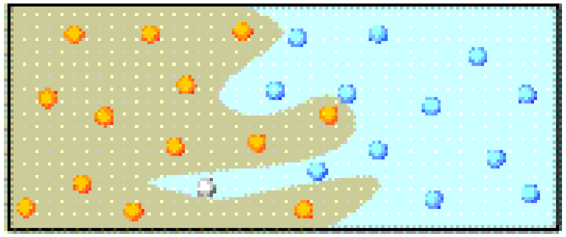
Chapter 19. Molecules in Motion

Transport Properties of a Substance

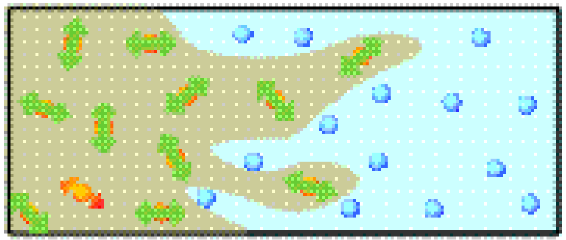
1. **Diffusion**: Migration of matter **down** **a concentration gradient**
   (IQ 50)

2. **Thermal Conduction**: Migration of energy down a temperature gradient
3. **Electrical Conduction**: Migration of electric charge along a potential gradient (**electronic + ionic**)
4. **Viscosity**: Migration of linear momentum down a velocity gradient

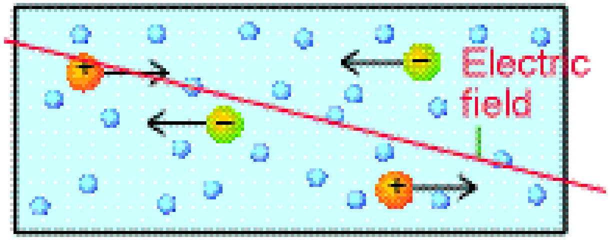
Transport Properties


(a)

Diffusion: Spreading of one species into another. **Atoms, Ions, Molecules, Ionized Molecules, & Electrons**

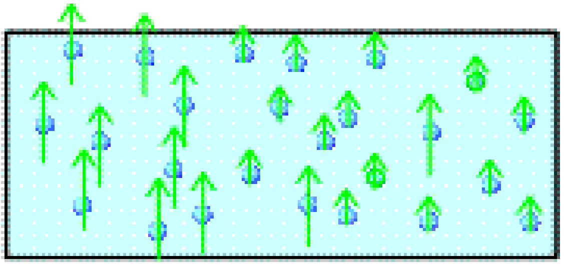

(b)

Thermal Conduction: Molecules with different energies of **thermal motion** (represented by the arrows) spread into each other's region. **Lattice & Electrons**



(c)

Electrical Conduction: **Ions + Electrons** migrate under the influence of an electric field


(d)

Viscosity: Molecules with different linear momenta (represented by the arrows) migrate.

19A.1. Transport Properties

- **Diffusion**
- **Thermal Conductivity**
- **Electrical Conductivity**
- **Viscosity**
- **Effusion**

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

- amount of property passing through **unit area per unit time**

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

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

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

↓

z-direction

Fick’s First Law of Diffusion

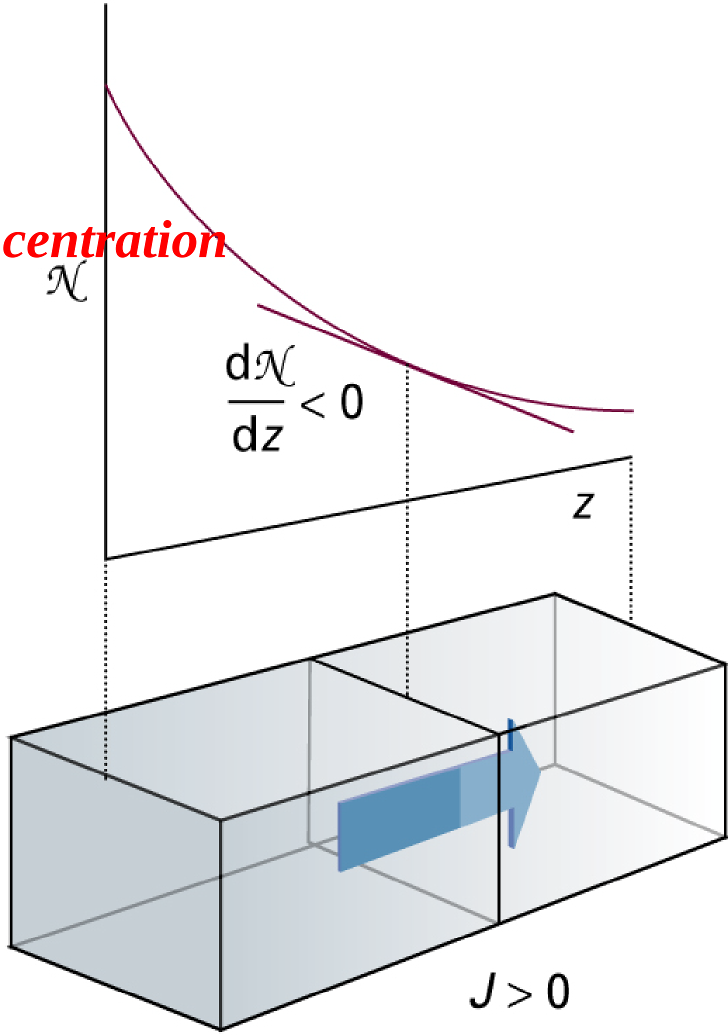
$$J_z(matter) = -D\left(\frac{d\tilde{N}}{dz}\right)$$

diffusion coefficient

The mass flow occurs down a concentration gradient. ***(IQ 50)***

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

the coefficient of thermal conductivity



concentration

Figure 19A.1

The Connection between the Flux of Momentum and Viscosity

- Particles are continuously moving between the laminars, and bringing with them the *x*-component of momentum.

- A laminar 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 laminars tend towards a uniform velocity, and we interpret **the retarding effect** of the slow layers on the fast ones as the fluid's viscosity.

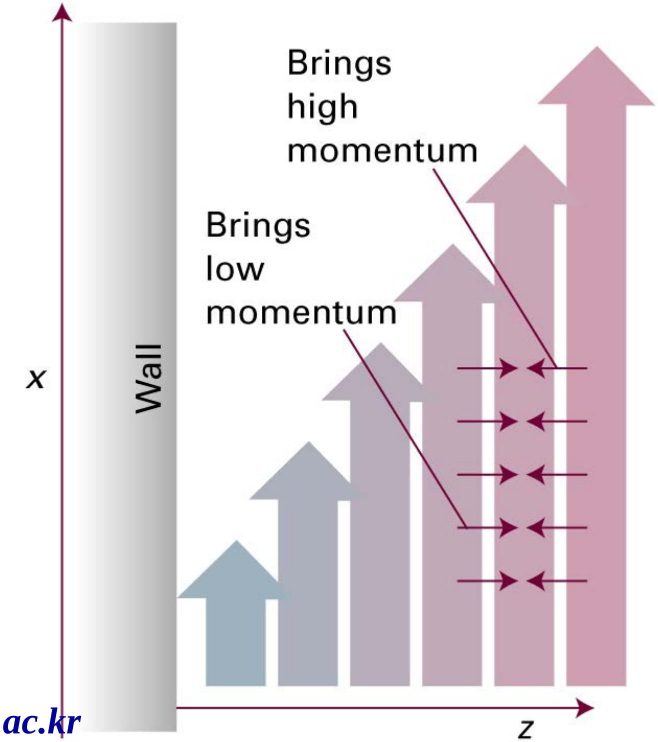


Figure 19A.2

Viscosity = Stickiness

- The effect depends on the transfer of *x*-momentum into the lamina of interest.
- So, the viscosity depends on the flux of *x*-momentum in the *z*-direction.
- This flux depends on the gradient of the *x*-component of velocity of the fluid:

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

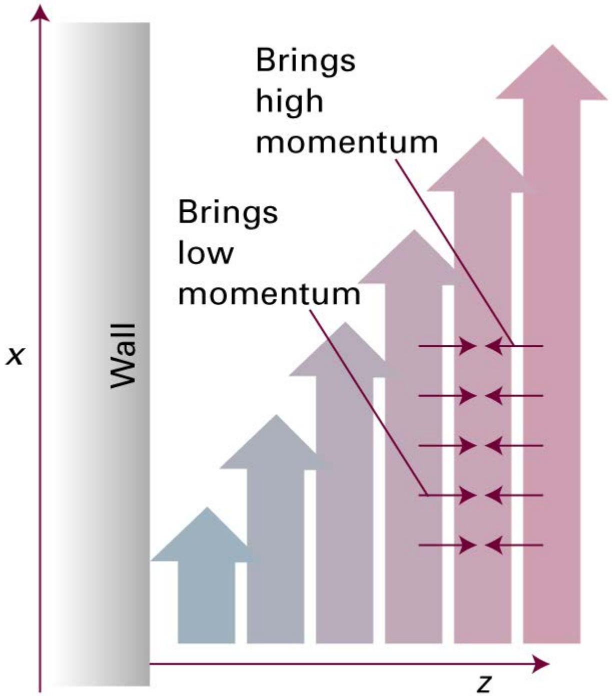
momentum flux

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

Linear-Momentum Viscosity

(19A.5)

[*η*] = kg / m s = poise



19A.2. The Kinetic Model of Gases – Collision Flux

Three Assumptions:

1. The gas consists of molecules of mass *m* in **ceaseless (elastic) random motion**.
2. The size of 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.

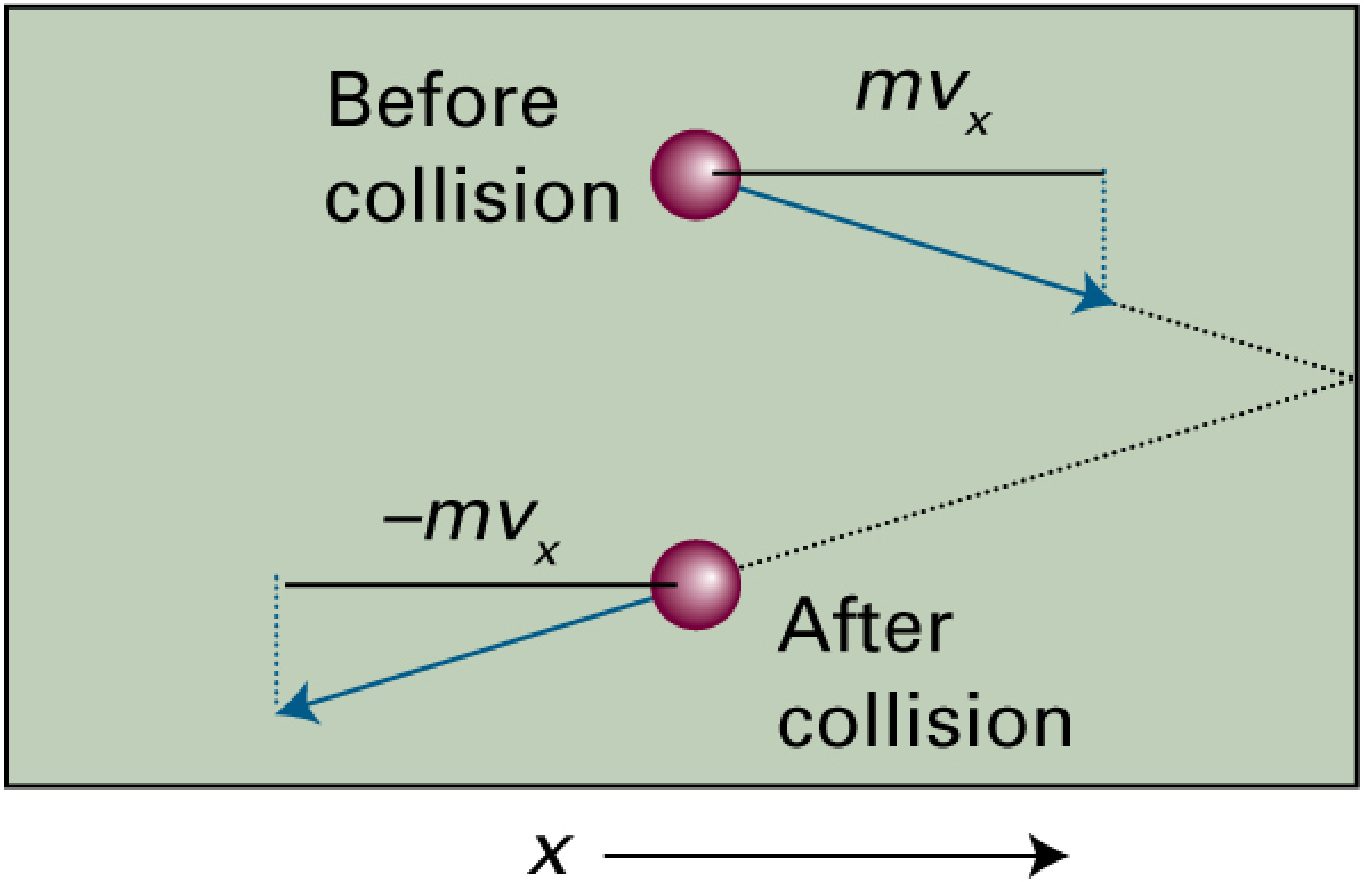
The **collision frequency**, z: the number of collisions made by a single particle per time

$z^{-1} = \tau$: Collision Time

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 $|2mv_x|$.



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.

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Collisions with Walls and Surfaces

The number of collisions in a time interval Δt (IQ 1,000)

$\cong$

The number of molecules able to reach in that time

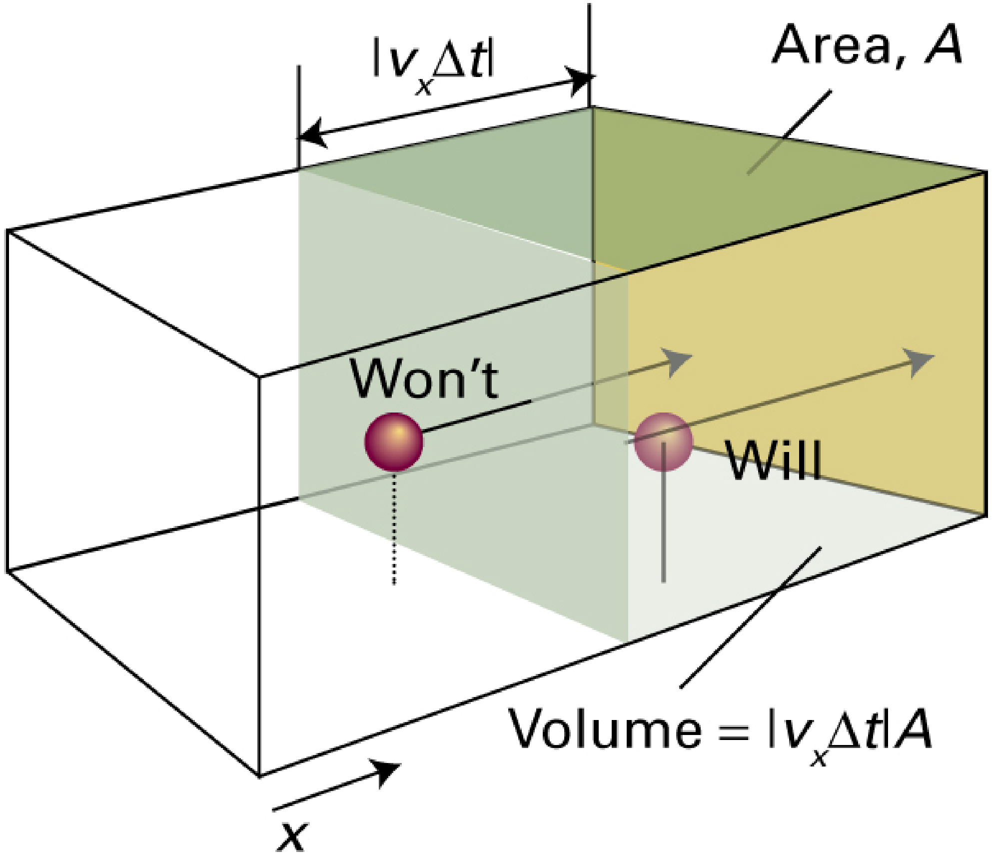


Figure 19A.3
A molecule will reach the wall on the right within an interval Δt if it is within a distance $v_x\Delta t$ of the wall and traveling to the right.

Collisions with Walls and Surfaces

flux J

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 the molecules in the volume $A v_x \Delta t$, with velocities in the right direction, will strike the wall in the interval Δt.

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

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

Chap. 1

where $f(v_x) = \left(\dfrac{m}{2\pi kT} \right)^{\frac{1}{2}} \exp\left(-\dfrac{m v_x^2}{2kT} \right)$

1-D

Maxwell-Boltzmann distribution

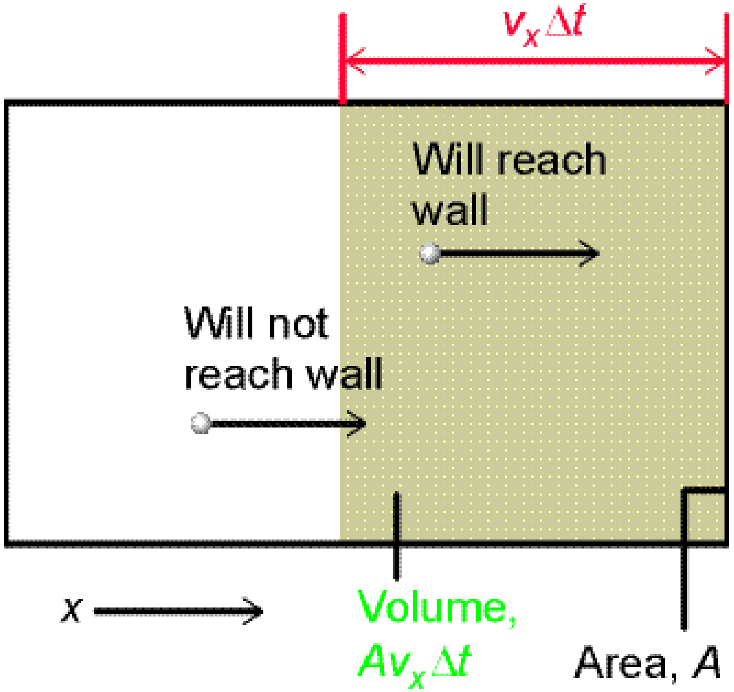
Total number of collisions = $\widetilde{N} A \Delta t \left(\frac{kT}{2\pi m}\right)^{\frac{1}{2}}$

∴ The number of collisions per unit time per unit area

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

$$= \frac{p}{(2\pi mkT)^{\frac{1}{2}}} \qquad \textbf{(19A.6)}$$

$$q^{t} = \frac{V}{\Lambda^{3}}, \qquad \Lambda = \frac{h}{(2\pi mkT)^{1/2}}$$



flux *J*

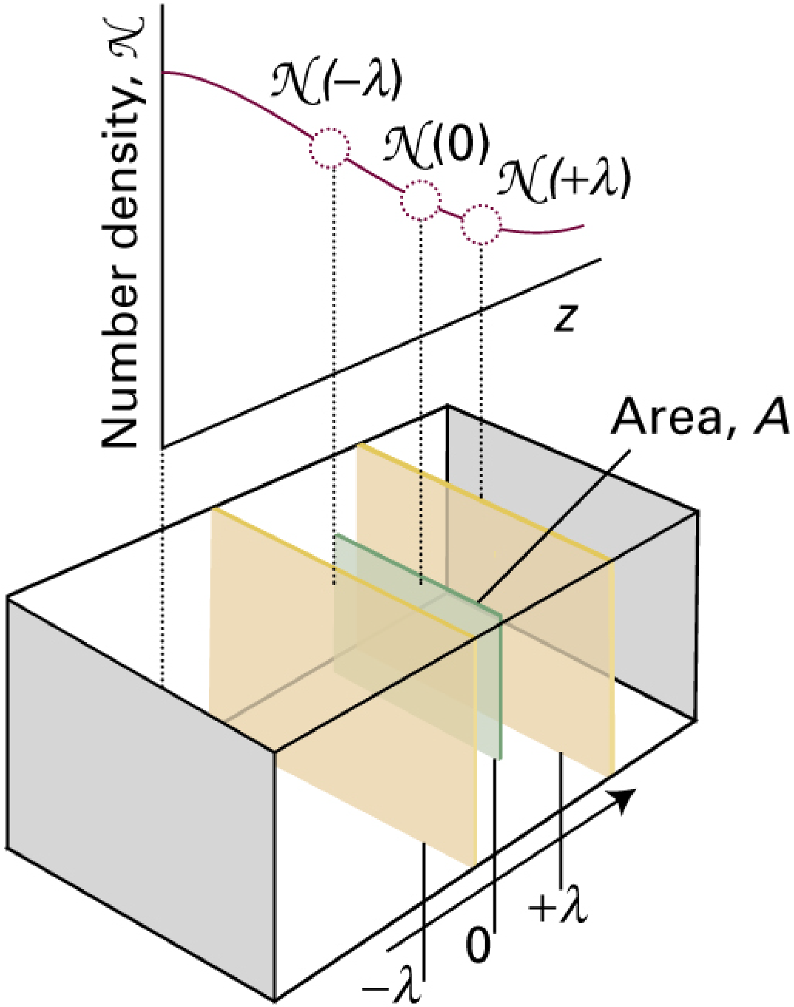
Only molecules within a distance $v_x\Delta t$ with v_x>0 can reach the wall on the right in an interval Δ*t*.

Effusion Cell

Molecular Beam Epitaxy (MBE)

19A.2(a). Diffusion Coefficient of a Perfect Gas

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



Diffusion Coefficient

= Diffusivity

Figure 19A.4. 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.

$$v_{rms} = \left(\frac{3kT}{m}\right)^{\frac{1}{2}}$$

The result of this modification

$$J_z = -\frac{1}{3}\lambda\bar{c}\left(\frac{d\tilde{N}}{dz}\right)_0 \quad \text{with} \quad J_z = -D\left(\frac{d\tilde{N}}{dz}\right)_0 \qquad \textbf{(19A.10)}$$

(교재)

$$D = \frac{1}{6}\lambda\bar{c} = \frac{1}{6}z\lambda^2$$

$$= \frac{1}{6}\left(\frac{1}{\sigma}\right)\left(\frac{kT}{p}\right)\left(\frac{8kT}{\pi m}\right)^{\frac{1}{2}} \quad \text{where } \sigma = \pi d^2$$

[Derivation on White Board]

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

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

$z = \Gamma = \tau^{-1}$: Jump Frequency = [Collision Time]$^{-1}$

Thermal Conductivity

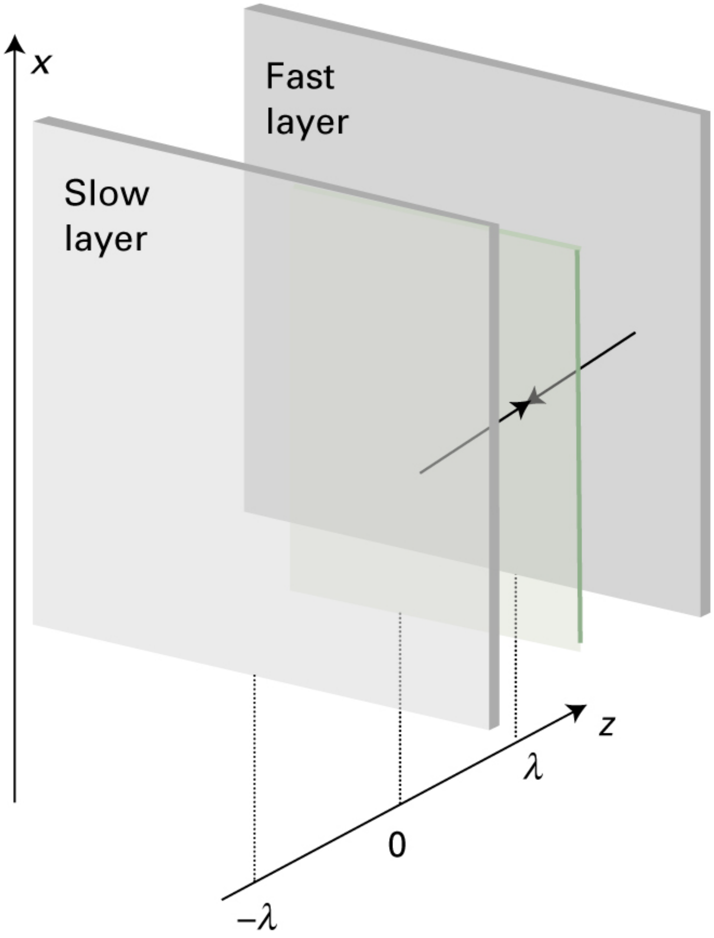
$$\kappa = \frac{1}{3}\lambda\bar{c}C_{V,m}[A] \qquad \textbf{(19A.13a)}$$

This shows that ***κ* 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

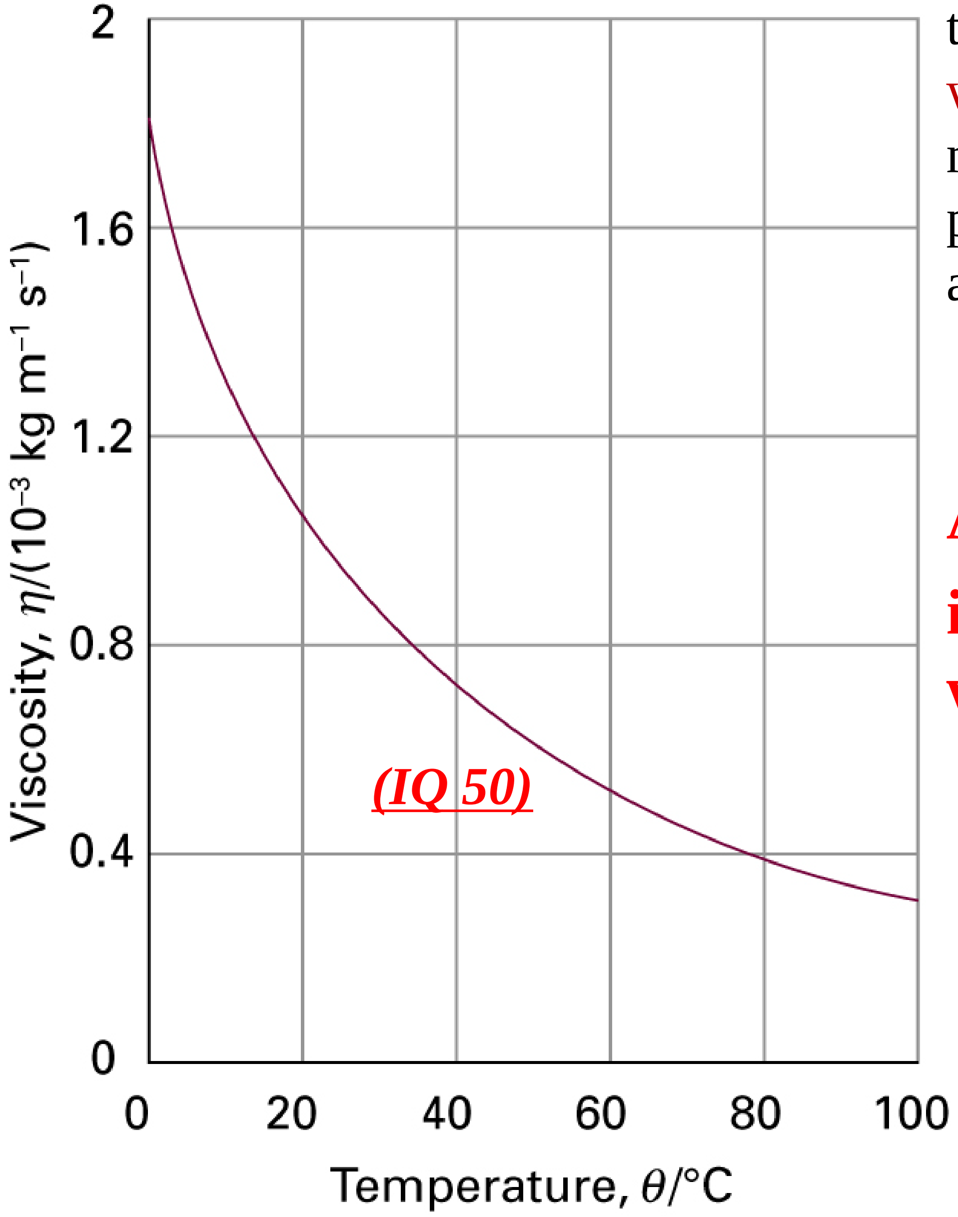
We have already seen that the coefficient of viscosity is determined by the rate at which momentum is transported.



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

(19A.16)

Figure 19A.6. 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.



(IQ 50)

Figure 19B.1. 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 $\log \eta$ vs. $1/T$ is (approximately) a straight line with a positive slope.

$$\eta = \eta_0 \ \exp\left(E_a/k_B T\right) \tag{19B.2}$$

Ideal Electrolyte = 100% Ionic Conductivity

19B.1(b). Conductivity of Electrolyte Solution

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 **: resistivity**

Electronic ***and/or*** ***Ionic***

σ ρ

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.

$\rho \approx 10^{-4}\ \Omega$ cm **$\sigma \approx 10^{6}\ S$/cm**

Transparent Conducting Oxide ***Cu, Ag, or Au***

Graphite

Electrolyte Solution

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

$$\Lambda_m = \frac{\kappa}{c} \tag{19B.4}$$

c = molar concentration (molarity) of the added electrolyte.

Λ_m : the molar conductivity

molarity = mole / $(10\text{ cm})^3$
= mole / liter

Two Types of Electrolytes

(1) Strong Electrolytes

- Molar conductivity depends weakly on the concentration of solute.

- The number of ions in the solution is (approximately) proportional to the concentration of the electrolyte.

- The conductivity is not exactly proportional to the number of ions present, due to the strong **ionic interactions**.

c = molarity

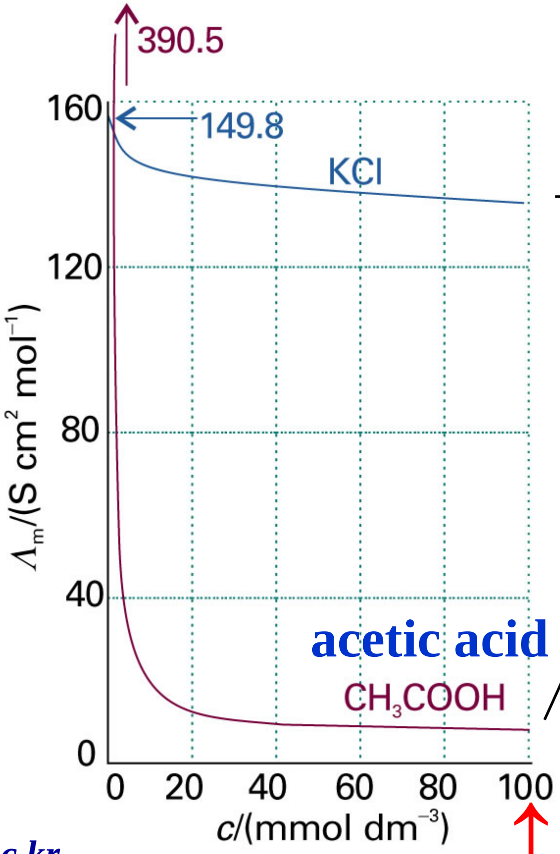
Kohlrausch's law

$$\Lambda_m(c) = \Lambda_m^0 - Kc^{\frac{1}{2}} \quad \text{[skip]} \qquad \textbf{(19B.5)}$$

Λ_m^0 : the limiting molar conductivity

K : the coefficient depends on the nature of the salt

Concentration Dependence of Molar Conductivities



acetic acid

→ ***Strong Electrolyte***

Weak Electrolyte

(~1% dissociation)

↑ **0.1 M**

Limiting molar conductivity (*c* = molarity ~ 0)

$$\Lambda_m^0 = \nu_+\lambda_+^0 + \nu_-\lambda_-^0 \qquad \textbf{(19B.6)}$$

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

***c*: molarity**
ν_+: number of cations

(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 dissociation**.

19B.2(a). Drift Velocity and Mobility

l : distance of electrode

$\Delta\phi$: potential difference

$\Delta\phi/l$: potential gradient

The magnitude of force is proportional to the potential gradient:

$F = zeE$

c: molarity
ν_+: number of cations
ze: charge of an ion

F : force

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

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

The force acting on an ion accelerates it. However, 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 velocity** of the ion in solution, and is denoted as $s = v_d$

Since the drift velocity governs the rate of conduction, we expect that **the conductivity decreases with the increasing viscosity**.

c: molarity
ν_+: number of cations
ze: charge of an ion
$s = v_d$: drift velocity

- -

Stokes formula [skip]

the frictional force = $6\pi a\eta\ s$

a: the radius of a spherical object

η: the viscosity of a medium

$$6\pi a\eta s \cong zeE$$

$$\therefore s \cong \frac{zeE}{6\pi a\eta} \quad (19B.9)$$

19B.2(b). The Mobility of Ions [by Electric Field]

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

$$s_\pm = |\boldsymbol{v}_{d\pm}|.$$

$s_\pm \propto E$ E : **electric field**

$s_\pm = \mu_\pm E$ $\mu_\pm$: **mobility of ion and/or electron**

***c*: molarity**
ν_+: number of cations
***ze*: charge of an ion**
$s = v_d$: drift velocity

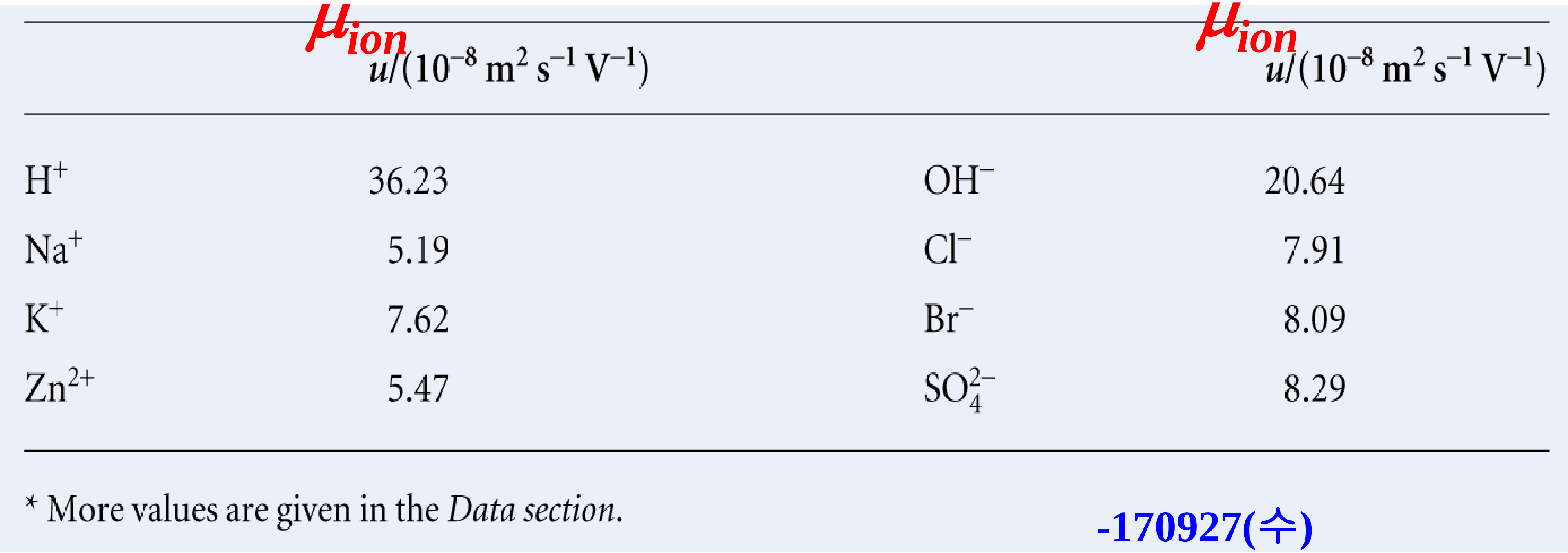
$$\overrightarrow{v_d} \equiv \mu \overrightarrow{E}$$

(19.B.11)

[electron mobility] = cm^2 / V s

Silicon: $\mu_{electron}$ = 1400 cm^2 / V s μ_{hole} = 500 cm^2 / V s

Table 19B.2 Ionic Mobilities in Water at 298 K



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

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-171011(수) Quiz 1
Chaps. 15-19A (pp. 604-797)

Drift Velocity

Mobility

재료상변태 (atoms)

μ **: chemical potential**

$$\vec{J} \equiv -D\nabla c \qquad \vec{J} = c\vec{v}_d \qquad \vec{v}_d \equiv -M\nabla\mu$$

전자기적성질 (ions and/or electrons)

$$\vec{J} = -\sigma\nabla\phi = \sigma\vec{E}$$

$$\vec{J} = ne\vec{v}_d \qquad \vec{v}_d \equiv \mu\vec{E}$$

E_F

$$\sigma = ne\mu \quad (= ne^2\tau/m^*)$$

free electron model

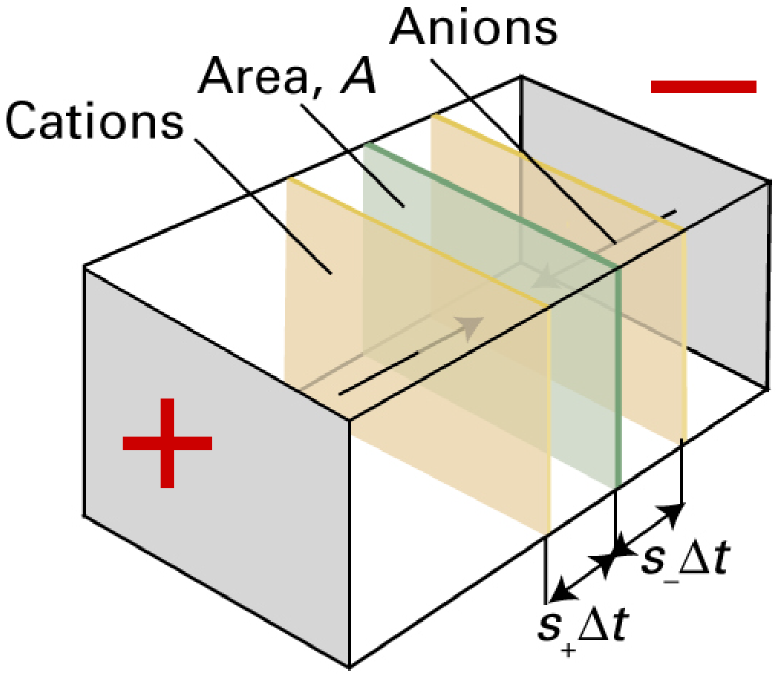
$z^{-1} = \tau$ **: Collision Time = [Jump frequency]**$^{-1}$

Electronic Conductivity

The relation between mobility and conductivity

Consider a solution of a salt of concentration c (molar concentration in moles per unit volume) so that it contains **$v_+ c N_A$ cations and $v_- c N_A$ anions per volume**. The cations have charge z_+e and the anions z_-e.

c: molarity
v_+: number of cations
ze: charge of an ion
$s = v_d$: drift velocity



$\nu_+ = 1 \quad \nu_- = 2$

$z_+ = 2 \quad z_- = 1$

for $MgCl_2$

Figure 19B.3
Calculating the charge flux.

Volume (cation): $s_+\Delta t A$

Cation number that passes through: $(s_+\Delta t A) \times v_+ c N_A$

Cation number that passes through: $(s_+\Delta t A) \times v_+ c N_A$

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

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

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

$$\underline{J_{(total\ ions)}} = v_+ s_+ z_+ c e N_A + v_- s_- |z_-| c e N_A$$

$$= \underline{(\mu_+ v_+ z_+ + \mu_- v_- |z_-|) c F \mathcal{E}}$$

conductivity **$\sigma = ne\mu$**

(Justific. 19B.1)

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

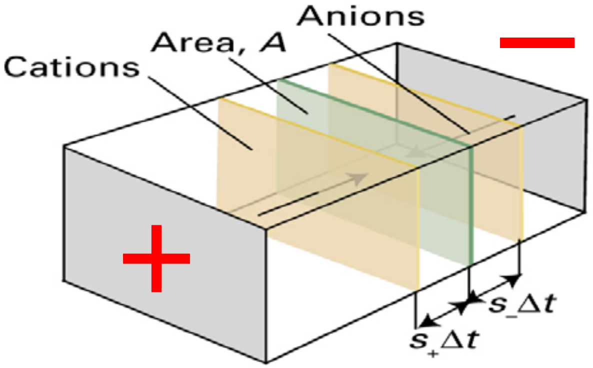
$$\underline{s_\pm = \mu_\pm\ \mathcal{E}}$$

$v_d = \mu E$

$\nu_+ = 1 \quad \nu_- = 2$

$z_+ = 2 \quad z_- = 1$

for $MgCl_2$



c: molarity
v_+: number of cations
ze: charge of an ion
$s = v_d$: drift velocity
$F = eN_A$: Faraday constant

$$J_{(total\ ions)} = (\mu_+ \nu_+ z_+ + \mu_- \nu_- |z_-|)cFE$$

$J = \sigma E$

$\sigma_{electron} = ne\mu$

Comparison of these two expressions

$$\kappa = (\nu_+ \mu_+ z_+ + \nu_- \mu_- |z_-|)cF$$ **= Ionic Conductivity**

Molar conductivity

$$\Lambda_m = (\nu_+ \mu_+ z_+ + \nu_- \mu_- |z_-|)F$$

***c*: molarity**
v_+: number of cations
***ze*: charge on an ion**
$s = v_d$: drift velocity
$F = eN_A$: Faraday constant

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

$$\Lambda_m = z(\mu_+ + \mu_-)F \qquad \textbf{(19B.14b)}$$

$\nu_+ = 1 \quad \nu_- = 2$

$z_+ = 2 \quad z_- = 1$

for $MgCl_2$

19C.1. Fundamental Aspects of Molecular Transport

Diffusion: Thermodynamic View

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

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

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

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

In classical mechanics

$$dw = -\,force\ \ dx$$

The gradient of chemical potential acts like a force.

(19C.1)

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

$$\upsilon_d \equiv -M \nabla \mu$$ (atoms)

$$\upsilon_d \equiv \mu E = -\mu \nabla \phi$$

(electric)

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

$$J \equiv -D \nabla c$$

c: # of atoms/cm^3

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

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

$$Force = -\frac{d}{dx}(\mu^{\circ} + RT \ln c) = -\left(\frac{RT}{c}\right)\left(\frac{dc}{dx}\right)$$ (19C.2b)

- -

Chap. 5 $$\mu_i(P, T, n_A, n_B, n_C, ...) = \mu_i^0(P, T) + RT \ln a_i$$

$$a_i(T, p, x_j) = x_i$$ *Ideal solution*

19C.1. Fick's First Law of Diffusion

The flux of diffusing particles is motion in response to a thermodynamic force arising from a concentration gradient.

isotope

$$J_x(\text{matter}) = -D\frac{dc}{dx}$$

The particle flux *J* is proportional to the drift velocity

c = moles per volume
{*textbook*}

$$J = cs = -D\left(\frac{dc}{dx}\right)$$

$s = v_d$: drift velocity

(atoms)

$$\boldsymbol{J \equiv -D\nabla c}$$

$$\boldsymbol{J = c\upsilon_d}$$

(19C.5)

$$\boldsymbol{J = ne\upsilon_d}$$

Ideal Solution => Diffusivity and Mobility

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

(19C.2b)
ppt 19-32

$$\therefore J = cs = -D\left(\frac{dc}{dx}\right) = -cM\frac{d\mu}{dx} = -cM\left(\left(\frac{RT}{c}\right)\left(\frac{dc}{dx}\right)\right)$$

$J_{atom} = cv_d$

Diffusivity D
Drift velocity $s = v_d$

Atomic Mobility $M = D/RT$

$v_d \equiv -M\nabla\mu$

(skip)

Ideal Solution of Ions => Diffusivity and Ionic Mobility

The mobility of an ion is related to the electrical force on it. Since the mobility is defined through $s = \mu_{ion}E$, and since the electrical force is ezE, so that the force per mole is zFE (since $F = e N_A$),

$$v_d = s = \mu_{ion}E = \left(\frac{\mu_{ion}}{zF}\right)(zFE)$$

(D/RT) Force $= (\mu_{ion}/zF)$ Force

$v_d \equiv \mu E$

$$\therefore \frac{\mu_{ion}}{zF} = \frac{D}{RT} \qquad \therefore D = \frac{\mu_{ion}RT}{zF} = \frac{\mu_{ion}k_BT}{ze}$$

Einstein relation **(19B.16)**

(skip)

19B.2(c). The Relation between Mobility and Viscosity

$$s = \frac{ezE}{6\pi\eta a} \qquad s = uE \qquad \textbf{(19B.15)}$$

By equating two equations,

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

Since the Einstein relation is $u = \dfrac{ezD}{kT}$ **(in ideal solution)**

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

Stokes-Einstein relation

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.

19C.2. Diffusion Equation

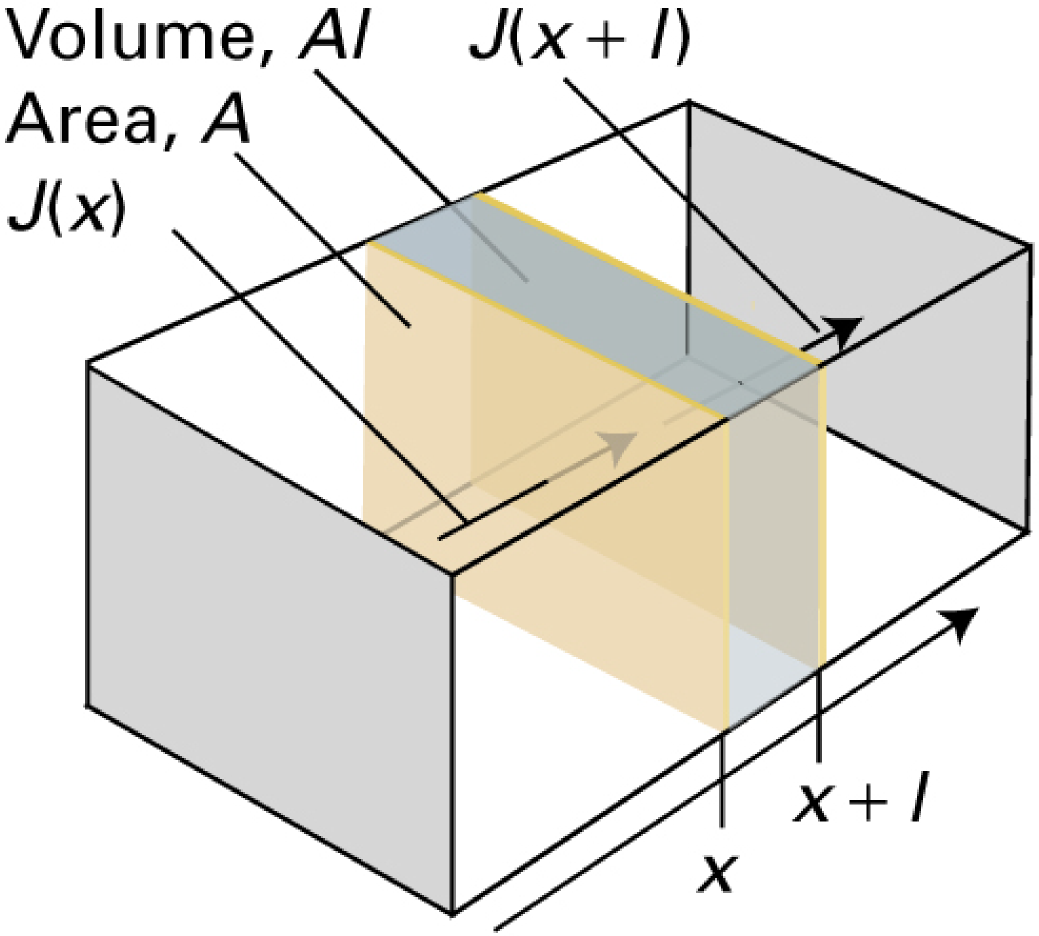


Figure 19C.1

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).

$$\nabla \cdot J + \frac{\partial c}{\partial t} = 0$$

$\nabla \cdot J$ **= divergence *J***

True all the time

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

Fick's 2nd law of diffusion

(19C.7)

only when *D* is independent of *c*

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

19C.2(b). Diffusion with Convection

(skip)

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

When the fluid is flowing at a velocity *v*

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

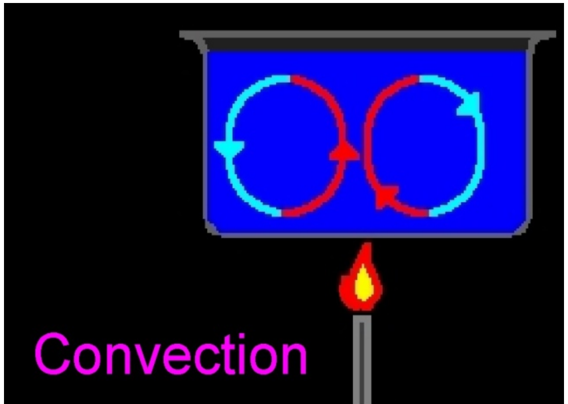
J: the convection flux

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,

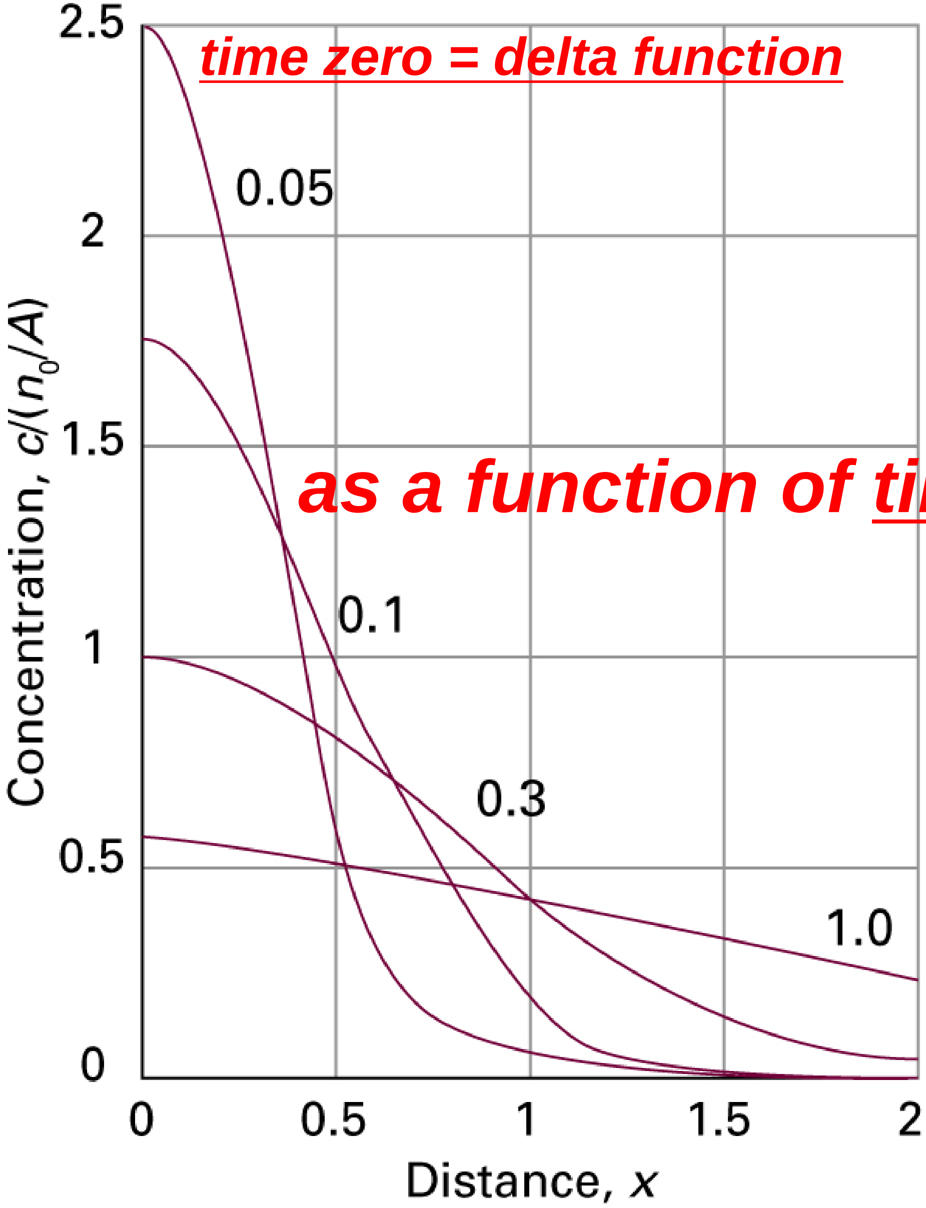
$$\frac{\partial c}{\partial t} = \frac{J - J'}{l} = \left\{ c - \left[c + \left(\frac{\partial c}{\partial x} \right) l \right] \right\} \frac{v}{l} = -v \frac{\partial c}{\partial x}$$

generalized diffusion equation

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} - v \frac{\partial c}{\partial x} \qquad \text{(19C.10)}$$



19C.2(c). Solutions of Diffusion Equation – *D* independent of *c* $D > 0$



time zero = delta function

as a function of time

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

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

(19C.11)

Figure 19C.4 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.

$\sqrt{Dt}$ The mean distance through which the solute has spread after a time *t*

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

(Example 19C.1)

$$\langle x \rangle = \frac{1}{\sqrt{\pi D t}} \int_0^\infty x e^{\frac{-x^2}{4Dt}} = 2\left(\frac{Dt}{\pi}\right)^{\frac{1}{2}}$$

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

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

$z^{-1} = \tau$: Collision Time

The **mean free path** λ,

$$\lambda = \frac{\bar{c}}{z} = \frac{1}{\sigma\left(\frac{N}{V}\right)} \qquad z = \bar{c}\,\sigma\left(\frac{N}{V}\right)$$

For a perfect gas,

$$\lambda = \frac{1}{\sigma\left(\frac{p}{kT}\right)} = \left(\frac{1}{\sigma}\right)\left(\frac{kT}{p}\right) \qquad \textbf{(1B.13)}$$

The mean free path is inversely proportional to the pressure.

v = 500 m/s $\quad$ τ = 1 ns (= 0.5 ns)

$v\,\tau$ = 300 nm at 300 K + 1 atm

10^{-5} atm ↔ ~1 cm

at 300 K

Problems from Chap. 19

E 19A.8(b) 19A.9(b) 19A.10(b)

E 19B.3(b) 19B.4(b) 19B.5(b)

D 19C.2

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