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Molecular motion in gases

The simplest types of molecular motion

- the random motion of molecules of a perfect gas
- the largely uniform motion of ions in solution in an electric field

Transport properties of a substance

- **Diffusion**: the migration of matter down a concentration gradient
- **Thermal conduction**: the migration of energy down a temperature gradient
- **Electric conduction**: the migration of electric charge along an electrical potential gradient
- **Viscosity**: the migration of linear momentum down a velocity gradient
- **Effusion**: the emergence of a gas from a container through a small hole

21.1 The kinetic model of gases

Three assumptions of the kinetic model

1. The gas consists of molecules of mass m in endless random motion
2. The size of molecules is negligible
→ diameters of molecules \ll average distance traveled between collisions
3. The molecules interact only through brief, infrequent, and elastic collisions

(a) Pressure and molecular speeds

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

- M : molar mass ($M = mN_A$)

- c : **root mean square speed**

$$c = \langle v^2 \rangle^{1/2}$$



21.1 The kinetic model of gases

Justification 21.1 *The pressure of a gas according to the kinetic model*

When a particle of mass m and velocity v_x collides with the wall, (see Fig. 21.1)

- Linear momentum : mv_x (before collision), $-mv_x$ (after collision)
- x-component of momentum change : $2mv_x$ & collision interval : Δt
- Traveling distance : $v_x \Delta t$, volume : $A \times v_x \Delta t$
 - all the molecules within $A \times v_x \Delta t$ will strike the wall (see Fig. 21.2)
- The number density : nN_A/V , the number of molecules in $A \times v_x \Delta t$: $(nN_A/V) \times Av_x \Delta t$
- The average number of collisions : $(1/2)nN_A Av_x \Delta t$ ^{1/V}

$$\begin{aligned} \text{Momentum change} &= \frac{nN_A Av_x \Delta t}{2V} \times 2mv_x \\ &= \frac{nmAN_A v_x^2 \Delta t}{V} = \frac{nMAv_x^2 \Delta t}{V} \end{aligned}$$

$$\text{Rate of change of momentum} = \frac{nMAv_x^2}{V}$$

Rate of change of momentum
= force (by Newton's second law of motion)

$$\text{Pressure} = \frac{nMv_x^2}{V} \quad p = \frac{nM \langle v_x^2 \rangle}{V}$$

(p : average pressure, $\langle v_x \rangle$: average velocity)

By random motion of molecules,

$$c = \left(\langle v_x^2 \rangle + \langle v_y^2 \rangle + \langle v_z^2 \rangle \right)^{1/2} = \left(3 \langle v_x^2 \rangle \right)^{1/2}$$

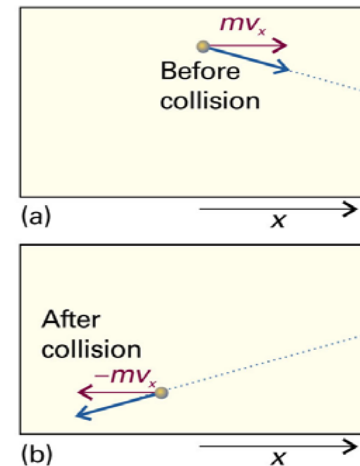


Fig. 21.1 The pressure of a gas arises from the impact of its molecules on the walls. In an elastic collision of a molecule with a wall perpendicular to the x -axis, the x -component of velocity is reversed but the y - and z -components are unchanged.

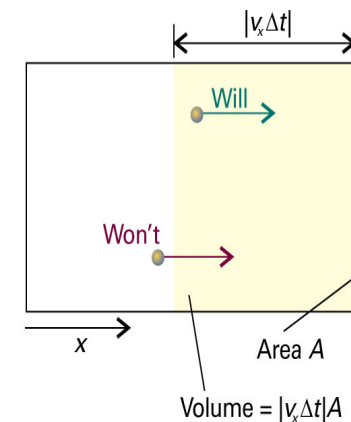


Fig. 21.2 A molecule will reach the wall on the right within an interval Δt if it is within a distance $v_x \Delta t$ of the wall and travelling to the right.



21.1 The kinetic model of gases

For a perfect gas at constant T , $pV = \text{constant}$ (by Boyle's law) $= nRT$

$$pV = \frac{1}{3} nMc^2 = nRT \quad \longrightarrow \quad c = \left(\frac{3RT}{M} \right)^{1/2} \quad c \propto (T)^{1/2}, \quad c \propto \left(\frac{1}{M} \right)^{1/2}$$

- $T \uparrow \rightarrow c \uparrow$
- heavy molecules travel more slowly than light molecules

In an actual gas,

- c span a wide range \rightarrow collisions redistribute c continually
- the fraction of molecules at the speed range from v to $v + dv$

$f(v)dv \rightarrow \mathbf{f(v)}$: **distribution of speeds**

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

Maxwell distribution of speeds
(driven by J.C. Maxwell)

- the range of speeds broads as $T \uparrow$ (see Fig. 21.3)
- lighter molecules have a broader distribution of speeds than heavier molecules

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

: area under the graph of f as a function of v (see Fig. 21.4)

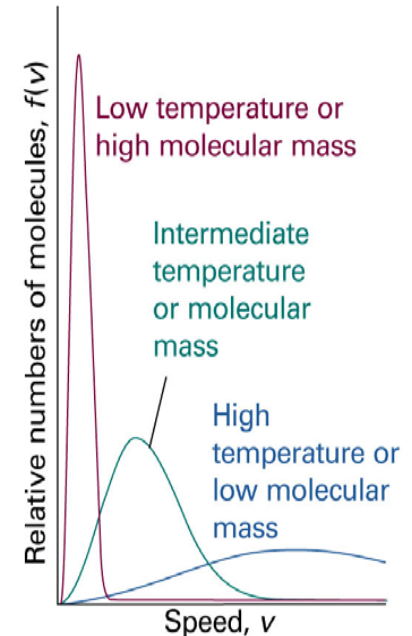


Fig. 21.3 The distribution of molecular speeds with temperature and molar mass. Note that the most probable speed (corresponding to the peak of the distribution) increases with temperature and with decreasing molar mass, and simultaneously the distribution becomes broader.



21.1 The kinetic model of gases

Justification 21.2 *The Maxwell distribution of speeds*

Using the Boltzmann distribution and $E = \frac{1}{2}mv_x^2 + \frac{1}{2}mv_y^2 + \frac{1}{2}mv_z^2$

$$f = Ke^{-E/kT} = Ke^{-(\frac{1}{2}mv_x^2 + \frac{1}{2}mv_y^2 + \frac{1}{2}mv_z^2)/kT}$$

$$= Ke^{-mv_x^2/2kT} e^{-mv_y^2/2kT} e^{-mv_z^2/2kT}$$

Since $f = f(v_x)f(v_y)f(v_z)$,

$$f(v_x) = K^{1/3}e^{-mv_x^2/2kT} \rightarrow \text{in the range } -\infty < v_x < \infty, \quad \int_{-\infty}^{\infty} f(v_x)dv_x = 1$$

$$1 = K^{1/3} \int_{-\infty}^{\infty} e^{-mv_x^2/2kT} dv_x = K^{1/3} \left(\frac{2\pi kT}{m} \right)^{1/2}$$

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

$$\rightarrow f(v_x)f(v_y)f(v_z)dv_xdv_ydv_z = \left(\frac{M}{2\pi RT} \right)^{3/2} e^{-Mv_x^2/2RT} dv_xdv_ydv_z$$

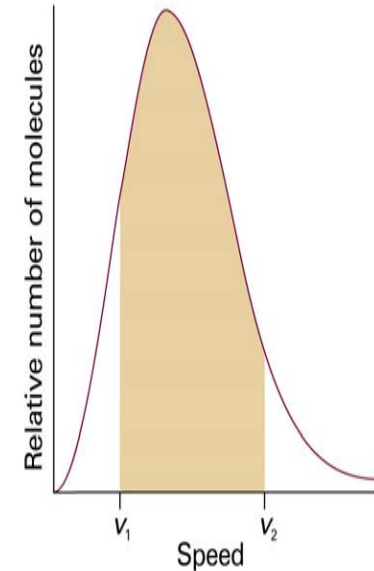


Fig. 21.4 To calculate the probability that a molecule will have a speed in the range v_1 to v_2 , we integrate the distribution between those two limits; the integral is equal to the area of the curve between the limits, as shown shaded here.



21.1 The kinetic model of gases

$f(v)dv$ in the range of v to $v+dv$
 : forming a spherical shell of
 radius v and thickness dv (see Fig. 21.5)

(see Example 21.1)

$$\bar{c} = \int_0^{\infty} vf(v)dv = 4\pi \left(\frac{M}{2\pi RT} \right)^{3/2} \int_0^{\infty} v^3 e^{-Mv^2/2RT} dv$$

$$\therefore \bar{c} = \left(\frac{8RT}{\pi M} \right)^{1/2} \quad \bar{c} : \text{the mean speed of the molecules in a gas}$$

At $f'(v) = 0$, (see Fig 21.6)

$$c^* = \left(\frac{2RT}{M} \right)^{1/2} \quad c^* : \text{the most probable speed}$$

$$\bar{c}_{rel} = 2^{1/2} \bar{c} \quad \bar{c}_{rel} : \text{the relative mean speed}$$

(see Fig 21.7)

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

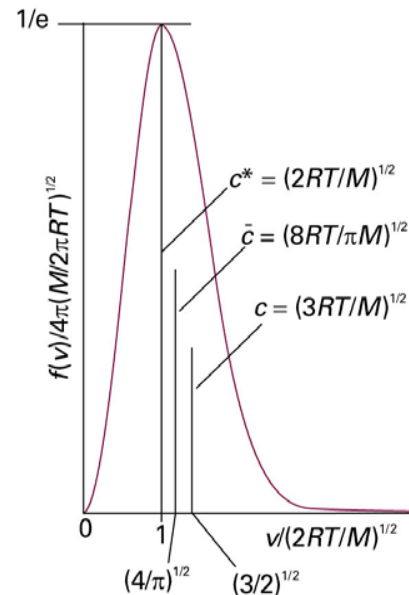


Fig. 21.6 A summary of the conclusions that can be deduced from the Maxwell distribution for molecules of molar mass M at a temperature T : c^* is the most probable speed, \bar{c} is the mean speed, and c is the root mean square speed.

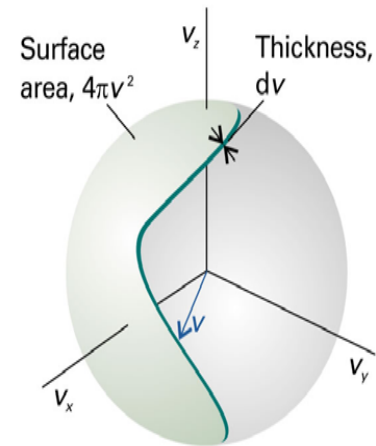


Fig. 21.5 To evaluate the probability that a molecule has a speed in the range v to $v + dv$, we evaluate the total probability that the molecule will have a speed that is anywhere on the surface of a sphere of radius $v = (v_x^2 + v_y^2 + v_z^2)^{1/2}$ by summing the probabilities that it is in a volume element $dv_x dv_y dv_z$ at a distance v from the origin.

21.1 The kinetic model of gases

The concept of the relative mean speed

In case of two dissimilar molecules of masses m_A and m_B ,

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

- k : Boltzmann's constant ($k=R/N_A$)
- μ : reduced mass

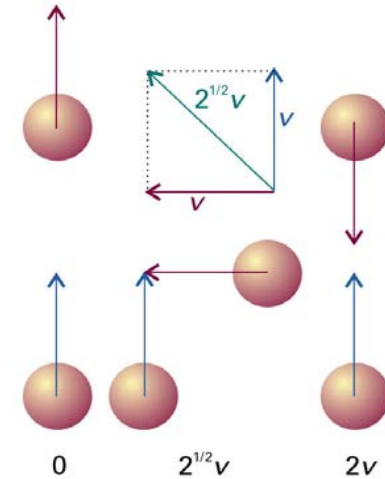


Fig. 21.7 A simplified version of the argument to show that the mean relative speed of molecules in a gas is related to the mean speed. When the molecules are moving in the same direction, the mean relative speed is zero; it is $2v$ when the molecules are approaching each other. A typical mean direction of approach is from the side, and the mean speed of approach is then $2^{1/2}v$. The last direction of approach is the most characteristic, so the mean speed of approach can be expected to be about $2^{1/2}v$. This value is confirmed by more detailed calculation.

21.1 The kinetic model of gases

(b) The collision frequency

The collision frequency (z): The number of collisions made by one molecule during the time interval when N molecules exist in a volume V

$$z = \sigma \bar{c}_{\text{rel}} \mathcal{N}, \text{ where } \sigma \text{ is the collision cross-section}$$

In terms of the pressure,
$$z = \frac{\sigma \bar{c}_{\text{rel}} p}{kT}$$

Justification 21.3 Using the kinetic model to calculate the collision frequency

One mobile molecule travels through the gas with a mean relative speed \bar{c}_{rel} for Δt (see Fig. 21.9)

- the volume of collision tube (area \times length) : $\sigma \bar{c}_{\text{rel}} \Delta t$
- the number of stationary molecules : the number density ($\mathcal{N} = N/V$) \times the volume = $\mathcal{N} \sigma \bar{c}_{\text{rel}} \Delta t$
- the number of collisions divided by the time interval : $z = \mathcal{N} \sigma \bar{c}_{\text{rel}}$
- in terms of pressure (using perfect gas equation)

$$\frac{N}{V} = \frac{nN_A}{V} = \frac{pN_A}{RT} = \frac{p}{kT} \rightarrow z = \frac{\sigma \bar{c}_{\text{rel}} p}{kT}$$

Synoptic table 21.1* Collision cross-sections

	σ/nm^2
C_6H_6	0.88
CO_2	0.52
He	0.21
N_2	0.43

* More values are given in the Data section.

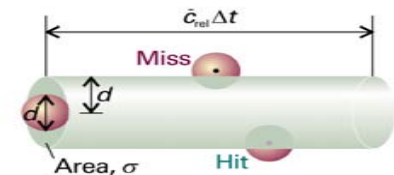


Fig. 21.9 In an interval Δt , a molecule of diameter d sweeps out a tube of radius d and length $\bar{c}_{\text{rel}} \Delta t$. As it does so it encounters other molecules with centres that lie within the tube, and each such encounter counts as one collision. In reality, the tube is not straight, but 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.



21.1 The kinetic model of gases

(c) The mean free path

The mean free path (λ) : the average distance a molecule travels between collisions

$$\lambda = \frac{c}{z} \quad \lambda = \frac{kT}{2^{1/2} \sigma p} \quad - \text{If a molecule collides with frequency } (z), \text{ it spends a time } 1/z \text{ in free flight between collisions, and therefore travels a distance } \lambda$$

- In a sample of constant volume, $T/p = \text{constant}$ as $T \uparrow$

→ the mean free path is independent of T in a constant V

→ the distance between collisions is determined by the number of molecules (not the speed)

21.2 Collisions with walls and surfaces

The collision flux (Z_w) : the number of collisions with the area in a given time interval divided by the area and the duration of the interval

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

(When $p=100 \text{ kPa}$ and $T=300\text{K}$, $Z_w \approx 3 \times 10^{23} \text{ cm}^{-1} \text{ s}^{-1}$)

Justification 21.4 The collision flux

When a molecule strikes the wall within Δt , area = A , distance = $v_x \Delta t$

$$\text{Number of collisions} = \mathcal{N} A \Delta t \int_0^\infty v_x f(v_x) dx \quad Z_w = \mathcal{N} \int_0^\infty v_x f(v_x) dx \quad (\because \text{collision flux} = \text{number of collisions} / A \cdot \Delta t)$$

$$\int_0^\infty v_x f(v_x) dv_x = \left(\frac{m}{2\pi kT} \right)^{1/2} \int_0^\infty v_x e^{-mv_x^2/2kT} dv_x = \left(\frac{kT}{2\pi m} \right)^{1/2} \therefore Z_w = \mathcal{N} \left(\frac{kT}{2\pi m} \right)^{1/2} = \frac{p}{(2\pi mkT)^{1/2}} = \frac{1}{4} \bar{c} \mathcal{N}$$

$$(\because \mathcal{N} = nN_A/V = p/kT)$$



21.3 The rate of effusion

Graham's law of effusion

: the rate of effusion is inversely proportional to the square root of the molar mass

- The mean speed of molecules $\propto 1/M^{1/2} \rightarrow$ the rate of striking the area of hole $\propto 1/M^{1/2}$
- When a gas at p and T is separated from a vacuum by a small hole,

$$\text{Rate of effusion} = Z_w A_0 = \frac{pA_0}{(2\pi mkT)^{1/2}} = \frac{pA_0 N_A}{(2\pi MRT)^{1/2}}$$

$$(\because A_0 = \text{area of a hole}, R = N_A k, M = mN_A)$$

- \rightarrow The basis of the **Knudsen method** for the determination of the (very low) vapour pressures of liquids and solids
(**Knudsen method** : The rate of escaping molecules through a small hole can be used to calculate vapour pressure of a liquid or solid)
- \rightarrow If the vapour pressure of the sample is p , and it is enclosed in a cavity with a small hole, then the rate of loss of mass from the container is proportional to p .



21.4 Transport properties of a perfect gas

(a) The phenomenological equations

Flux (J) : the quantity of migration passing through a given area in a given time interval divided by the area and the duration of the interval

- matter flux (molecules/m²s) and energy flux (joules/m²s)
- the flux of matter diffusing parallel to the z-axis of a container is found to be proportional to the first derivative of the concentration

$$: J(\text{matter}) \propto \frac{d\mathcal{N}}{dz} \quad (J [\text{atoms/m}^2\cdot\text{s}]) \quad J(\text{energy}) \propto \frac{dT}{dz} \quad (J [\text{Joules/m}^2\cdot\text{s}])$$

- if the concentration varies steeply with position, then diffusion will be fast
- no net flux if the concentration is uniform ($d\mathcal{N}/dz=0$)

→ **Fick's first law of diffusion**

$$J(\text{matter}) = -D \frac{d\mathcal{N}}{dz} \quad J(\text{energy}) = -\kappa \frac{dT}{dz}$$

- Because matter flows down a concentration gradient, from high concentration to low concentration, J is positive if $d\mathcal{N}/dz$ is negative. (see Fig. 21.10) → writing $(-D)$

- D : the diffusion coefficient [$\text{m}^2\cdot\text{s}^{-1}$],
- κ : the coefficient of thermal conductivity [$\text{JK}^{-1}\cdot\text{m}^{-1}\cdot\text{s}^{-1}$]

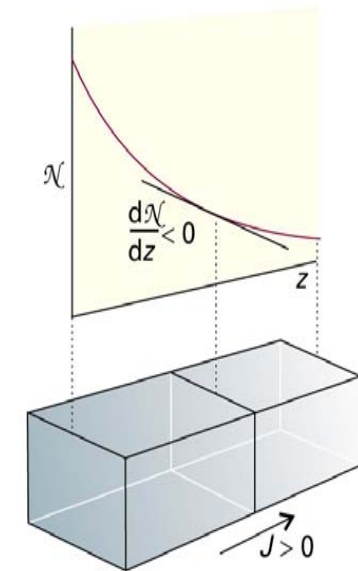


Fig. 21.10 The flux of particles down a concentration gradient. Fick's first law states that the flux of matter (the number of particles passing through an imaginary window in a given interval divided by the area of the window and the duration of the interval) is proportional to the density gradient at that point.



21.4 Transport properties of a perfect gas

The connection between the flux of momentum and the viscosity

- **Newtonian flow** (can be imagined as occurring by a series of layers moving past one another - see Fig. 21.11)

→ the layer next to the wall of the vessel is stationary, and the velocity of successive layers varies linearly with distance z , from the wall

→ retarding effect

- a layer is retarded by molecules from slowly moving layer with a low momentum in the x -direction

: the viscosity \propto the flux of x -component in the z -direction

$$J(x - \text{component of momentum}) = -\eta \frac{dv_x}{dz}$$

- η : the coefficient of viscosity [kg/m·s]

: reported in poise(P), 1P=10⁻¹kgm⁻¹s⁻¹ (see Table 21.2)

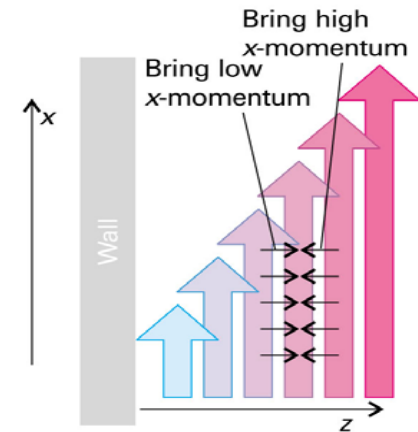


Fig. 21.11 The viscosity of a fluid arises from the transport of linear momentum. In this illustration the fluid is undergoing laminar flow, and particles bring their initial momentum when they enter a new layer. If they arrive with high x -component of momentum they accelerate the layer; if with low x -component of momentum they retard the layer.

Synoptic table 21.2* Transport properties of gases at 1 atm

	κ /(J K ⁻¹ m ⁻¹ s ⁻¹)	η /(μ P) [†]	
	273 K	273 K	293 K
Ar	0.0163	210	223
CO ₂	0.0145	136	147
He	0.1442	187	196
N ₂	0.0240	166	176

* More values are given in the *Data section*.
[†] 1 μ P = 10⁻⁷ kg m⁻¹ s⁻¹.



21.4 Transport properties of a perfect gas

(b) The transport parameters

The value of the transport coefficient of a perfect gas

$$D = \frac{1}{3} \lambda \bar{c} \quad (\text{see Further information 21.1 and Table 21.3})$$

- As $p \uparrow$, the mean free path $\lambda \downarrow$
: $D \downarrow \rightarrow p \uparrow$ (the gas molecules diffuse more slowly)
- As $T \uparrow$, the mean speed, \uparrow
: $D \uparrow \rightarrow T \uparrow$ (the molecules in a hot sample diffuse more quickly than those in a cool sample)
- As the collision cross-section (σ) \downarrow , $\lambda \uparrow$
: D (small sample) $>$ D (large sample)

Table 21.3 Transport properties of perfect gases

Property	Transported quantity	Simple kinetic theory	Units
Diffusion	Matter	$D = \frac{1}{3} \lambda \bar{c}$	$\text{m}^2 \text{s}^{-1}$
Thermal conductivity	Energy	$\kappa = \frac{1}{3} \lambda \bar{c} C_{V,m} [A]$ $= \frac{\bar{c} C_{V,m}}{3\sqrt{2} \sigma N_A}$	$\text{J K}^{-1} \text{m}^{-1} \text{s}^{-1}$
Viscosity	Linear momentum	$\eta = \frac{1}{3} \lambda \bar{c} m \mathcal{N}$ $= \frac{m \bar{c}}{3\sqrt{2} \sigma}$	$\text{kg m}^{-1} \text{s}^{-1}$



21.4 Transport properties of a perfect gas

$$\kappa = \frac{1}{3} \lambda \bar{c} C_{V,M} [A], \text{ where } C_{V,M} \text{ is the molar heat capacity at constant volume.}$$

1. $\lambda \propto$ pressure, and $\lambda \propto \frac{1}{\text{The molar concentration of the gas}}$

”Thermal conductivity is independent of the pressure”

However, at very low pressure, $\kappa \propto p$, because λ exceeds the dimensions of the apparatus.

2. The thermal conductivity is greater for gases with a high heat capacity.

$$\eta = \frac{1}{3} M \lambda \bar{c} [A]$$

[A] : The molar concentration of the gas molecules
M : Molar mass

1. $\lambda \propto \frac{1}{p}$, $[A] \propto p$, $\eta \propto \bar{c}$, η is independent of the pressure
2. $\bar{c} \propto T^{1/2}$, $\eta \propto T^{1/2}$, the viscosity of a gas increases with temperature



21.4 Transport properties of a perfect gas

Two techniques for measuring viscosities of gases.

1. Depends on the rate of damping of the torsional oscillations of a disc.

(The half life of the decay of the oscillation depends on the viscosity and design of the apparatus.)

2. Poiseuille's formula. (for the rate of flow of a fluid through a tube of radius, r.)

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

Where, V : the volume flowing

p_1, p_2 : the pressure at each end of the tube

l : the length of tube.

p_0 : the pressure at which the volume is measured.



Molecular motion in liquids

21.5 Experimental results

The method measuring the motion of molecules in liquids

- NMR or ESR
- Inelastic neutron scattering

Viscosity measurement (see Table 21.4)

- For a molecule in a liquid to escape from neighbours, at least a min. energy is required

- The probability that a molecule has an energy E_a , probability \propto

$$e^{E_a / RT}$$

-The coefficient of viscosity (η) is inversely proportional to the mobility of the particles :

- The viscosity should decrease sharply with increasing temperature
- a variation of η in small temperature ranges (see Fig. 21.13)

$$\eta \propto e^{E_a / RT}$$

Synoptic table 21.4* Viscosities of liquids at 298 K

	$\eta / (10^{-3} \text{ kg m}^{-1} \text{ s}^{-1})$
Benzene	0.601
Mercury	1.55
Propane	0.224
Water†	0.891

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

† The viscosity of water corresponds to 0.891 cP.

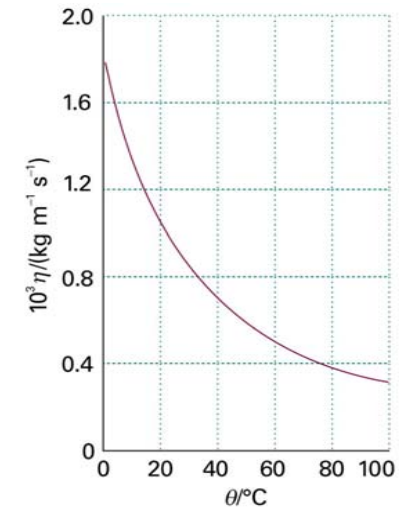


Fig. 21.13 The experimental temperature dependence of the viscosity of water. As the temperature is increased, more molecules are able to escape from the potential wells provided by their neighbours, and so the liquid becomes more fluid. A plot of $\ln \eta$ against $1/T$ is a straight line (over a small range) with positive slope.



21.6 The conductivities of electrolyte solutions

(a) Conductance and conductivity

The fundamental measurement of the motion of ions

- **Resistance** (R) : ohms [Ω]
- **Conductance** ($G = 1/R$) : *mho* [Ω^{-1}] or siemens [$1\text{S} = 1\Omega^{-1} = 1\text{CV}^{-1}\text{s}^{-1}$]

$$G = \frac{\kappa A}{l} \quad - \kappa : \text{the conductivity [S/m]}$$

$$\Lambda_m = \frac{\kappa}{c} \quad - \Lambda_m : \text{the molar conductivity [S}\cdot\text{m}^2\text{/mol]}$$

- c : the molar concentration of the added electrolyte

The variation of Λ_m with the concentration

- the number of ions in the solution might not be proportional to the concentration of the electrolyte
- strong interaction of ions

The concentration dependence of molar conductivities (two classes)

- strong electrolyte : Λ_m depends only slightly on the molar concentration
- weak electrolyte : Λ_m falls sharply to low values as the concentration increases (see Fig. 21.14)

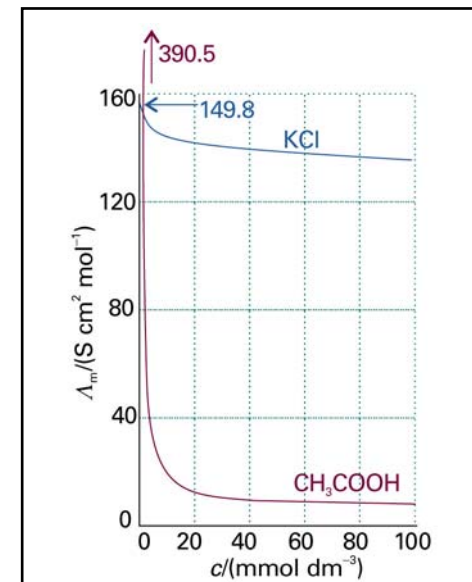


Fig. 21.14 The concentration dependence of the molar conductivities of (a) a typical strong electrolyte (aqueous potassium chloride) and (b) a typical weak electrolyte (aqueous acetic acid).



21.6 The conductivities of electrolyte solutions

(b) Strong electrolytes

: the substances that are virtually fully ionized in solution (ionic solids and strong acids)

At low concentrations,

$$A_m = A_m^{\circ} - \mathcal{K}c^{1/2} \quad : \text{Kohlrausch's law}$$

- A_m° : the limiting molar conductivity (in the zero concentration)
: the sum of contributions from its individual ions

$$A_m^{\circ} = \nu_+ \lambda_+ + \nu_- \lambda_- \quad : \text{Kohlrausch's law of the independent migrations of ions}$$

- λ_+ : the limiting molar conductivity of the cations (See Table 21.5)
- λ_- : the limiting molar conductivity of the anions
- ν_+ and ν_- : the numbers of cations and anions per formula unit of electrolyte (ex/ $\nu_+=\nu_-=1$ for HCl and $\nu_+=1, \nu_-=2$ for MgCl_2)

Synoptic table 21.5* Limiting ionic conductivities in water at 298 K

	$\lambda / (\text{mS m}^2 \text{ mol}^{-1})$		$\lambda / (\text{mS m}^2 \text{ mol}^{-1})$
H^+	34.96	OH^-	19.91
Na^+	5.01	Cl^-	7.63
K^+	7.35	Br^-	7.81
Zn^{2+}	10.56	SO_4^{2-}	16.00

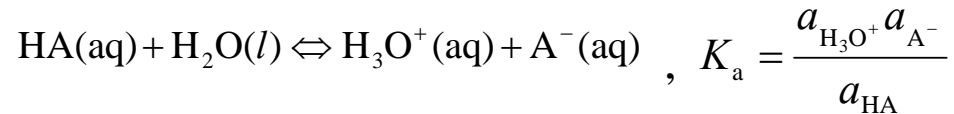
* More values are given in the *Data section*.



21.6 The conductivities of electrolyte solutions

(c) Weak electrolytes

: The substances that are not fully ionized in solution



- The conductivity depends on the numbers of ions in the solution

For the acid HA at a molar concentration at equilibrium,

$$[\text{H}_3\text{O}^+] = \alpha c \quad [\text{A}^-] = \alpha c \quad [\text{HA}] = (1 - \alpha)c \quad - \alpha : \text{the degree of ionization}$$

If activity coefficients are ignored,

$$K_a = \frac{\alpha^2 c}{1 - \alpha} \quad \longrightarrow \quad \alpha = \frac{K_a}{2c} \left\{ \left(1 + \frac{4c}{K_a} \right)^{1/2} - 1 \right\}$$

Using $\Lambda_m = \alpha \Lambda_m^\circ$ and $\frac{1}{\alpha} = 1 + \frac{\alpha c}{K_a}$

$$\frac{1}{\Lambda_m} = \frac{1}{\Lambda_m^\circ} + \frac{\Lambda_m c}{K_a (\Lambda_m^\circ)^2}$$

Ostwald's dilution law

- If $1/\Lambda_m$ is plotted against $c\Lambda_m$, then the intercept at $c = 0$ will be $1/\Lambda_m^\circ$ (see Fig.21.15)

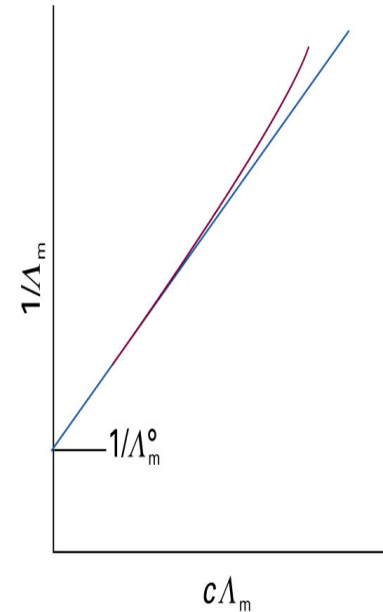


Fig. 21.15 The graph used to determine the limiting value of the molar conductivity of a solution by extrapolation to zero concentration.



21.7 The mobilities of ions

(a) The drift speed

When the potential difference between two electrodes a distance l apart is $\Delta\phi$, the uniform electric field

$$: \mathcal{E} = \frac{\Delta\phi}{l}$$

In such a field, an ion of charge ze experiences a force of magnitude

$$\mathcal{F} = ze\mathcal{E} = \frac{ze\Delta\phi}{l}$$

- anions and cations accelerated by the electric field experience a frictional retarding force ($\mathcal{F}_{\text{fric}}$)
- application of the Stokes formula (in eqn 19.12)

$$\mathcal{F}_{\text{fric}} \propto s \rightarrow \mathcal{F}_{\text{fric}} = fs \quad f = 6\pi\eta a \quad (s : \text{speed, } f : \text{the frictional coefficient, } a : \text{radius of sphere})$$

- the force by electric field and the frictional force are in opposite directions
- the ions quickly reach a terminal speed

$$ze\mathcal{E} = fs \rightarrow s = \frac{ze\mathcal{E}}{f} \quad \text{the drift speed}$$

- $s \propto$ the strength of the applied field $\rightarrow s = u\mathcal{E}$

$$s = \frac{ze\mathcal{E}}{f} = u\mathcal{E} \rightarrow \therefore u = \frac{ze}{f} = \frac{ze}{6\pi\eta a} \quad (u : \text{the mobility of ion})$$

(see Table 21.6)

Synoptic table 21.6* Ionic mobilities in water at 298 K

	$u/(10^{-8} \text{ m}^2 \text{ s}^{-1} \text{ V}^{-1})$		$u/(10^{-8} \text{ m}^2 \text{ s}^{-1} \text{ V}^{-1})$
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.



21.7 The mobilities of ions

(b) Mobility and conductivity

The relation between an ion's mobility and molar conductivity :

$$\lambda = zuF \quad - F : \text{the Faraday constant } (F = N_A e)$$

Justification 21.5 *The relation between ionic mobility and molar conductivity*

Consider a solution of a fully dissociated strong electrolyte at a molar concentration c (see Fig. 21.17)

- the molar concentration = vc & the number of density = vcN_A

→ the number density of ions = $s\Delta tAvcN_A$

$$J(\text{ions}) = \frac{s\Delta tAvcN_A}{A\Delta t} = svcN_A \quad \rightarrow \text{each ion carries a charge } ze$$

$$\therefore J(\text{charge}) = zsvcN_A = zsvcF$$

Because $s = uE$, $J(\text{charge}) = zuvcFE \rightarrow$ The current (I)

$$\therefore I = JA = zuvcFEA$$

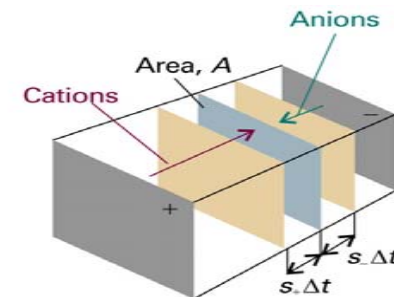


Fig. 21.17 In the calculation of the current, all the cations within a distance $s_+ \Delta t$ (that is, those in the volume $s_+ A \Delta t$) will pass through the area A . The anions in the corresponding volume the other side of the window will also contribute to the current similarly.

21.7 The mobilities of ions

$$\text{By } E = \Delta\phi/l, \quad I = \frac{zuvcFA\Delta\phi}{l} \quad \rightarrow \text{ by Ohm's law and } G = \kappa A/l, \quad I = \frac{\Delta\phi}{R} = G\Delta\phi = \frac{\kappa A\Delta\phi}{l}$$

$$I = \frac{zuvcFA\Delta\phi}{l} = \frac{\kappa A\Delta\phi}{l} \rightarrow k = zuvcF \rightarrow \text{both sides } \div vc : \quad \therefore \lambda = zuF \quad \text{-eq 21.44}$$

For the solution itself in the limit of zero concentration, $\Lambda_m^{\circ} = (z_+ u_+ v_+ + z_- u_- v_-)F$

For a symmetrical z:z electrolyte, $\Lambda_m^{\circ} = z(u_+ + u_-)F$

(c) Transport numbers

The fraction of total current carried by the ions of a specified type

$$: t_{\pm} = \frac{I_{\pm}}{I} \quad (t_{\pm} : \text{the transport number})$$

- I_{\pm} : the current by the cation (I_+) or anion (I_-)
 - I : the total current through the solution $\rightarrow t_+ + t_- = 1$

For the limit of zero concentration of the electrolyte solution, (using $I = \frac{zuvcFA\Delta\phi}{l}$)

$$t_{\pm}^{\circ} = \frac{z_{\pm} v_{\pm} u_{\pm}}{z_+ v_+ u_+ + z_- v_- u_-} \quad t_{\pm}^{\circ} = \frac{u_{\pm}}{u_+ + u_-} \quad (\because z_+ v_+ = z_- v_-)$$



21.7 The mobilities of ions

Because the ionic conductivities are related to the mobilities by $\lambda = zuF$,

$$t_{\pm}^{\circ} = \frac{v_{\pm}\lambda_{\pm}}{v_{+}\lambda_{+} + v_{-}\lambda_{-}} = \frac{v_{\pm}\lambda_{\pm}}{A_m^{\circ}}$$

For each type of ion,

$$v_{\pm}\lambda_{\pm} = t_{\pm}^{\circ} A_m^{\circ}$$

The method for measuring transport numbers
: **the moving boundary method**

In Fig. 21.18

a sharp boundary between the two solutions

- MX : the leading solution
- NX (denser solution) : the indicator solution
 - the mobility : M ions > N ions
- if M ions diffuse into the lower solution, they will be pulled upwards
 - the boundary moves from AB to CD
- The relation between the distance (l) moved by the boundary in the time Δt for which a current I is passed for Δt : $t_{+} = \frac{z_{+}c\lambda F}{I\Delta t}$

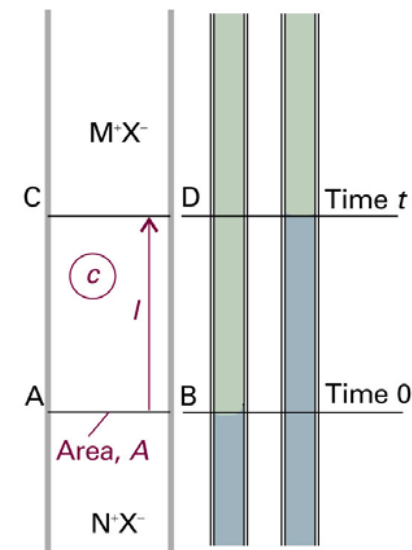


Fig. 21.18 In the moving boundary method for the measurement of transport numbers the distance moved by the boundary is observed as a current is passed. All the M ions in the volume between AB and CD must have passed through CD if the boundary moves from AB to CD. One procedure is to add bromothymol blue indicator to a slightly alkaline solution of the ion of interest and to use a cadmium electrode at the lower end of the vertical tube. The electrode produces Cd^{2+} ions, which are slow moving and slightly acidic (the hydrated ion is a Brønsted acid), and the boundary is revealed by the colour change of the indicator.



21.8 Conductivities and ion-ion interactions

The $c^{1/2}$ dependence of Kohlrausch's law by the ionic atmosphere

- **relaxation effect** (see Fig. 21.19)
 - : In a electric field, two charges are in opposite directions
 - retardation of the moving ion
- **electrophoretic effect**
 - : By the ionic atmosphere, a viscous drag of the moving ion \uparrow (the mobility \downarrow)

To obtain quantitative expressions,

- **Debye-Huckel-Onsager theory** (see Fig. 21.20 and Table 21.7)

$$\mathcal{K} = A + B\Lambda_m^0$$

$$A = \frac{z^2 e F^2}{3\pi\eta} \left(\frac{2}{\epsilon RT} \right)^{1/2} \quad B = \frac{qz^3 e F}{24\pi\epsilon RT} \left(\frac{2}{\epsilon RT} \right)^{1/2}$$

Synoptic table 21.7* Debye-Hückel-Onsager coefficients for (1,1)-electrolytes at 298 K

Solvent	$A/(\text{mS m}^2 \text{ mol}^{-1}/(\text{mol dm}^{-3})^{1/2})$	$B/(\text{mol dm}^{-3})^{-1/2}$
Methanol	15.61	0.923
Propanone	32.8	1.63
Water	6.02	0.229

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

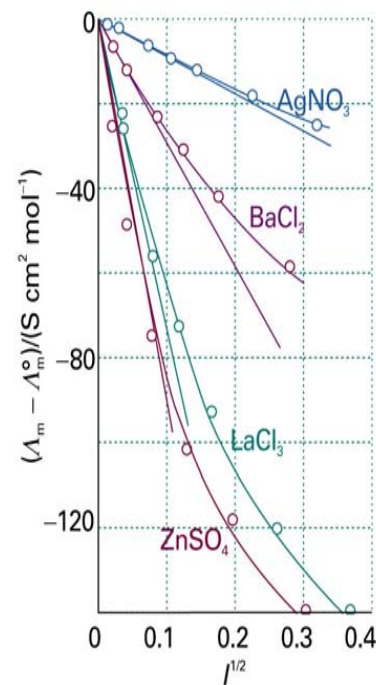


Fig. 21.20 The dependence of molar conductivities on the square root of the ionic strength, and comparison (straight lines) with the dependence predicted by the Debye-Hückel-Onsager theory.

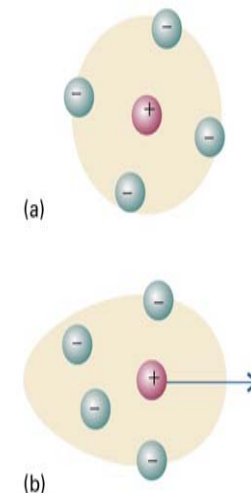


Fig. 21.19 (a) In the absence of an applied field, the ionic atmosphere is spherically symmetric, but (b) when a field is present it is distorted and the centres of negative and positive charge no longer coincide. The attraction between the opposite charges retards the motion of the central ion.



Diffusion

21.9 The thermodynamic view

At constant p and T , the maximum non-expansion work that can be done per mole when a substance moves from a location μ to a location $\mu + d\mu$,

$$dw = d\mu = \left(\frac{\partial \mu}{\partial x} \right)_{p,T} dx$$

General work against an opposing force : $dw = -\mathcal{F}dx$

By comparing these two expressions, the slope of μ can be interpreted as an effective force per mole of molecules

$$\mathcal{F} = - \left(\frac{\partial \mu}{\partial x} \right)_{p,T} \quad : \text{Thermodynamic force}$$

It may represent the spontaneous tendency of the molecules to disperse as a consequence of the 2nd Law and the hunt for maximum entropy.

(a) The thermodynamic force of a concentration gradient

In a solution, $\mu = \mu^\circ + RT \ln a$

If the solution is not uniform, the activity depends on the position : $\mathcal{F} = -RT \left(\frac{\partial \ln a}{\partial x} \right)_{p,T}$

For an ideal solution ($a = c$) : $\mathcal{F} = -\frac{RT}{c} \left(\frac{\partial c}{\partial x} \right)_{p,T}$



21.9 The thermodynamic view

(b) Fick's first law of diffusion $J \propto dc/dx$

Suppose the flux of diffusing particles is driven by a thermodynamic force due to a concentration gradient. The particles reaches a steady **drift speed** (s) when **the thermodynamic force F** is matched by the viscous drag. Then, $s \propto F$

However, the particle flux (J) is proportional to the drift speed ($J \propto s$), and the thermodynamic force is proportional to the concentration gradient ($F \propto dc/dx$)

$$\therefore J \propto s, s \propto F, \text{ and } F \propto dc/dx \rightarrow J \propto dc/dx$$

(c) The Einstein relation

Fick's first law : $J = -D \frac{dc}{dx}$ Because the flux is related to the drift speed, $J = sC$

$$\text{Therefore, } sC = -D \frac{dc}{dx} \rightarrow \text{Using } F = -\frac{RT}{c} \left(\frac{\partial c}{\partial x} \right)_{p,T} \quad s = -\frac{D}{c} \frac{dc}{dx} = \frac{DF}{RT}$$

When an ion in solution has a drift speed $s = uE$, a force ezE from electric field of strength E

$$F = N_A ezE = zFE$$

$$uE = \frac{zFE}{RT}$$

$$u = \frac{zFD}{RT}$$

$$\therefore D = \frac{uRT}{zF}$$

: **Einstein relation**

(relation between D and u (ionic mobility))



21.9 The thermodynamic view

(d) The Nernst-Einstein equation

The Einstein relation provides a link between the molar conductivity (λ) of an electrolyte and the diffusion coefficients (D) of its ions.

$$\text{For each ion, } \lambda = zuF = \frac{z^2 DF^2}{RT}$$

From $\Lambda_m^0 = \nu_+ \lambda_+ + \nu_- \lambda_-$, the limiting molar conductivity,

$$\Lambda_m^0 = (\nu_+ z_+^2 D_+ + \nu_- z_-^2 D_-) \frac{F^2}{RT} \quad \text{Nernst-Einstein equation}$$

(e) The Stokes-Einstein equation

By combining $u = \frac{ze}{f}$ with $D = \frac{uRT}{zF}$ by using $eR/F = k$,

$$D = \frac{kT}{f} \quad \text{Stokes-Einstein equation}$$

By Stokes's law for the frictional force, $f = 6\pi\eta a$, Then $D = \frac{kT}{6\pi\eta a}$

Since Stokes-Einstein equation makes no reference to the charge of the diffusing species, it applies to neutral molecules \rightarrow estimation of D for electrically neutral molecules by measuring viscosity (see Table 21.8)

Synoptic table 21.8* Diffusion coefficients at 298 K

	$D/(10^{-9} \text{ m}^2 \text{ s}^{-1})$
H ⁺ in water	9.31
I ₂ in hexane	4.05
Na ⁺ in water	1.33
Sucrose in water	0.522

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



21.9 The thermodynamic view

Walden's rule : product $\eta\Lambda_m$ is very approximately constant for the same ions in different solvents

$\Lambda_m \propto D$ and $D \propto 1/\eta$, so, $\Lambda_m \propto 1/\eta$

However, the role of solvation (*i.e.*, different solvents solvate the same ions to different extents) limits its applicability since hydrodynamic radius a & viscosity η change with the solvent.

21.10 The diffusion equation

Time-dependent diffusion process

ex) a metal bar heated at the end

the concentration distribution in a solvent to which solute is added

The rate of concentration changes at a point to the spatial variation of the concentration at that point

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} \quad \text{Fick's second law}$$

Justification 21.6 *The diffusion equation*

When the particles enter the slab, (see Fig. 21.24 in the next page.)

the amount in the infinitesimal interval dt : $JAdt$



21.10 The diffusion equation

$$\text{from ①, } \frac{\partial c}{\partial t} = \frac{J \Delta t}{A \Delta t} = \frac{J}{l} \quad \text{from ②, } \frac{\partial c}{\partial t} = -\frac{J' \Delta t}{A \Delta t} = -\frac{J'}{l}$$

$$\text{The net rate of change of concentration : } \frac{\partial c}{\partial t} = \frac{J - J'}{l}$$

Using Fick's first law,

$$J - J' = -D \frac{\partial c}{\partial x} + D \frac{\partial c'}{\partial x} = -D \frac{\partial c}{\partial x} + D \frac{\partial}{\partial x} \left\{ c + \left(\frac{\partial c}{\partial x} \right) l \right\} = D l \frac{\partial^2 c}{\partial x^2}$$

$$\therefore \frac{\partial c}{\partial t} = \frac{J - J'}{l} = \frac{D l (\partial^2 c / \partial x^2)}{l} = D \frac{\partial^2 c}{\partial x^2}$$

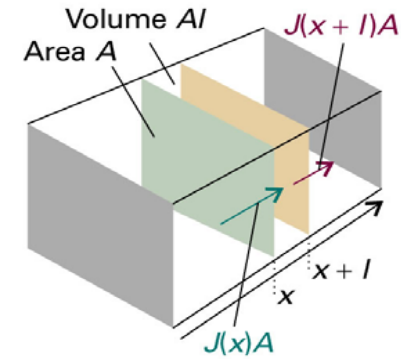


Fig. 21.24 The net flux in a region is the difference between the flux entering from the region of high concentration (on the left) and the flux leaving to the region of low concentration (on the right).

(a) Diffusion with convection

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

When the flux of particles flow through an area A in an interval Δt

(the velocity of the flowing fluid : v)

$$J = \frac{c A v \Delta t}{A \Delta t} = c v \quad (\mathbf{J : the convective flux})$$

$$\text{In a slab of thickness } l \text{ and area } A, \quad \frac{\partial c}{\partial t} = \frac{J - J'}{l} = \left\{ c - \left[c + \frac{\partial c}{\partial x} \right] l \right\} \frac{v}{l} = -v \frac{\partial c}{\partial x}$$



21.10 The diffusion equation

When both diffusion and convection occur,

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

This expression is important in chemistry because of the possibility that the concentrations of particles may change as a result of reaction

(b) Solutions of the diffusion equation

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

- a second-order differential eqn with respect to space
- a first-order differential eqn with respect to time

Consider a solvent in which the solute is initially coated on one surface of the container

- Initial condition at $t_0 = 0$, all N_0 particles are concentrated on yz -plane at $x = 0$
- The requirements for the two boundary conditions
 - 1) the concentration must everywhere be finite
 - 2) the total amount of particles is n_0 ($n_0 = N_0/N_A$) at all times
 - the flux = 0 at the top and bottom surfaces

$$c(x, t) = \frac{n_0}{A(\pi Dt)^{1/2}} e^{-x^2/4Dt}$$

the concentration spreads and tends to uniformity (see Fig. 21.26)

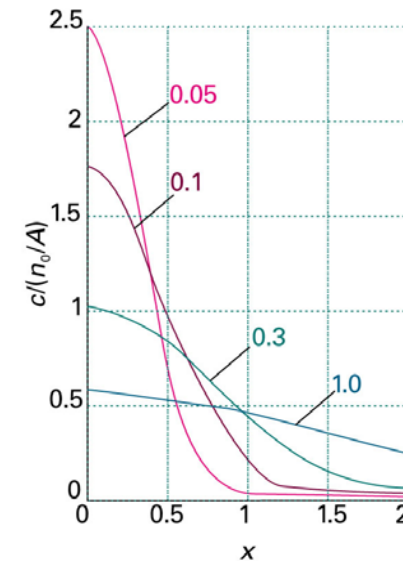


Fig. 21.26 The concentration profiles above a plane from which a solute is diffusing. The curves are plots of eqn 21.72 and are labelled with different values of Dt . The units of Dt and x are arbitrary, but are related so that Dt/x^2 is dimensionless. For example, if x is in metres, Dt would be in metres²; so, for $D = 10^{-9} \text{ m}^2 \text{ s}^{-1}$, $Dt = 0.1 \text{ m}^2$ corresponds to $t = 10^8 \text{ s}$.



21.10 The diffusion equation

For a localized concentration of solute in a three-dimensional solvent, the concentration of diffused solute is spherically symmetrical and at a radius r is

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

(c) The measurement of diffusion coefficients

(1) Capillary technique

- a capillary tube, open at one end and containing a solution, is immersed in a well stirred larger quantity of solvent → monitoring the change of c

(2) Diaphragm technique

- the diffusion occurs through the capillary pores of a sintered glass diaphragm separating the well-stirred solution → monitoring the change of c

(3) The dynamic light scattering technique (in Section 19.3)

(4) NMR (Nuclear Magnetic Resonance)



21.11 Diffusion probabilities

The net distance traveled on average by particles in a time t

- The number of particles in a slab of thickness dx and area A at x : $cAN_A dx$

- The probability that any of the $N_0 = n_0 N_A$ particles : $cAN_A dx / N_0$

- The mean distance : $\langle x \rangle = \int_0^\infty \frac{xcAN_A}{N_0} dx = \frac{1}{(\pi Dt)^{1/2}} \int_0^\infty xe^{-x^2/4Dt} dx = \frac{1}{(\pi Dt)^{1/2}} \frac{4Dt}{2} = 2 \left(\frac{Dt}{\pi} \right)^{1/2}$

- The root mean square distance traveled in the same time :

$$\begin{aligned} \langle x^2 \rangle &= \int_0^\infty \frac{x^2 cAN_A}{N_0} dx = \frac{1}{(\pi Dt)^{1/2}} \int_0^\infty x^2 e^{-x^2/4Dt} dx \\ &= \frac{1}{(\pi Dt)^{1/2}} \times \sqrt{\pi} (2 \times 4Dt)^{3/2} = 2Dt \end{aligned}$$

$$\therefore \langle x \rangle = 2 \left(\frac{Dt}{\pi} \right)^{1/2} \quad \therefore \langle x^2 \rangle^{1/2} = (2Dt)^{1/2} \quad (\text{see Fig. 21.28})$$

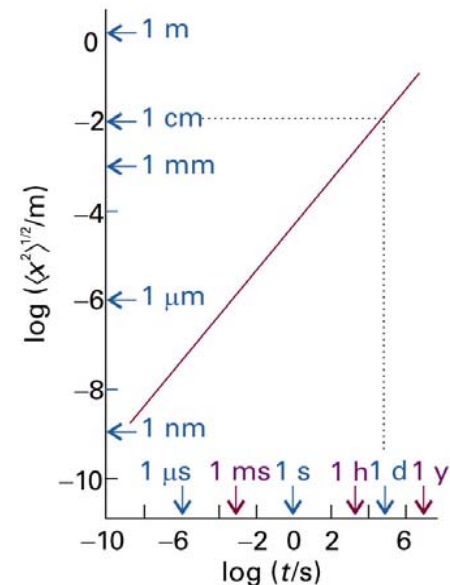


Fig. 21.28 The root mean square distance covered by particles with $D = 5 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$. Note the great slowness of diffusion.

- Fig. 21.28 shows how long it takes for diffusion to increase the net distance traveled on average to about 1cm in an unstirred solution



21.12 The statistical view

Assuming the particles to travel only along a straight line (the x -axis), and for each step to be through the same distance (λ) : **the one-dimensional random walk**

$$P = \left(\frac{2\tau}{\pi t} \right)^{1/2} e^{-x^2\tau/2t\lambda^2}$$

the probability of a particle being at a distance x from the origin after a time t

Justification 21.7 *The one-dimensional random network*

The number of ways of a one-dimensional random walk :

$$W = \frac{N!}{N_L!N_R!} = \frac{N!}{\left\{ \frac{1}{2}(N+n) \right\}! \left\{ \frac{1}{2}(N-n) \right\}!}$$

The probability of the net distance walked being $n\lambda$ is,

$$P = \frac{\text{number of paths with } N_R \text{ steps to the right}}{\text{total number of steps}} = \frac{W}{2^N} = \frac{N!}{\left\{ \frac{1}{2}(N+n) \right\}! \left\{ \frac{1}{2}(N-n) \right\}! 2^N}$$

By Stirling's approximation,

$$\ln x! \approx \ln(2\pi)^{1/2} + \left(x + \frac{1}{2}\right) \ln x - x$$



21.12 The statistical view

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

$$\text{Using } \ln(1 \pm x) \approx \pm x - \frac{1}{2} x^2 \quad \ln P \approx \ln \left(\frac{2}{\pi N} \right)^{1/2} - \frac{n^2}{2N} \quad \therefore P = \left(\frac{2\tau}{\pi t} \right)^{1/2} e^{-x^2 \tau / 2t \lambda^2}$$

$$\text{By two expressions } c(x, t) = \frac{n_0}{A(\pi D t)^{1/2}} e^{-x^2 / 4Dt} \quad \text{and} \quad P = \left(\frac{2\tau}{\pi t} \right)^{1/2} e^{-x^2 \tau / 2t \lambda^2}$$

The diffusion can be interpreted as the outcome of a large number of steps in random directions.

The relation of D to the step length λ and the rate at which the jumps occur :

$$e^{-x^2 / 4Dt} = e^{-x^2 \tau / 2t \lambda^2} \rightarrow \boxed{D = \frac{\lambda^2}{2\tau}} \quad \text{Einstein-Smoluchowski equation}$$

The central connection between the microscopic details of particle motion and the macroscopic parameters relating to diffusion

If we interpret λ/τ as the mean speed (c) and λ as a mean free path,

$$D = \frac{\lambda^2}{2\tau} = \frac{1}{2} c \lambda \quad \text{the diffusion of a perfect gas is a random walk with an average step size equal to the mean free path}$$

