\right)^{\frac{1}{2}} = \left(\frac{2kT}{3\pi^2\eta a}\right)^{\frac{1}{2}}\sqrt{t}$$

$$D = \frac{kT}{6\pi\eta a}$$

The root mean square distance: $\overline{x} = \sqrt{\langle x^2\rangle}$

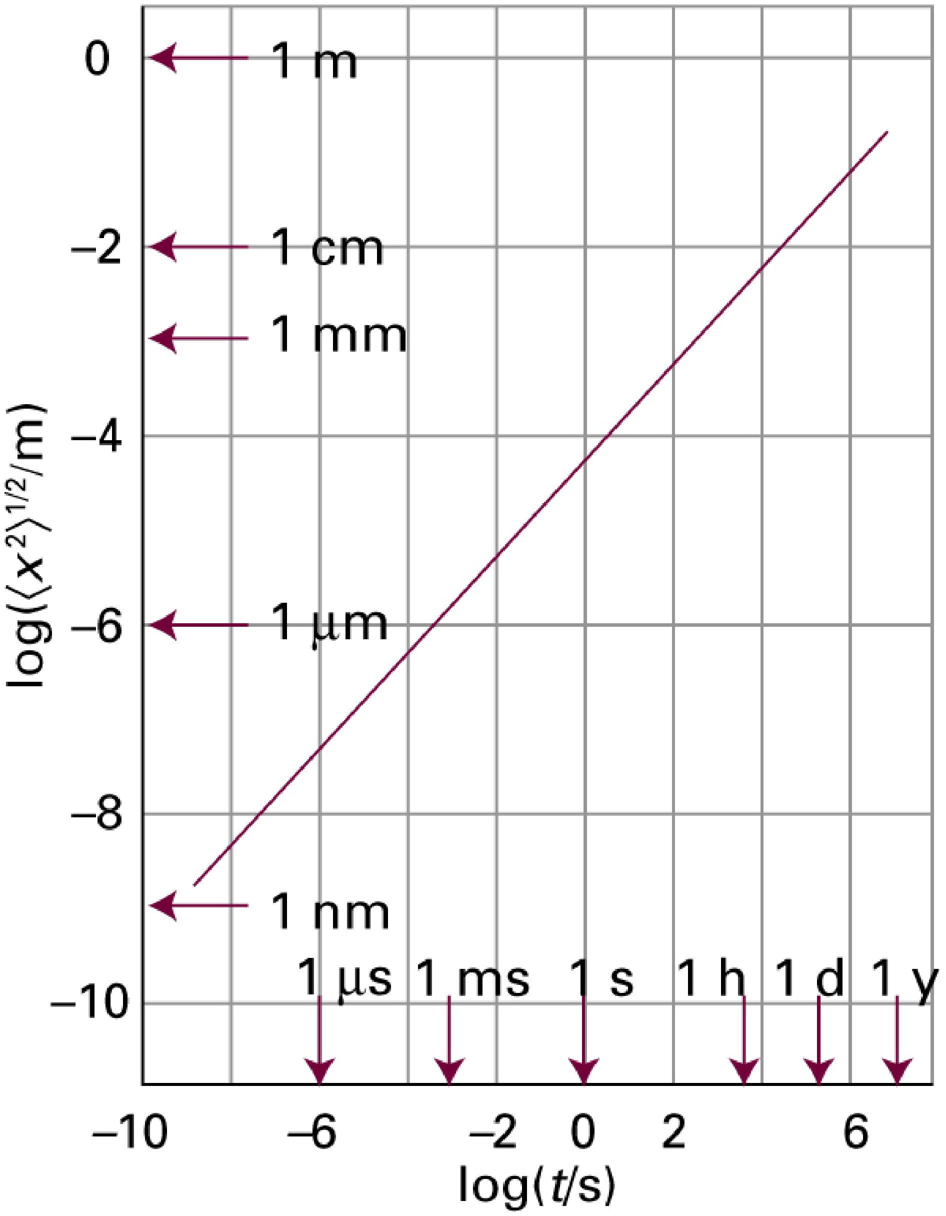
$$\boldsymbol{\overline{x} = \sqrt{\langle x^2\rangle} = \sqrt{\int_0^\infty \frac{x^2 cAN_A dx}{N_0}} = (2Dt)^{\frac{1}{2}}}$$

The number in all the slabs up to the one at $\overline{x}$

$$N(x \le \overline{x}, t) = \int_0^{\overline{x}} cAN_A dx = (0.68\cdots)(\frac{N_0}{A})$$

It follows that the proportion of molecules inside the range

$0 \le x \le \overline{x}$ is 0.68.



$$\bar{x} = \sqrt{\langle x^2 \rangle} = (2Dt)^{\frac{1}{2}}$$

Figure 20.23 The root mean square distance covered by particles with a typical diffusion coefficient $D = 5\times10^{-10}\ m^2 s^{-1}$. Note the great slowness of diffusion.

Diffusion : the statistical view

Consider a model of diffusion on the basis that the particles can jump through a distance d, and do so in a time τ. This means that the distance covered by a molecule in a time t is $\left(\frac{t}{\tau}\right)d$.

Also consider one-dimensional random walk.

Find the probability that a molecule will be formed at a distance x from the origin at a time t.

$$\frac{t}{\tau}(\text{steps}) = n$$

n_R: the number of steps to the right

n_L: the number of steps to the left

$$n = n_R + n_L$$

$$\therefore \text{ the net distance } x = n_R d - n_L d$$

The probability of being at x after n steps of length d is the probability that of the n steps, n_R occurred to the right, n_L occurred to the left, and

$$n_R - n_L = \frac{x}{d}$$

What is the total number of possibilities for left or right steps?
In other word, the total number of different journeys for a walk of n steps

$$\text{the total number} = 2^n$$

How many ways are there of taking n_R of the n steps to the right?
This is the same as the number of ways of choosing n_R objects from n possibilities, irrespective of the order:

$$\frac{n!}{n_R!(n-n_R)!}$$

We can check this in the case of 4 steps, and ask what is the total number of ways of taking 2 right steps:

2^4: possible step sequences

LLLL	LLLR	LLRR	LRRR	RRRR
	LLRL	LRLR	RLRR	
	LRLL	LRRL	RRLR	
	RLLL	RLLR	RRRL	
		RLRL		
		RRLL		

6 ways of taking 2 steps to the right and 2 steps to the left

$$\frac{4!}{2!2!} = 6$$

The probability that the particle is at the origin after 4 steps = $\frac{6}{16}$

The probability that it is at $x(=4d) = \frac{1}{16}$

Generally, the probability of being *x* after *n* steps

$$P(x) = \frac{n!}{n_R!(n-n_R)!2^n}$$

$$n = n_R + n_L, \qquad \frac{x}{d} = n_R - n_L$$

$$n_R = \frac{x}{d} + n_L = \frac{x}{d} + n - n_R$$

$$2n_R = \frac{x}{d} + n \qquad \therefore n_R = \frac{1}{2}\left(n + \frac{x}{d}\right)$$

$$\therefore P(x) = \frac{n!}{\left[\frac{1}{2}(n+s)\right]!\left[\frac{1}{2}(n-s)\right]!2^n} \quad \text{where } s = \frac{x}{d}$$

This equation becomes identical to the Gaussian distribution when we examine the limit in which the number of steps becomes very large.

Stirrling's approximation (more accurate)

$$\ln N! \approx (N+\frac{1}{2})\ln N - N + \ln(2\pi)^{\frac{1}{2}}$$

$$\ln P = \ln n! - \ln\left[\frac{1}{2}(n+s)\right]! - \ln\left[\frac{1}{2}(n-s)\right]! - n\ln 2$$

$$\ln P \cong (n+\frac{1}{2})\ln n - \cancel{n} + \ln\cancel{(2\pi)}^{\frac{1}{2}} - \left[\frac{1}{2}(n+s)+\frac{1}{2}\right]\ln\left[\frac{1}{2}(n+s)\right]$$

$$+\frac{1}{2}(\cancel{n}+\cancel{s}) - \ln\cancel{(2\pi)}^{\frac{1}{2}} - \left[\frac{1}{2}(n-s)+\frac{1}{2}\right]\ln\left[\frac{1}{2}(n-s)\right]$$

$$+\frac{1}{2}(\cancel{n}-\cancel{s}) - \ln(2\pi)^{\frac{1}{2}} - n\ln 2$$

$$= \ln\left(\frac{2}{\pi n}\right)^{\frac{1}{2}} - \frac{1}{2}(n+s+1)\ln(1+\frac{s}{n}) - \frac{1}{2}(n-s+1)\ln(1-\frac{s}{n})$$

If we allow *s*/*n* to be a small number (so that *x* must not be a great distance from the origin),

$$\ln(1+y) \approx y$$

$$\ln P \approx \ln\left(\frac{2}{\pi n}\right)^{\frac{1}{2}} - \frac{s^2}{2n}$$

$$\text{or}\quad P \approx \left(\frac{2}{\pi n}\right)^{\frac{1}{2}} \exp\left(-\frac{s^2}{2n}\right)$$

the Gaussian form

$$s \rightarrow \frac{x}{d}, \qquad n \rightarrow \frac{t}{\tau}$$

$$\boldsymbol{P(x,t) = \left(\frac{2\tau}{\pi t}\right)^{\frac{1}{2}} \exp\left(-\frac{x^2\tau}{2td^2}\right)}$$

$$\boldsymbol{c(x,t) = \frac{n_0}{A\sqrt{\pi D t}} \exp\left(-\frac{x^2}{4Dt}\right)}$$

This has precisely the form of c/n_0 as a solution of the diffusion equation. Therefore we can be confident that the diffusion can be interpreted as a result of a very large number of small steps in random directions.

Comparison of the two exponents leads to the identification,

$$\frac{2d^2}{\tau} = 4D$$

$$\therefore \boldsymbol{D} = \frac{\frac{1}{2}\boldsymbol{d}^2}{\boldsymbol{\tau}} \longleftarrow$$ Einstein-Smoluchowski equation

For if d/τ is interpreted as a mean velocity of the molecules undergoing diffusion, and the jump length d is called a mean free path and written λ, the Einstein-Smoluchowski equation reduces to $D = (1/2)\lambda\bar{c}$, which is the same as that obtained for the diffusion constant from the kinetic theory of gases.

Compare the eq.: $D = \frac{1}{3}\lambda\bar{c}$