Thermodynamics

Predicts the **direction** of everyday spontaneous processes:

- flow of heat from warmer to cooler regions
- expansion from higher to lower pressure
- mixing from higher to lower concentrations
- chemical reaction from higher to lower activities

But what are the **rates** of these important processes?

Chapter 17. Transport Processes

- most systems are not at equilibrium
- how rapidly does a non-equilibrium system reach equilibrium?
- need to know rates of transport of
    - mass (**Fick's law** of diffusion)
    - heat (**Fourier's law** of thermal conductivity)
    - momentum (**Newton's law** of viscosity)
    - charge (**Ohm's law** of electrical conductivity)

$$\boxed{J_x = -D\frac{\partial C}{\partial x}}$$

$$\boxed{J_x = -\kappa\frac{\partial T}{\partial x}}$$

$$\boxed{J_x = -\eta\frac{\partial v}{\partial z}}$$

$$\boxed{J_x = -\kappa\frac{\partial \phi}{\partial x}}$$

- flux J_x (quantity transported per unit area per unit time) is proportional to a transport coefficient and a driving gradient

Section 17.1 What is Transport?

- **equilibrium:** uniform temperature, pressure, and chemical potentials
- but most systems have **gradients** in temperature, pressure, composition, *etc*.
- **transport** refers to the flow of heat, momentum and matter to approach thermal, mechanical and chemical equilibrium
- practical applications describing the rates of physical and chemical processes in every branch of science and technology
- biochemical transport (*e.g*., O_2 carried hemoglobin) essential for multi-cellular plants and animals

Transport Equation

$$\boxed{J_x = -\alpha \frac{\partial(\text{property})}{\partial x}}$$

J_x = **flux density** (also called the flux): the amount of mass, energy, momentum, or charge flowing per unit area per unit time in the x-direction

α = **transport coefficient**

$\frac{\partial(\text{property})}{\partial x}$ = **gradient** in a system property **driving the flux**

Why the minus sign in transport equations? The flow is "down" the gradient, such as heat flowing from regions of higher to lower temperature.

Section 17.2 Mass Transport by Diffusion

Diffusion: transport of matter by random molecular motions

(***not by bulk flow***, such as stirring or pumped flow in a pipe)

Fick's Law of Diffusion

$$\boxed{J_x = -D\frac{\partial C}{\partial x}}$$

J_x = flux density of molecules diffusing in the x-direction

D = diffusion coefficient

$\frac{\partial C}{\partial x}$ = concentration gradient

Fick’s Law of Diffusion

$$\boxed{J_x = -D\frac{\partial C}{\partial x}}$$

Applies to gases, liquids and solids.

J_x = **flux density**, SI units: m^{-2} s^{-1} (for molecules)

$\dfrac{\partial C}{\partial x} = \dfrac{\partial (N/V)}{\partial x}$ = **concentration gradient**, SI units: m^{-4}

D = **diffusion coefficient**, SI units: m^{2} s^{-1}

Fick's Law of Diffusion

$$\boxed{J_x = -D\frac{\partial C}{\partial x}}$$

Provides **mixing on the molecular level**.

Studied in every branch of science and technology.

Applications:

- chemical kinetics. Molecules must diffuse together to react. Some reactions rates are diffusion-limited, such as $H^+ + OH^- \rightarrow H_2O$.
- rates of mass transfer, such as gas absorption and dissolution
- transport across membranes, metabolic rates
- transmission of nerve impulses
- rates of nuclear fission (neutron transport in reactors)
- waste management

Diffusion Coefficients at 300 K and 1 bar

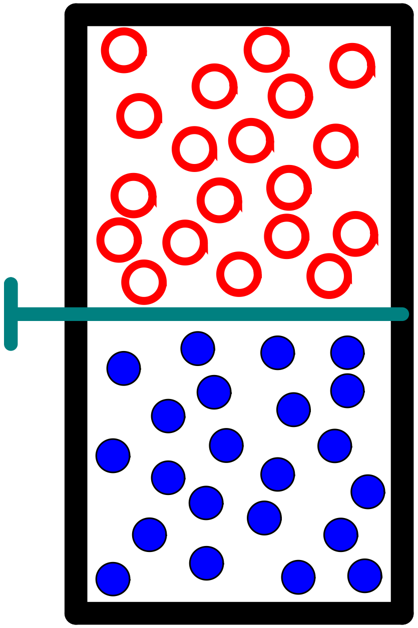
	D / m^2 s^{-1}
helium (g)	4.4×10^{-5}
argon (g)	1.1×10^{-5}
water (g)	0.28×10^{-5}
water (*l*)	2.3×10^{-9}
benzene (*l*)	2.2×10^{-9}
n-hexane (*l*)	4.1×10^{-9}
helium in water (*l*)	6.3×10^{-9}
aluminum (s)	1.3×10^{-34}

Values of D range over many orders of magnitude, from as low as 10^{-35} m^2 s^{-1} for solids up to about 10^{-4} m^2 s^{-1} for gases, with intermediate values for liquids.

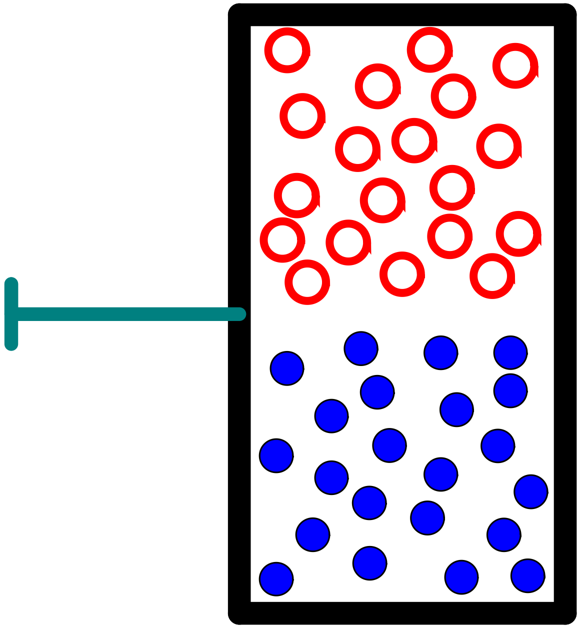
Diffusion Measurements

Many techniques are used. **Example:** Loschmidt gas diffusion cell

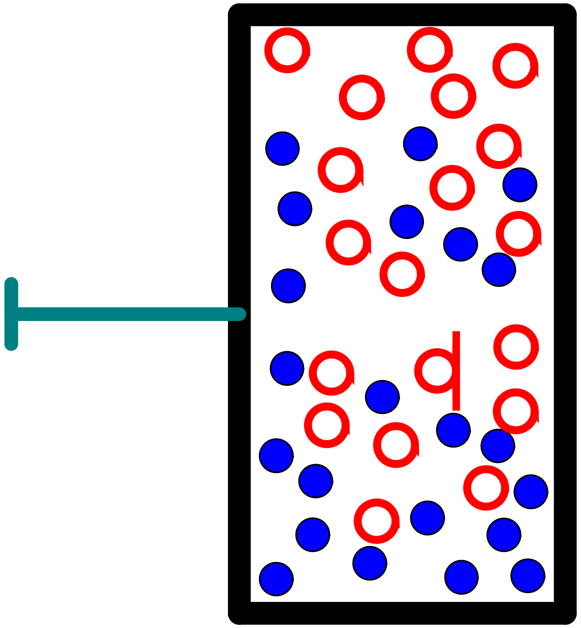
load cell



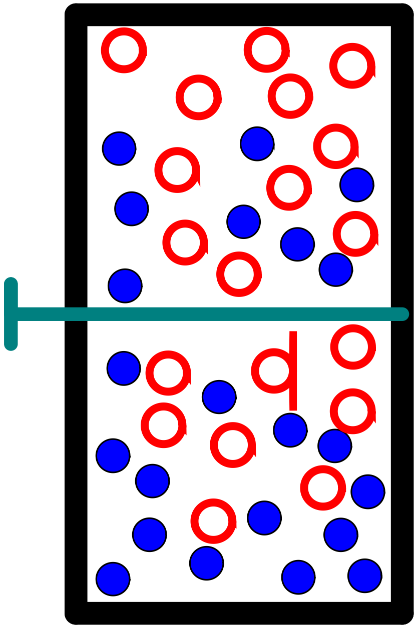
start diffusion



diffusion for a timed interval



stop diffusion, analyze upper and lower mixtures to calculate *D*

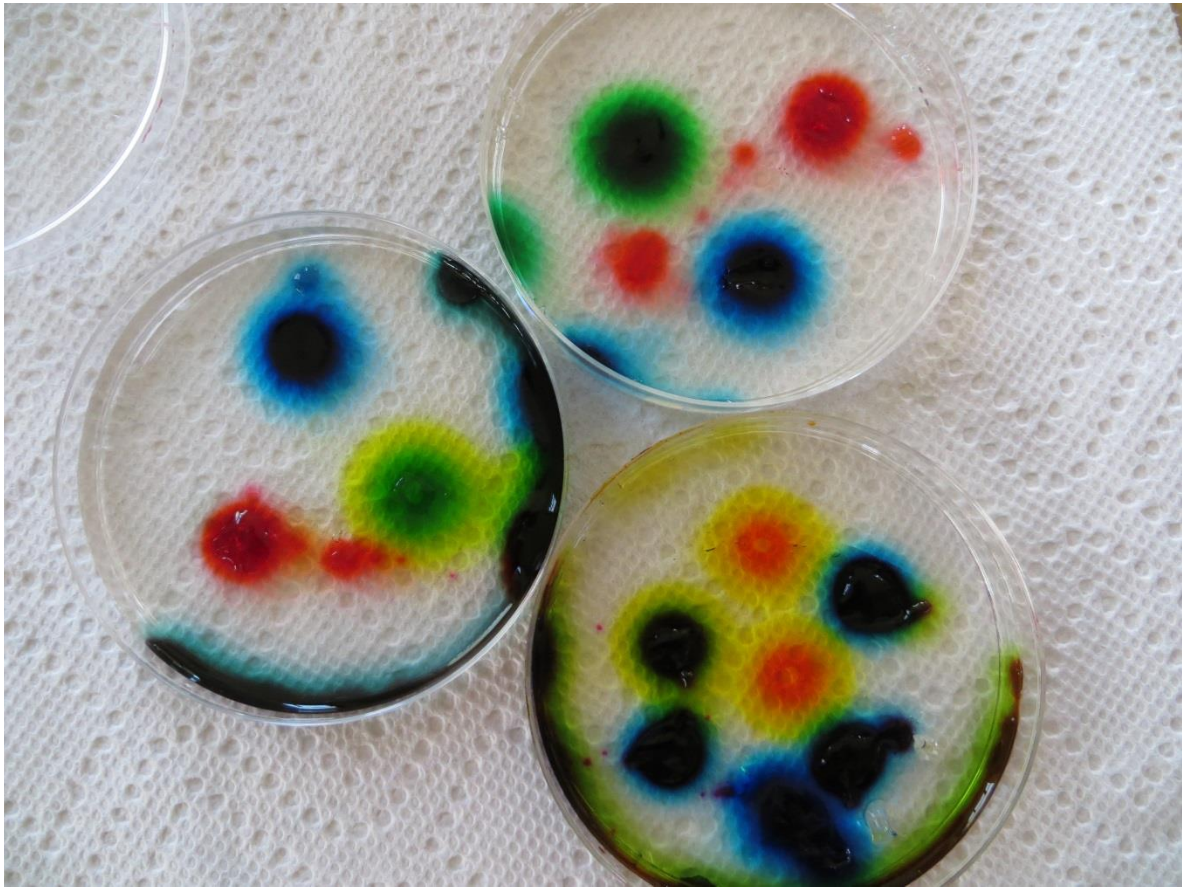


Avoid convection (stirring) during diffusion measurements!

Not diffusion!

Put denser solutions underneath less dense solutions.

Use narrow tubes or gels to prevent convection.



Example For argon at 298 K and 1 atm: $D = 1.1 \times 10^{-5}\ \text{m}^2\ \text{s}^{-1}$. The concentration gradient in the *x*-direction is 0.25 mol $\text{L}^{-1}\ \text{cm}^{-1}$. Calculate the flux density J_x of argon atoms.

$$\frac{\partial C}{\partial x} = \frac{\partial (N/V)}{\partial x} = (0.25\,\frac{\text{mol}}{\text{L cm}})\ (6.022\times 10^{23}\,\frac{1}{\text{mol}})\ (10^3\,\frac{\text{L}}{\text{m}^3})\ (10^2\,\frac{\text{cm}}{\text{m}})$$

concentration gradient (SI units)

$$\frac{\partial C}{\partial x} = 1.50 \times 10^{28}\ \text{m}^{-4}$$

molecules per unit volume per unit length

flux density

$$J_x = -D\frac{\partial C}{\partial x} = -(1.1 \times 10^{-5}\ \text{m}^2\ \text{s}^{-1})\,(1.50 \times 10^{28}\ \text{m}^{-4})$$

$$\boxed{J_x = -1.65 \times 10^{23}\ \text{m}^{-2}\ \text{s}^{-1} \qquad \text{(flux density of argon atoms)}}$$

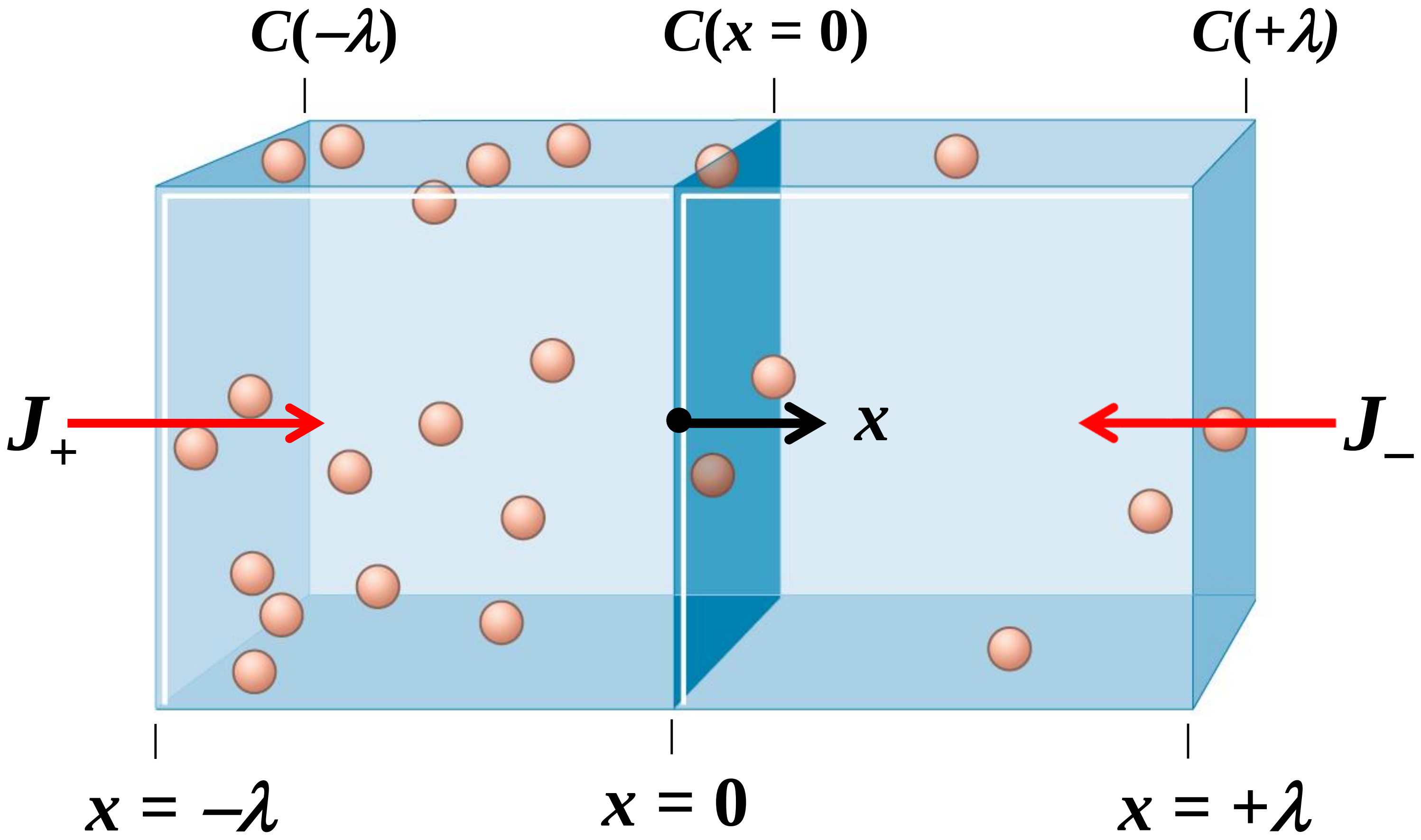
$$J_{x\text{m}} = -0.273\ \text{mol m}^{-2}\ \text{s}^{-1} \qquad \text{(molar flux density of argon} = J_x/N_\text{A}\text{)}$$

Gas Diffusion Coefficients from Kinetic Theory

$$J_x = -D\frac{\partial C}{\partial x}$$

- Need to know how equilibrium velocity distributions are changed by non-equilibrium concentration gradients
- Accurate calculations are complicated
- Can get a good qualitative understanding of gas diffusion using the hard-sphere model developed in the previous Chapter
- Simplified treatments of thermal conductivity and viscosity can also be developed

Why important: Theory is used to understand macroscopic transport processes on a <u>molecular level</u>.



$$\boxed{J_+ = \left[C(x=0) - \lambda\frac{\partial C}{\partial x}\right]\frac{<v>}{4}}$$

$$\boxed{J_- = \left[C(x=0) + \lambda\frac{\partial C}{\partial x}\right]\frac{<v>}{4}}$$

Where is this from? Collision rate with a wall: $Z_c = (N/V)<v>/4 = C<v>/4$

Diffusion Coefficients from Kinetic Theory

$$\boxed{J_x = -D\frac{\partial C}{\partial x}}$$

Net diffusion flux of molecules in the *x*-direction at *x* = 0:

$$J_x = J_+ - J_-$$

$$\approx \left[C(x=0) - \lambda\frac{\partial C}{\partial x}\right]\frac{<v>}{4} - \left[C(x=0) + \lambda\frac{\partial C}{\partial x}\right]\frac{<v>}{4}$$

$$= -\lambda\frac{<v>}{2}\frac{\partial C}{\partial x}$$

$$= -D\frac{\partial C}{\partial x}$$

approximate diffusion coefficient:

$$\boxed{D_{\text{approx}} \approx \frac{1}{2}\lambda <v> = \sqrt{\frac{kT}{\pi m}}\,\frac{1}{C\sigma}}$$

Why approximate? Molecules collide and scatter over distances of λ.

Diffusion Coefficients from Kinetic Theory

$$\boxed{J_x = -D\frac{\partial C}{\partial x}}$$

<u>Exact</u> diffusion coefficient for a gas of hard-sphere molecules:

$$\boxed{D = \frac{3\pi}{8}\frac{1}{2}<v>\lambda = \frac{3\pi}{8}\sqrt{\frac{kT}{\pi m}}\ \frac{1}{C\sigma}}$$

The diffusion coefficient is proportional to the average speed and the mean free path of the molecules. As a result:

D is proportional to $T^{1/2}$, $m^{-1/2}$, C^{-1}, and σ^{-1}. Does this make sense?

Example: Calculate the diffusion coefficient of argon gas at 298 K and 1 atm.

Data: cross sectional area $\sigma = 0.36 \times 10^{-18}\ \mathrm{m^2}$

$$\boxed{D = \frac{3\pi}{8}\sqrt{\frac{kT}{\pi m}}\ \frac{1}{C\sigma^2} = \frac{3\pi}{8}\sqrt{\frac{RT}{\pi M}}\ \frac{1}{C\sigma}}$$

$$C = \frac{N}{V} = \frac{p}{kT} = \frac{101325\ \mathrm{Pa}}{(1.381 \times 10^{-23}\ \mathrm{J\ K^{-1}})\ (298\ \mathrm{K})} = 2.46 \times 10^{25}\ \mathrm{m^{-3}}$$

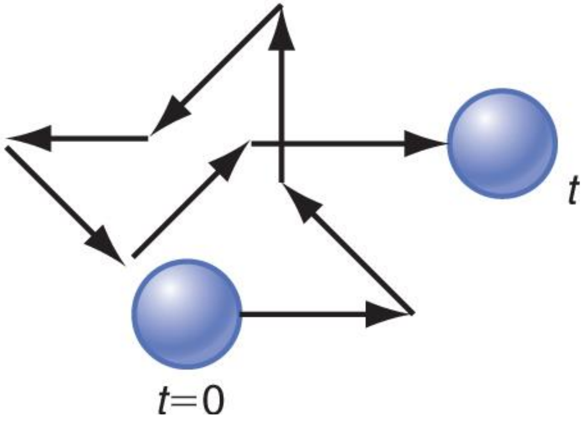
$$D = \frac{3\pi}{8}\sqrt{\frac{RT}{\pi M}}\ \frac{1}{C\sigma}$$

$$D = \frac{3\pi}{8}\sqrt{\frac{(8.314\ \mathrm{J\ K^{-1}\ mol^{-1}})\ (298\ \mathrm{K})}{\pi\,(0.03995\ \mathrm{kg\ mol^{-1}})}}\ \frac{1}{(2.46\times10^{25}\ \mathrm{m^{-3}})\ (0.36\times10^{-18}\ \mathrm{m^2})}$$

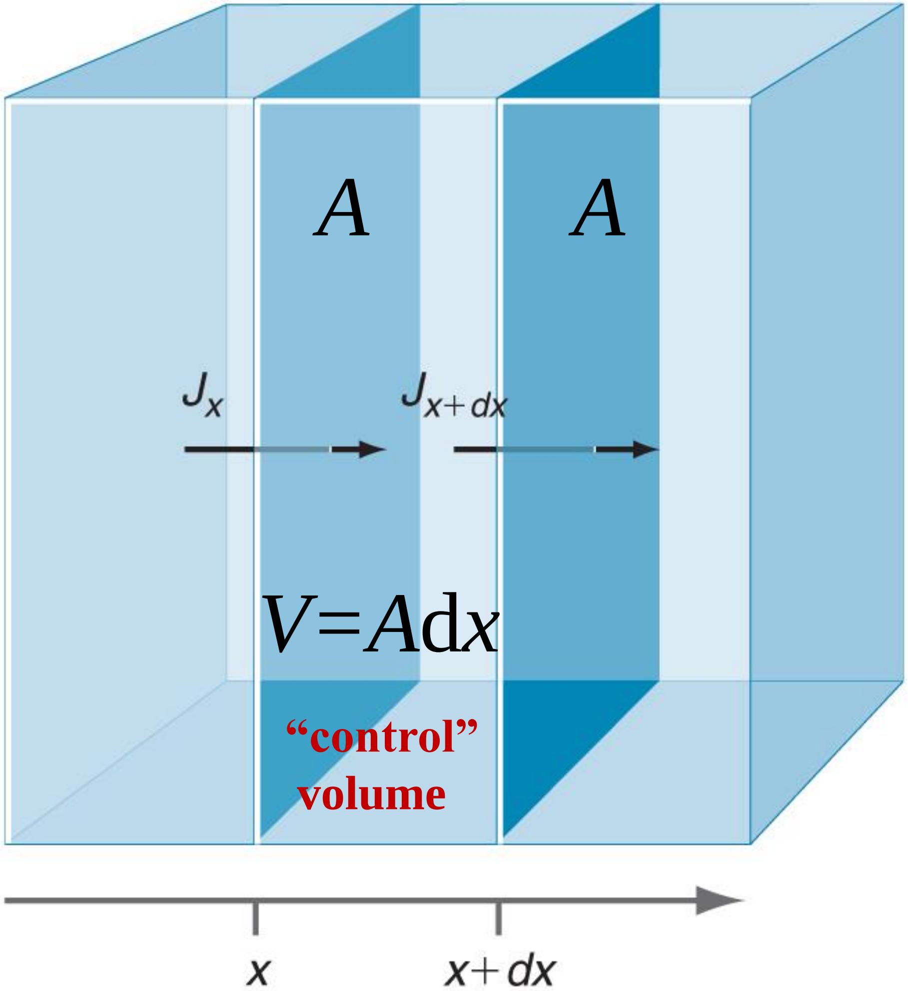
$$D = 1.87 \times 10^{-5}\ \mathrm{m^2\ s^{-1}}$$

Section 17.3 Time Evolution of Diffusion

- a concentration gradient causes molecules to diffuse
- given an initial concentration distribution at time $t = 0$, what is the distribution of molecules at a later time t ?
- how long does it take for molecules to diffuse a given distance?
- diffusion motions are random – is there a statistical interpretation?



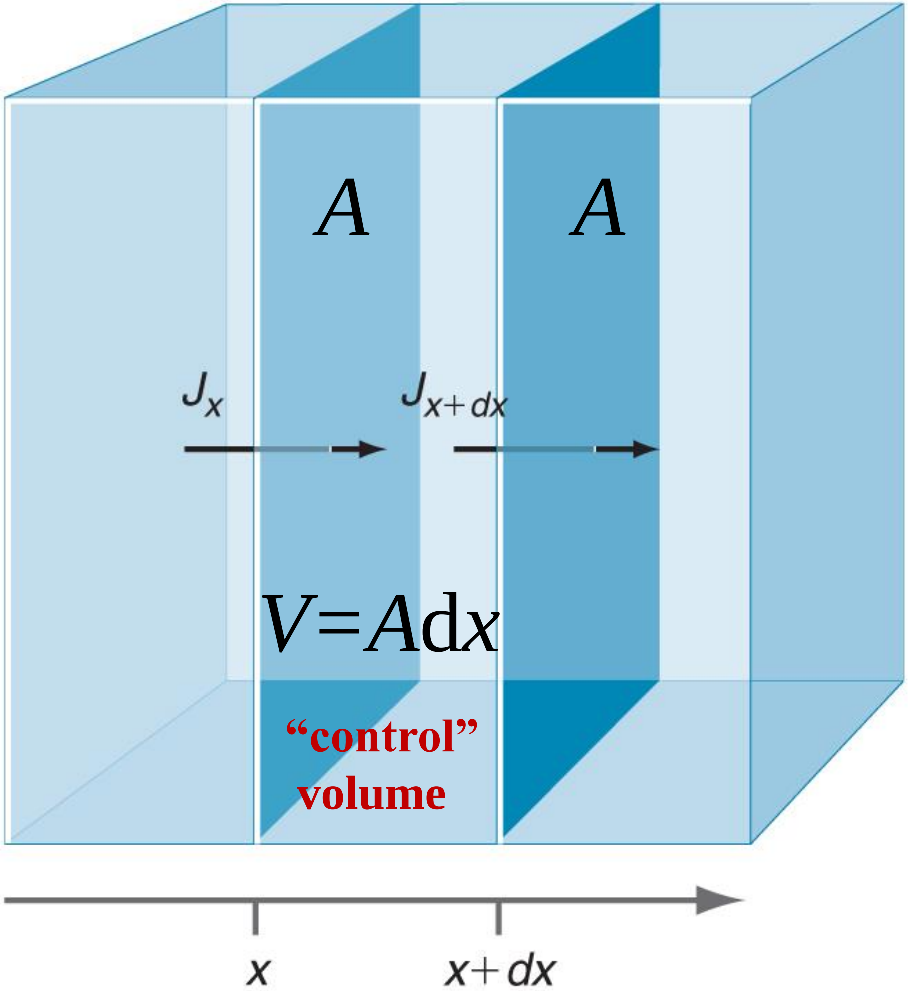
Mass Balance: Important for Analyzing Diffusion Processes



N is the number of molecules in in the volume $A\mathrm{d}x$ between positions x and $x + \mathrm{d}x$.

The number of molecules diffusing into volume $A\mathrm{d}x$ from the left (x) minus the number of molecules diffusing out of the volume on the right ($x + \mathrm{d}x$) gives $\mathrm{d}N/\mathrm{d}t$.

$$\boxed{\frac{\mathrm{d}N}{\mathrm{d}t} = \text{rate molecules enter} - \text{rate molecules leave}}$$



mass balance on the volume $A\mathrm{d}x$ between x and $x + \mathrm{d}x$:

$$\frac{\mathrm{d}N}{\mathrm{d}t} = J_x(x)A - J_x(x+\mathrm{d}x)A$$

$$\frac{1}{A\mathrm{d}x}\frac{\mathrm{d}N}{\mathrm{d}t} = \frac{J_x(x) - J_x(x+\mathrm{d}x)}{\mathrm{d}x}$$

Use $C = N/V = N/(A\mathrm{d}x)$ to get :

Continuity Equation

$$\boxed{\frac{\partial C}{\partial t} = -\frac{\partial J_x}{\partial x}}$$

Time Evolution of Concentration Gradients: Fick's Second Law of Diffusion

Combine $J_x = -D\partial C/\partial x$ and $\partial C/\partial t = -\partial J_x/\partial x$:

$$\frac{\partial C}{\partial t} = -\frac{\partial}{\partial x}(J_x) = -\frac{\partial}{\partial x}\left(-D\frac{\partial C}{\partial x}\right)$$

Why use partial derivatives?

If the concentration changes aren't too large, the diffusion coefficient can be treated as a constant to get

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

Fick's Second Law of Diffusion

The time derivative of the concentration $C(x, t)$ is proportional to the second x-derivative (the "curvature") of $C(x, t)$.

Time Evolution of Concentration Gradients: Fick’s Second Law of Diffusion

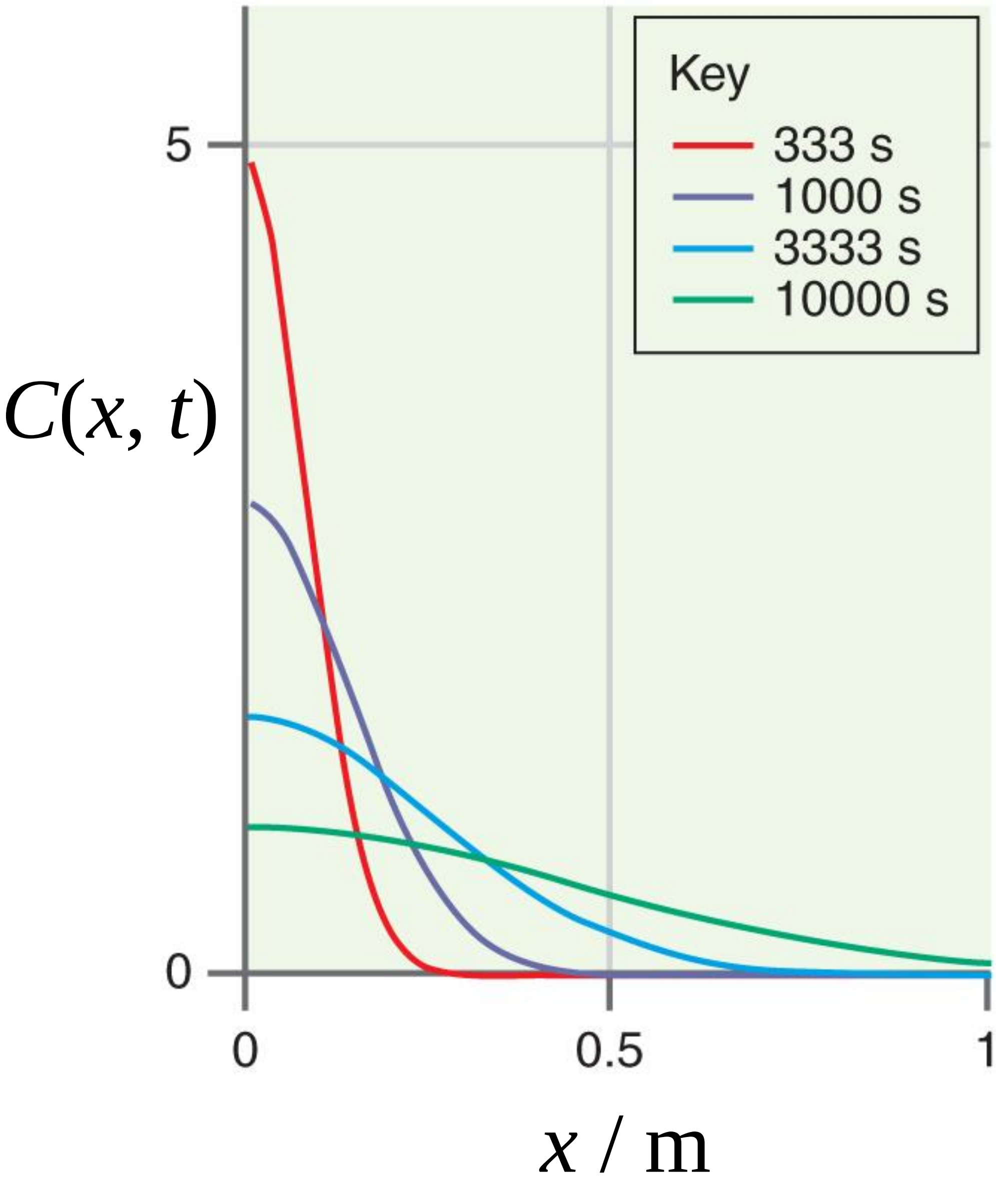
Application: Tracer Diffusion

Suppose N_0 molecules are initially located at position $x = 0$ at time $t = 0$ in a column of cross-sectional area A.

After diffusion for time t, where are the molecules?

Solving Fick’s Second Law $\frac{\partial C(x,t)}{\partial t} = D\frac{\partial^2 C(x,t)}{\partial x^2}$ gives

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



Tracer Diffusion

$$D = 10^{-5}\ \mathrm{m^2\ s^{-1}}$$

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

(*Does this look familiar?*)

Conservation of mass:

$$N_0 = A\int_{-\infty}^{+\infty} C(x,t)\,\mathrm{d}x$$

Section 17.4 Statistical Interpretation of Diffusion

Compare the **Gaussian probability distribution of random errors**

$$f(\varepsilon) = \frac{1}{\sigma\sqrt{2\pi}}\, e^{-\varepsilon^2/2\sigma^2}$$

and the **concentration distribution of randomly diffusion molecules**

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

Important Result

The randomly diffusing molecules form a Gaussian distribution with **variance $\langle x^2\rangle = 2Dt$.**   ***Statistics strikes again*!**

Statistical Interpretation of Diffusion

Gaussian distribution of random errors

average error $< \varepsilon > \; = \; 0$

average squared error $< \varepsilon^2 > \; = \; \sigma^2$

Gaussian distribution of randomly diffusing molecules

average displacement from $< x > \; = \; 0$

average squared displacement $< x^2 > \; = \; \sigma^2 \; = 2Dt$

Application: Diffusion Coefficient Measurements

Determine average squared displacements of molecules using:

- radioactive isotopes
- nuclear magnetic resonance spectroscopy
- uv, visible or IR absorbance spectroscopy
- conductivity changes (for electrolytes)

etc.

Calculate diffusion coefficients:

$$D = \langle x^2 \rangle / 2t$$

Example: Calculate the **root-mean-square displacement*** of argon atoms at 298 K and 1 atm after diffusion for 1, 100, and 10,000 s. *Data*: $D = 1.87 \times 10^{-5}\ \mathrm{m^2\ s^{-1}}$

$$\text{rms displacement} = \sqrt{<x^2>} = \sqrt{2Dt}$$ (in one dimension)

$\boxed{t = 1\ \mathrm{s}}$

$$\sqrt{<x^2>} = \sqrt{2\,(1.87\times 10^{-5}\ \mathrm{m^2\ s^{-1}})\,(1\ \mathrm{s})} = 0.00611\ \mathrm{m}$$

$\boxed{t = 10^2\ \mathrm{s}}$

$$\sqrt{<x^2>} = \sqrt{2\,(1.87\times 10^{-5}\ \mathrm{m^2\ s^{-1}})\,(100\ \mathrm{s})} = 0.0611\ \mathrm{m}$$

$\boxed{t = 10^4\ \mathrm{s}}$

$$\sqrt{<x^2>} = \sqrt{2\,(1.87\times 10^{-5}\ \mathrm{m^2\ s^{-1}})\,(10^4\ \mathrm{s})} = 0.611\ \mathrm{m}$$

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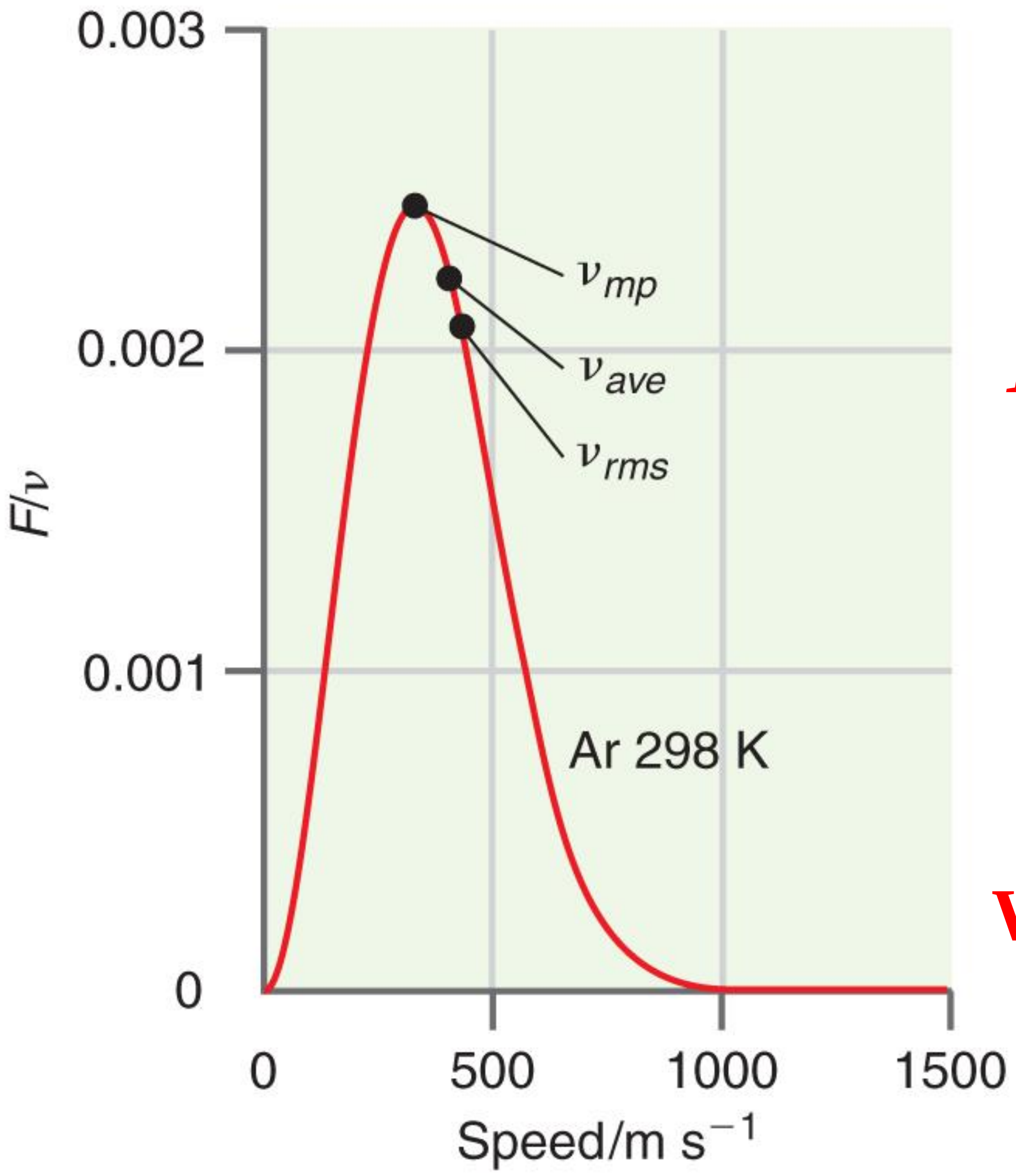
*Why not use the “rsm” displacement = $\sqrt{<x>^2}$ **?**

Comparison of Diffusion and Molecular Speeds



Argon atoms diffuse about 1 cm per second.

But wait!

Argon atoms are moving at average speeds of hundreds of meters per second.

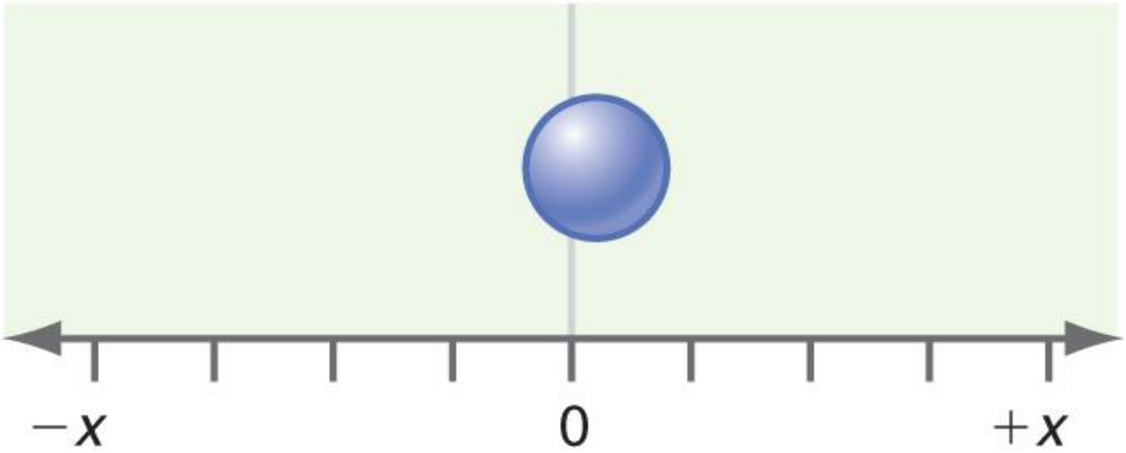
Why is diffusion so slow?

Diffusion as a Random Walk

A useful interpretation of diffusion can be developed by treating molecular motions as a series of steps in random directions.

Suppose a molecule is located at position $x = 0$ at time $t = 0$.

Model Every τ seconds the molecule takes a step of length λ. Steps in the positive- and negative x-direction are equally probable.



Diffusion as a Random Walk

After diffusion for time t and $N = t/\tau$ diffusion steps randomly left or right, a statistical analysis shows the probability $P(x)\mathrm{d}x$ of finding the molecule between x and $x + \mathrm{d}x$ is

$$P(x)\mathrm{d}x = \frac{1}{\sqrt{2\pi N\lambda^2}}\,\mathrm{e}^{-x^2/2N\lambda^2} = \frac{1}{\sqrt{2\pi t\lambda^2/\tau}}\,\mathrm{e}^{-x^2\tau/2\lambda^2 t}$$

Compare this result with the concentration distribution calculated by solving Fick's law of diffusion

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

Diffusion as a Random Walk

Conclusion: A diffusing molecule taking steps of length λ every τ seconds has diffusion coefficient

$$\boxed{D = \frac{\lambda^2}{2\tau}}$$

Accounts qualitatively for the larger diffusion coefficients of gases (longer step length) relative to liquids.

Diffusion in solids is even smaller: short step length and lower step frequency (high activation energy)

Diffusion and Thermodynamics

The negative gradient of a potential energy is a force.

Example The gravitational potential energy of mass *m* at height *h* is *mgh*. The gravitational force is –d(*mgh*)/d*h* = –*mg* (negative, acting downward).

Similarly, the **driving force for diffusion**

$$\boxed{-\frac{\partial \mu}{\partial x} = -\frac{\partial \mu}{\partial C}\frac{\partial C}{\partial x}}$$

is the negative gradient in the chemical potential. Substances diffuse from higher to lower chemical potential.

Diffusion and Thermodynamics

The **mobility** Λ of a molecule
is defined as the diffusion velocity
generated per unit driving force:

$$\boxed{\Lambda = \frac{v_{\text{diff}}}{\text{driving force}}}$$

diffusion flux density:

$$J_x = C v_{x,\text{diff}} = C\Lambda \times (\text{driving force}) = C\Lambda \times \left(-\frac{\partial \mu}{\partial x}\right) = -\Lambda C \frac{\partial \mu}{\partial C} \frac{\partial C}{\partial x}$$

compare with Fick’s law of diffusion:

$$J_x = -D \frac{\partial C}{\partial x}$$

Find:

$$\boxed{D = (\text{mobility}) \times (\text{thermodynamic factor}) = (\Lambda) \times \left(C \frac{\partial \mu}{\partial C} \right)}$$

Diffusion and Thermodynamics

$$D = \Lambda C \frac{\partial \mu}{\partial C}$$

For an ideal system (activity coefficient = 1):

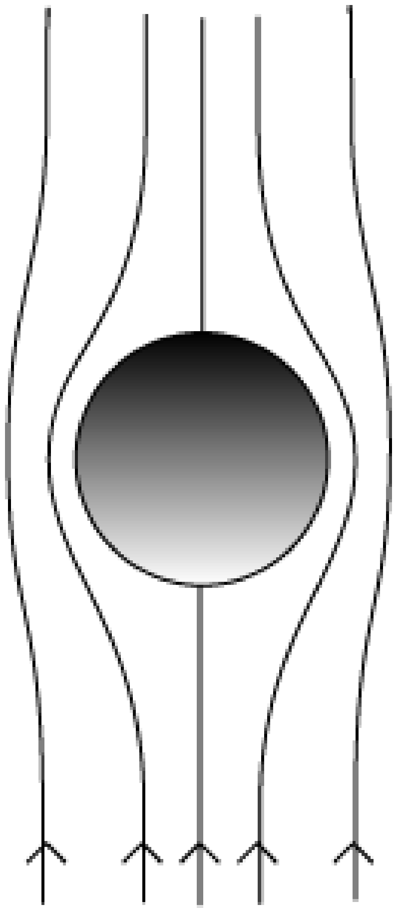
$$D = \Lambda C \frac{\partial(\mu^{\circ} + kT \ln C)}{\partial C} = kT\Lambda$$

Stokes-Einstein equation

Application: diffusion and sedimentation in liquids

Small, compact molecules in low-viscosity solvents have relatively large mobilities and diffusion coefficients.

Use diffusion measurements to determine mobilities and the sizes and shapes of molecules in solutions.



Drop a steel ball bearing of radius *r*
into a jar of honey or thick oil of viscosity η.

The gravitational force on the ball bearing (down) balanced by an equal frictional force in the opposite direction (up).

The ball bearing reaches a constant "terminal velocity" as it drops.

From hydrodynamics, the mobility of the ball bearing is:

$$\Lambda = \frac{1}{6\pi r \eta}$$

Spherical molecule of radius r in a **liquid** of viscosity η

mobility

$$\Lambda = \frac{1}{6\pi r \eta}$$

diffusion coefficient

$$D = kT\Lambda = \frac{kT}{6\pi r \eta}$$

Do molecules exist?

Seeing is believing.

Use a microscope to follow the random zig-zag motion of particles diffusing in water (**Brownian motion**).

Measure the average squared displacement $<x^2>$ of particles of measured radius r after diffusion for time t in a solvent of viscosity η.

$$D = \frac{< x^2 >}{2t} = \frac{kT}{6\pi r \eta}$$

Calculate microscopic *Boltzmann constant k* from macroscopic diffusion measurements and Avogadro's number from the *molar gas constant* : R/k.

We’ll consider diffusion in one-dimension only.

In general, diffusion fluxes are three-dimensional **vectors** with *x*, *y* and *z* components.

$$\vec{J} = J_x\hat{i} + J_y\hat{j} + J_z\hat{k}$$

$$\vec{J} = D\vec{\nabla}C$$

$$\frac{\partial C(x,y,z)}{\partial t} = D\left(\frac{\partial^2 C}{\partial x^2} + \frac{\partial^2 C}{\partial y^2} + \frac{\partial^2 C}{\partial z^2}\right) = D\nabla^2 C(x,y,z)$$

$$\text{rms displacement} = \sqrt{< x^2 > + < y^2 > + < z^2 >} = \sqrt{6Dt}$$

Section 17.5 Thermal Conductivity

Transport of energy by the conduction of heat driven by a temperature gradient.

Fourier's Law of Heat Conduction

$$\boxed{J_x = -\kappa \frac{\partial T}{\partial x}}$$

J_x = flux density of heat in the x-direction [$\mathrm{J\ m^{-2}\ s^{-1}}$]

κ = thermal conductivity [$\mathrm{J\ K^{-1}\ m^{-1}\ s^{-1} = W\ K^{-1}\ m^{-1}}$]

$\frac{\partial T}{\partial x}$ = temperature gradient [$\mathrm{K\ m^{-1}}$]

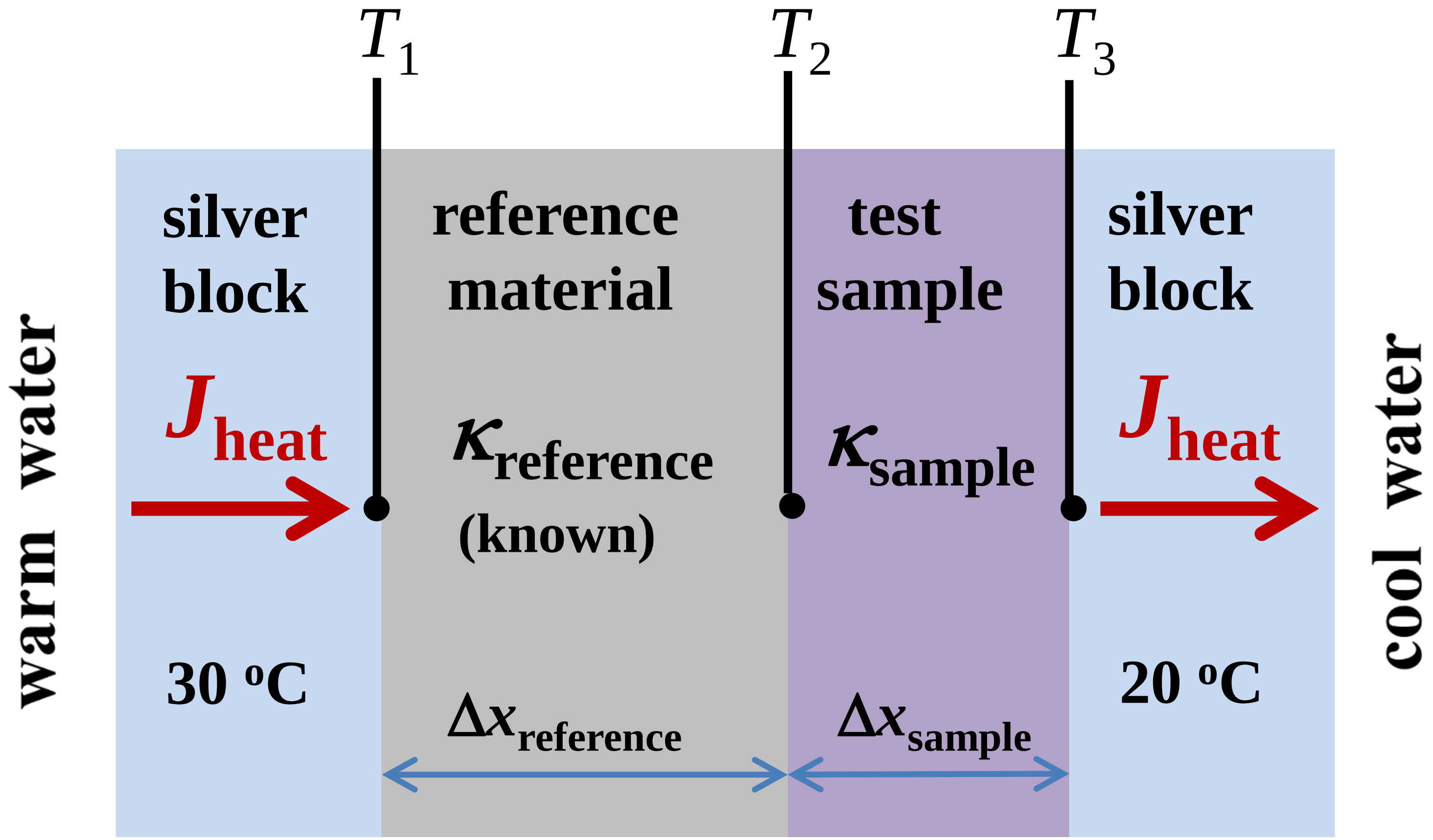
Thermal Conductivities at 300 K and 1 bar

	κ / J K^{-1} m^{-1} s^{-1}
argon (g)	0.018
air	0.026
hydrogen (g)	0.18
fiberglass insulation	0.045
water (g)	0.016
water (*l*)	0.61
aluminum	250
copper	400
silver	430
stainless steel	16
graphite	25 to 500
diamond	2200
diamond (^{12}C-enriched)	3200

Thermal Conductivity – Applications

- rates of heat transfer – how fast systems warm up or cool down
- design of heat exchangers in furnaces, refrigerators, heat pumps, radiators, chemical reactors, …
- thermal insulation to reduce heat transfer
- performance of advanced computer chips is limited by how rapidly heat can be dissipated
- how long does it take to bake and roast food – when’s dinner?
- thermal conductivities provide information about transport of energy by vibrations in solids and molecular collisions in fluids

Thermal Conductivity – Measurement



T_1 T_2 T_3

warm water

silver block

J_{heat}

30 °C

reference material

$\kappa_{\text{reference}}$ (known)

$\Delta x_{\text{reference}}$

test sample

κ_{sample}

Δx_{sample}

silver block

J_{heat}

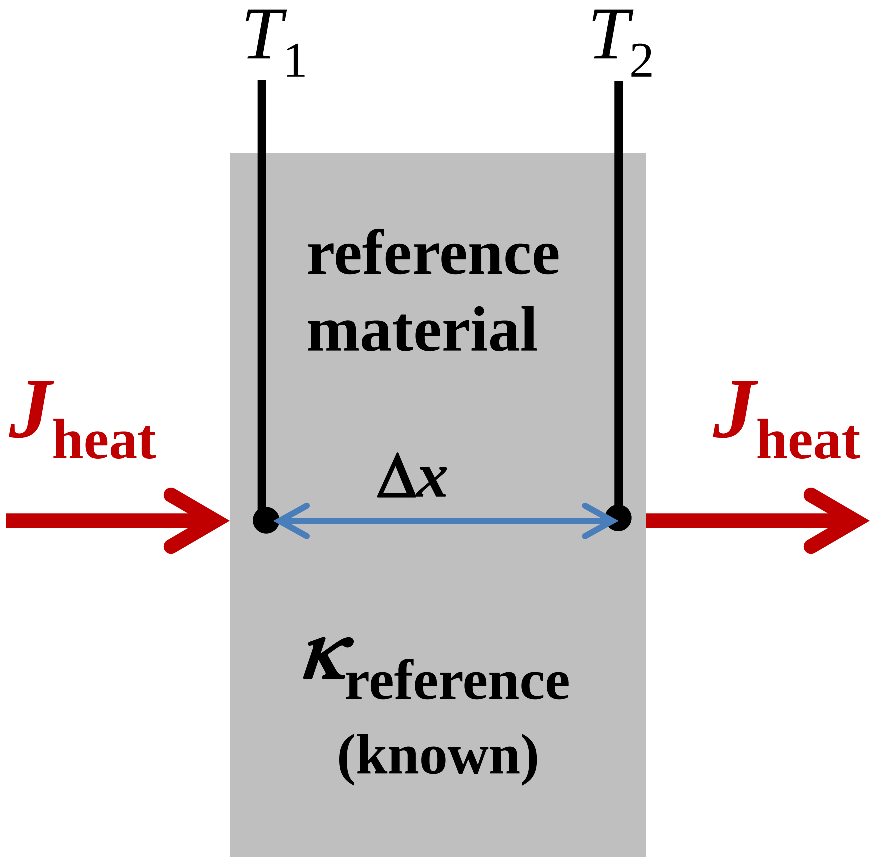
20 °C

cool water

$$J_{\text{heat}} = -\kappa_{\text{reference}} \frac{T_2 - T_1}{\Delta x_{\text{reference}}} = -\kappa_{\text{sample}} \frac{T_3 - T_2}{\Delta x_{\text{sample}}}$$

$$\boxed{\kappa_{\text{sample}} = \kappa_{\text{reference}} \frac{T_2 - T_1}{T_3 - T_2} \frac{\Delta x_{\text{sample}}}{\Delta x_{\text{reference}}}}$$

Heat Flow Sensor

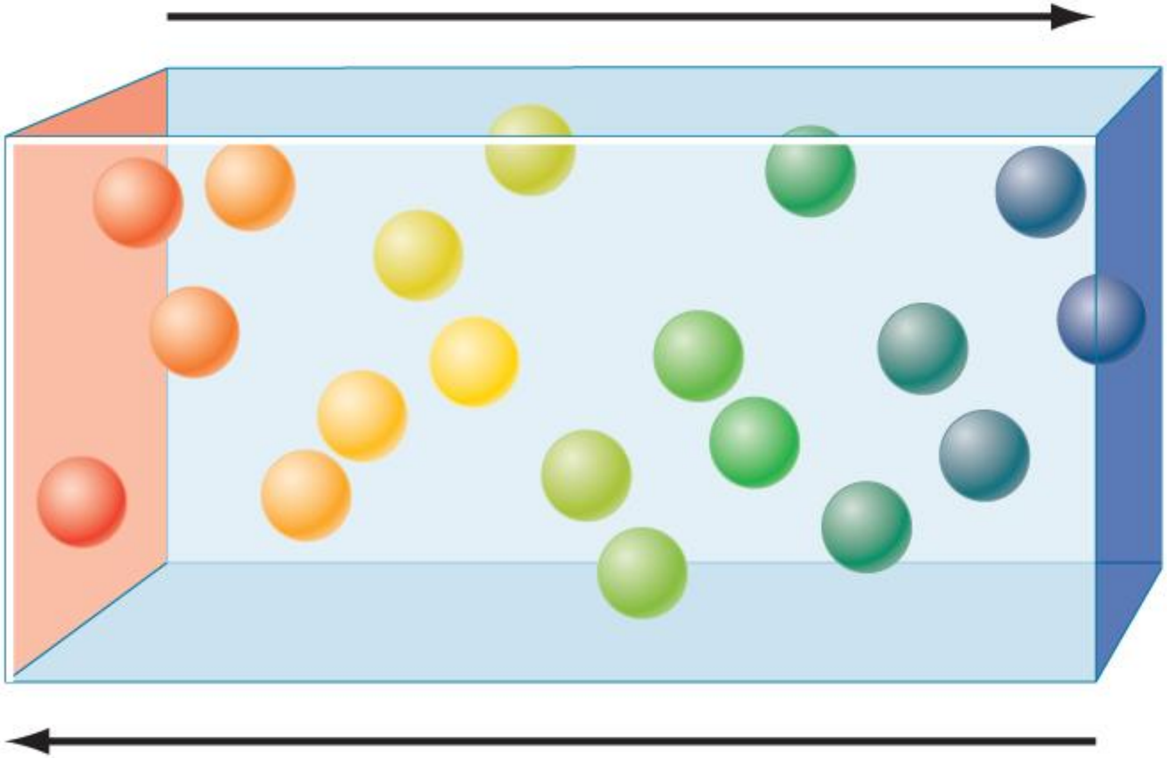


$$J_{\text{heat}} = -\kappa_{\text{reference}}\,(T_2 - T_1)/\Delta x$$

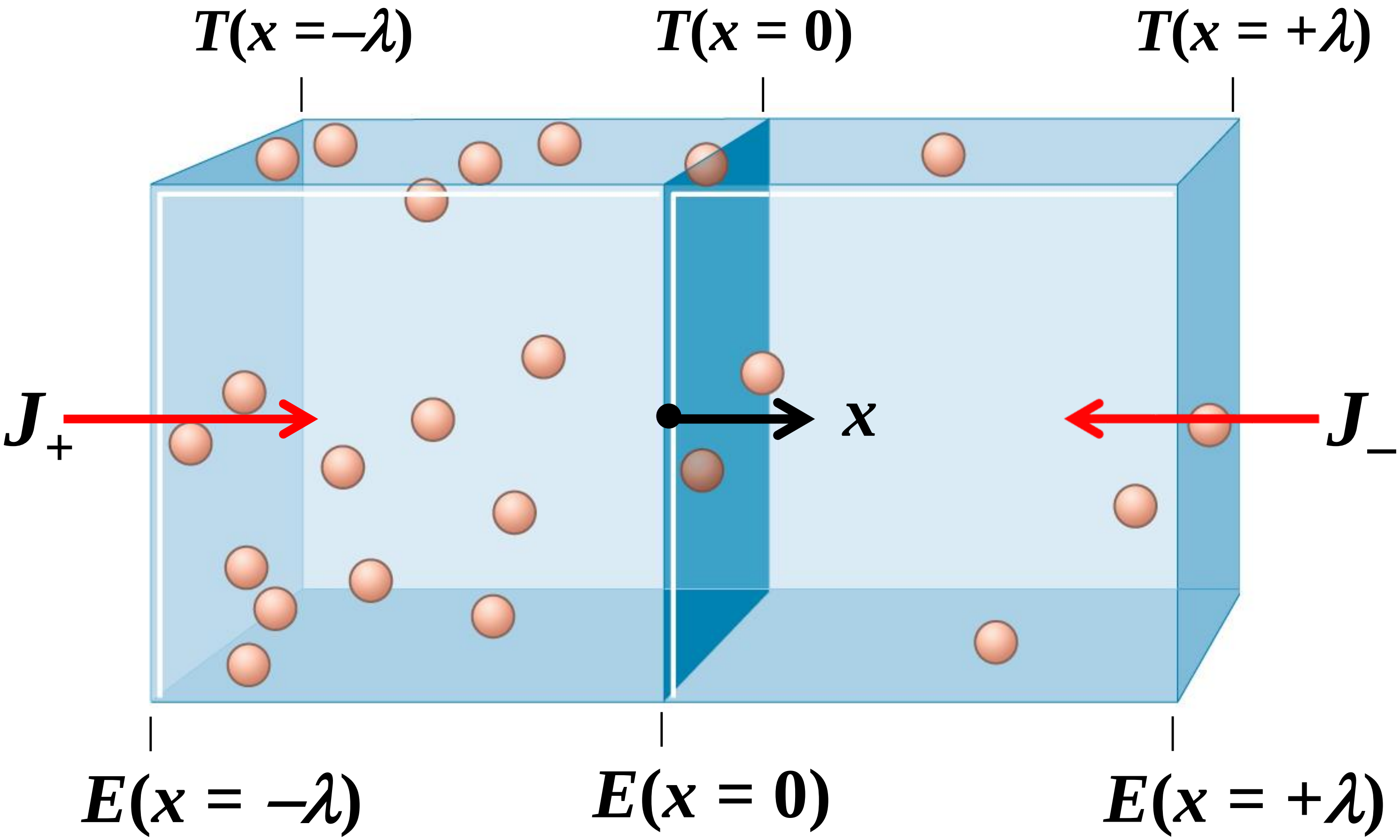
Heat Flow Sensors

Thermal Conductivity of Gases

heat flow $J_x = -\kappa \partial T/\partial x$



temperature



$$\boxed{J_+ = \left[E(x=0) - \lambda\frac{\partial E}{\partial x}\right] C\frac{<v>}{4}}$$

$$\boxed{J_- = \left[E(x=0) + \lambda\frac{\partial E}{\partial x}\right] C\frac{<v>}{4}}$$

***E* = average energy per molecule**

Thermal Conductivities from Kinetic Theory

$$\boxed{J_x = -\kappa \frac{\partial T}{\partial x}}$$

Net heat flux in the *x*-direction:

$$J_x = J_+ - J_-$$

$$\approx \left[E(x=0) - \lambda \frac{\partial E}{\partial x} \right] C \frac{<v>}{4} - \left[E(x=0) + \lambda \frac{\partial E}{\partial x} \right] C \frac{<v>}{4}$$

$$= -\lambda \frac{<v>}{2} C \frac{\partial E}{\partial x}$$

***approximate* thermal conductivity**:

$$= -\lambda \frac{<v>}{2} C \frac{\partial E}{\partial T} \frac{\partial T}{\partial x}$$

$$\boxed{\kappa_{\mathrm{a}} \approx \frac{1}{2} \lambda <v> C \frac{\partial E}{\partial T}}$$

$$= -\kappa \frac{\partial T}{\partial x}$$

Why approximate? Molecules collide and scatter over distances of λ.

Thermal Conductivities of Gases from Kinetic Theory

$$\boxed{J_x = -\kappa \frac{\partial T}{\partial x}}$$

$C = N/V = p/kT$

For hard spheres (translational kinetic energy only) $E = 3kT/2$ and $\partial E/\partial T = 3k/2$.

$$\kappa_{\mathrm{a}} \approx \frac{1}{2}\lambda < v > C \frac{\partial E}{\partial T} = \sqrt{\frac{kT}{\pi m}}\,\frac{1}{\sigma}\,\frac{3}{2}k$$

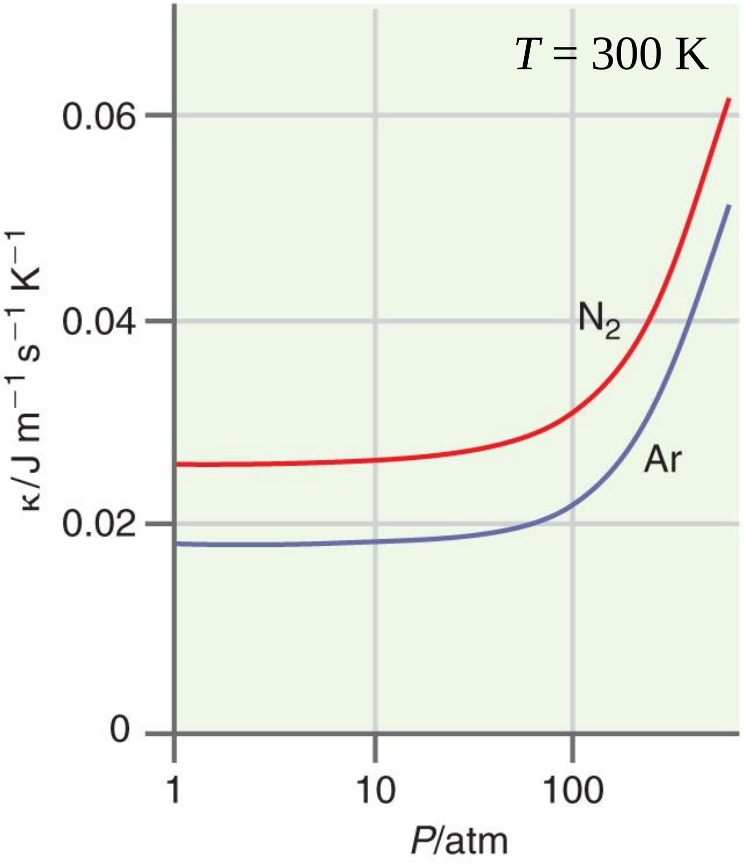
exact **thermal conductivity for hard spheres**:

$$\boxed{\kappa = \frac{25\pi}{32}\sqrt{\frac{kT}{\pi m}}\,\frac{1}{\sigma}\,\frac{3}{2}k}$$

Thermal Conductivities of Gases from Kinetic Theory

$$\boxed{\kappa \propto \lambda < v > C}$$

Give two reasons why helium has a relatively high thermal conductivity.



The predicted thermal conductivity is independent of pressure for ideal gases.

Why?

Section 17.5 Viscosity

Transport of momentum caused by friction between layers of fluid moving at different speeds.

Newton's Law of Viscosity

$$\boxed{J_z = -\eta \frac{\partial v_x}{\partial z}}$$

J_z = flux density of momentum [kg m^{-1} s^{-2} = N m^{-2}] in the z-direction, perpendicular to the velocity in the x-direction

η = viscosity [kg m^{-1} s^{-1} = Pa s]

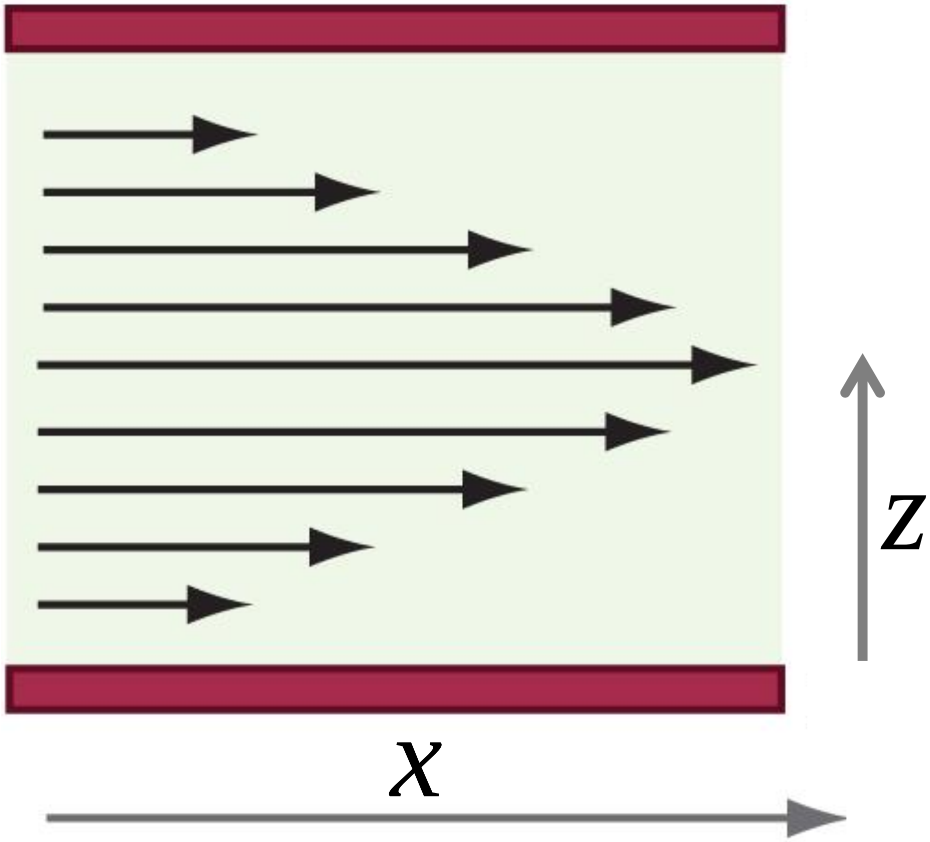
$\frac{\partial v_x}{\partial z}$ = velocity gradient in the z-direction [s^{-1}]

Viscosity and *Fluid Mechanics*

- flow of fluids (liquids and gases) in tubes and pipes, in porous media, around objects …
- design of pumps, plumbing, turbines, chemical reactors …
- circulatory systems (atmospheric, oceanic, physiological …)
- shock waves, explosions and ballistics
- computational fluid dynamics (CFD)
- aerodynamics
- ***rocket science !***

Example: Gas or Liquid Flowing Between Stationary Plates

Friction causes the fluid velocity to drop to zero at the plate surfaces.



minimum $v_x = 0$

maximum v_x (centerline)

minimum $v_x = 0$

similar to the flow of water in a creek

Selected Viscosities at 298 K and 1 bar

	η / Pa s
helium (g)	$20. \times 10^{-6}$
hydrogen (g)	9.0×10^{-6}
argon (g)	$23. \times 10^{-6}$
carbon dioxide (g)	$15. \times 10^{-6}$
air	$19. \times 10^{-6}$
water (*l*)	8.9×10^{-4}
benzene (*l*)	6.0×10^{-4}
acetone (*l*)	3.1×10^{-4}
mercury (*l*)	$15. \times 10^{-4}$
motor oil (SAE 10) (*l*)	0.065
motor oil (SAE 40) (*l*)	0.32
glycerol (*l*)	1.2
thick tar	$\approx 10^{8}$
upper mantle (2000 K)	$\approx 10^{21}$ (continental drift!)

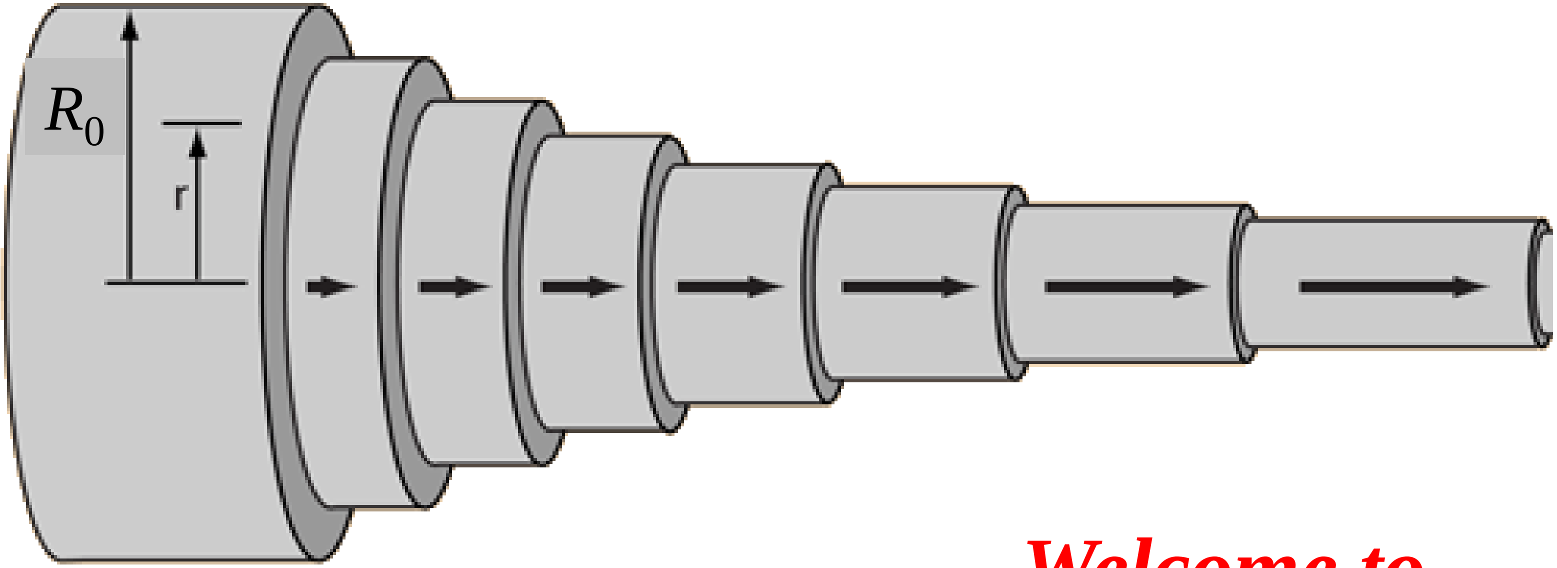
Viscosities of Air and Water at Different Temperatures

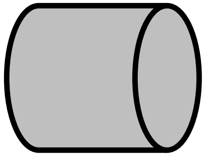
temperature / °C	**η (air, g) / 10^{-6} Pa s**	**η (H_2O, *l*) / 10^{-3} Pa s**
0	17.2	1.79
25	18.4	0.891
50	19.5	0.547
75	20.6	0.379
100	21.7	0.283

?

Flow of Fluid in a Tube of Radius R_0

Flow rate? Required pressure? Flow pattern?

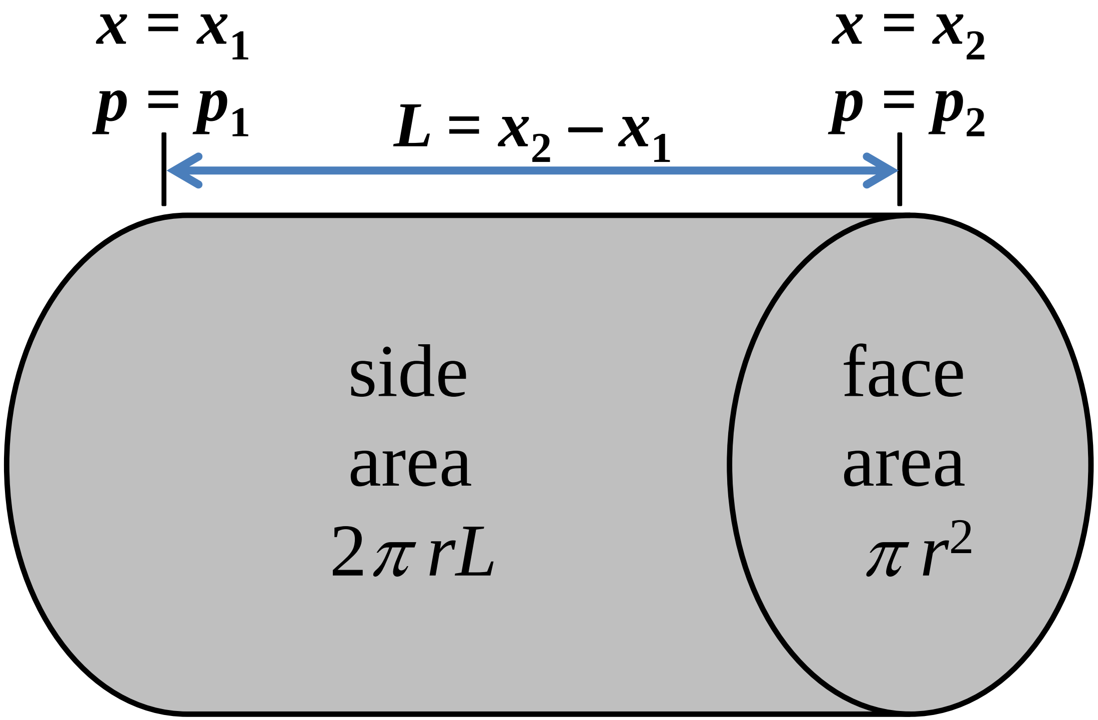




Welcome to
Fluid Mechanics !

Flow of Fluid in a Tube of Radius R_0

- assume **steady laminar flow** (no acceleration or turbulence)
- apply **force balance** to a cylinder of radius *r* and length *L*

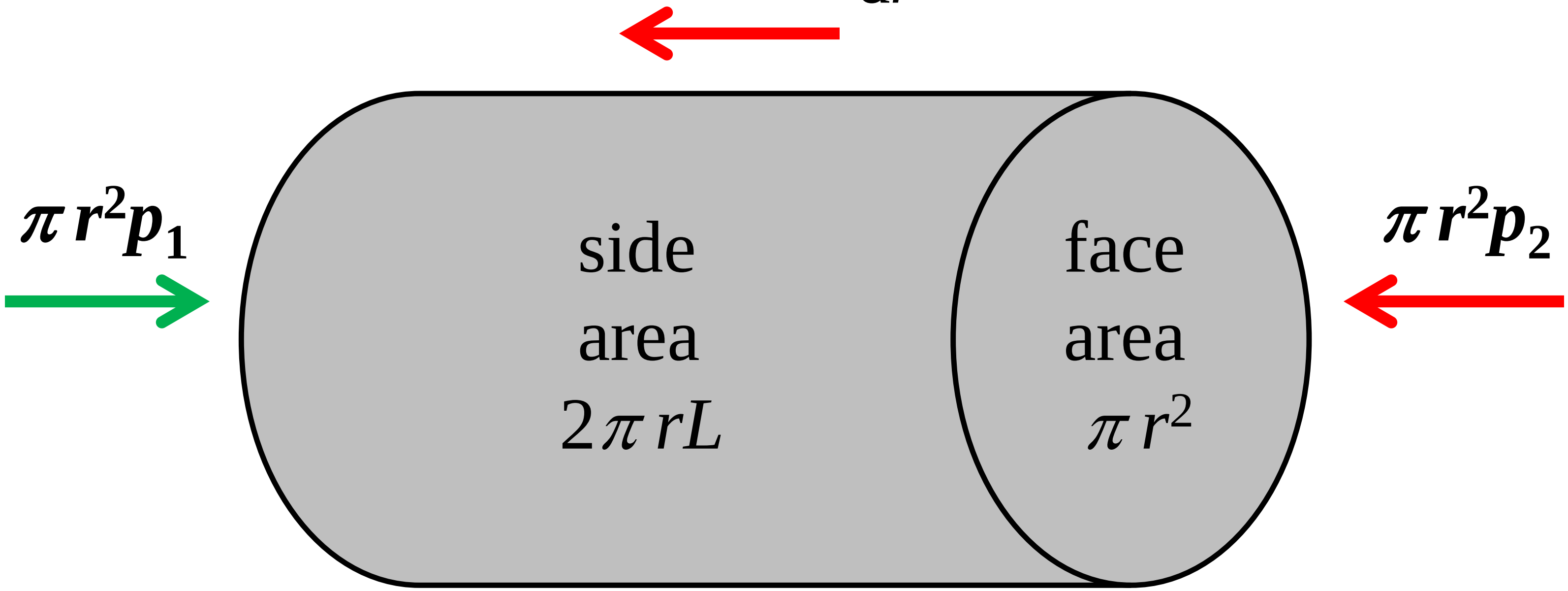


Flow of Fluid in a Tube of Radius R_0

$$\boxed{\pi r^2 p_1 - \pi r^2 p_2 + (2\pi rL)\eta \frac{\mathrm{d}v_x}{\mathrm{d}r} = 0}$$

force balance

frictional force $(2\pi rL)\eta \frac{\mathrm{d}v_x}{\mathrm{d}r}$ on side area



$\boldsymbol{\pi r^2 p_1}$

side area $2\pi rL$

face area πr^2

$\boldsymbol{\pi r^2 p_2}$

Flow of Fluid in a Tube of Radius R_0

$$\pi r^2 p_1 \; - \; \pi r^2 p_2 \; + \; (2\pi rL)\eta \frac{\mathrm{d}v_x}{\mathrm{d}r} \; = \; 0$$

divide by $4\pi r^2 L\eta$

$$\frac{1}{2r}\frac{\mathrm{d}v_x}{\mathrm{d}r} \; = \; \frac{1}{4\eta}\frac{p_2 - p_1}{L}$$

use $2r\mathrm{d}r = \mathrm{d}r^2$ to get

$$\frac{\mathrm{d}v_x}{\mathrm{d}r^2} \; = \; \frac{1}{4\eta}\frac{\mathrm{d}p}{\mathrm{d}x}$$

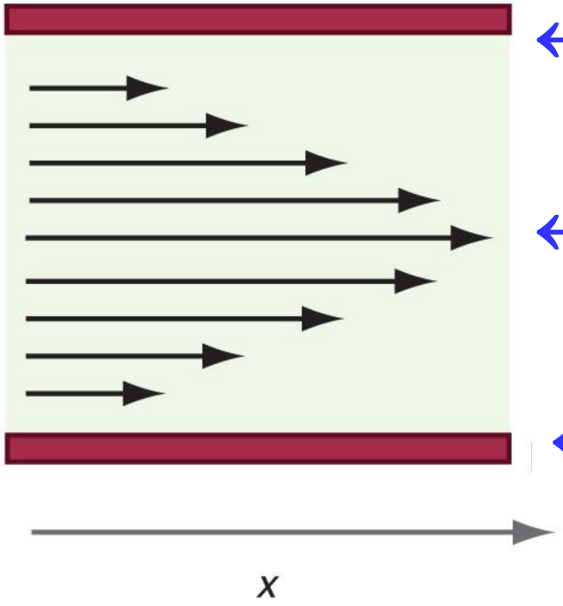
integrate from
$v_x = 0$ at the
tube wall ($r = R_0$)

$$\int_0^{v(r^2)} \mathrm{d}v_x \; = \; \frac{1}{4\eta}\frac{\mathrm{d}p}{\mathrm{d}x}\int_{r^2=R_0^2}^{r^2} \mathrm{d}r^2$$

Velocity Profile in a Tube of Radius R_0

$$\boxed{v_x(r) = \frac{1}{4\eta}\frac{\mathrm{d}p}{\mathrm{d}x}\left(r^2 - R_0^2\right) = v_{\max}\left(1-\frac{r^2}{R_0^2}\right)}$$

parabolic velocity profile



← $r = R_0$

← $r = 0$

← $r = R_0$

maximum velocity (at the tube centerline):

$$\boxed{v_{\max} = v_x(r=0) = -\frac{R_0^2}{4\eta}\frac{\mathrm{d}p}{\mathrm{d}x}}$$

Total Volume Flow Rate (for liquids)

Volume flow rate through a ring from r to r + dr of area $2\pi r\mathrm{d}r$ is $2\pi r v_x(r)\mathrm{d}r$. Integrate:

$$\frac{\mathrm{d}V}{\mathrm{d}t} = \int_0^{R_0} 2\pi r v_x(r)\mathrm{d}r = \frac{2\pi}{4\eta}\frac{\mathrm{d}p}{\mathrm{d}x}\int_0^{R_0} r(r^2 - R_0^2)\mathrm{d}r$$

Total Volume Flow Rate

$$\boxed{\frac{\mathrm{d}V}{\mathrm{d}t} = -\frac{\pi R_0^4}{8\eta}\frac{\mathrm{d}p}{\mathrm{d}x}}$$

Poiseuille Equation for liquids

total volume flow rate proportional to

- $R_0{}^4$
- $1/\eta$ (the **fluidity**)
- pressure gradient $-\mathrm{d}p/\mathrm{d}x$

Valid for laminar flow of incompressible liquids (“liter in, liter out”).

Try This A tube radius is reduced by 10 %. Show that the pressure gradient must be increased by 52 % to maintain the same volume flow rate. (Important cardiovascular implications.)

Try This The volume flow rate of fluid in a tube is

$$\frac{\mathrm{d}V}{\mathrm{d}t} = (\text{area}) \times (\text{average flow speed}) = \pi R_0^2 v_{\text{average}}$$

Show that the average flow speed is:

$$v_{\text{average}} = \frac{v_{\text{max}}}{2} = -\frac{R_0^2}{8\eta}\frac{\mathrm{d}p}{\mathrm{d}x}$$

Example Liquid water is pumped through a 30 cm length of chromatography tubing (inner diameter of 0.010 inch) at a flow rate of 1.00 mL per minute. Calculate the pressure drop.
Data: $\eta = 0.000891$ Pa s.

flow rate
$$\frac{\mathrm{d}V}{\mathrm{d}t} = \frac{1.00\ \mathrm{cm}^3}{60\ \mathrm{s}}\ \frac{10^{-6}\ \mathrm{m}^3}{\mathrm{cm}^3} = 1.67 \times 10^{-8}\ \mathrm{m}^3\ \mathrm{s}^{-1}$$

tube radius
$$R_0 = \frac{0.010\ \mathrm{inch}}{2}\ \frac{2.54\ \mathrm{cm}}{\mathrm{inch}}\ \frac{0.01\ \mathrm{m}}{\mathrm{cm}} = 1.27 \times 10^{-4}\ \mathrm{m}$$

$$\frac{\mathrm{d}p}{\mathrm{d}x} = -\frac{8\eta}{\pi R_0^4}\frac{\mathrm{d}V}{\mathrm{d}t} = -\frac{8\,(0.000891)}{\pi\,(0.000127)^4}\,(1.67 \times 10^{-8}) = -1.45 \times 10^{-5}\ \frac{\mathrm{Pa}}{\mathrm{m}}$$

(all SI units)

$$\frac{\mathrm{d}p}{\mathrm{d}x} = -1.45 \times 10^{-5}\ \frac{\mathrm{Pa}}{\mathrm{m}} = \frac{p_2 - p_1}{x_2 - x_1} = \frac{p_2 - p_1}{0.30\ \mathrm{m}}$$

$$p_2 - p_1 = -\,44{,}000\ \mathrm{Pa} = -\,0.44\ \mathrm{bar}$$

Flow Rates for Gases

The volume flow rate of gases is not constant, even for steady flows. **Gases are compressible!** For example, a liter in at p_1 produces two liters of gas downstream at p_2 if $p_1/p_2 = 2$.

But for **steady flow**: $\frac{\mathrm{d}N}{\mathrm{d}t} = \text{constant at any tube cross section}$

At any cross section along the tube (constant pressure p):

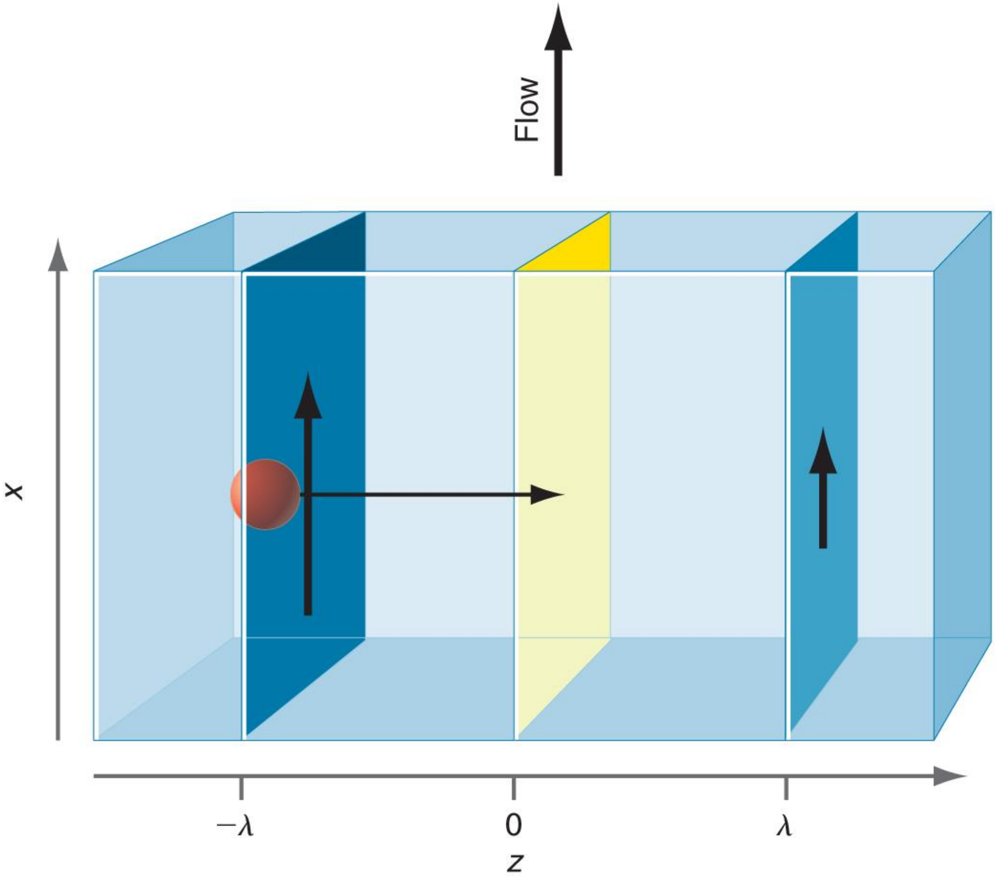
$$\frac{\mathrm{d}N}{\mathrm{d}t} = \frac{\mathrm{d}(pV/kT)}{\mathrm{d}t} = \frac{p}{kT}\frac{\mathrm{d}V}{\mathrm{d}t} = -\frac{p}{kT}\frac{\pi R_0^4}{8\eta}\frac{\mathrm{d}p}{\mathrm{d}x} = -\frac{1}{kT}\frac{\pi R_0^4}{16\eta}\frac{\mathrm{d}p^2}{\mathrm{d}x}$$

Flow rate of gas molecules proportional to dp^2/dx (*not to* dp/dx).

$$\boxed{\frac{\mathrm{d}N}{\mathrm{d}t} = -\frac{1}{kT}\frac{\pi R_0^4}{16\eta}\frac{\mathrm{d}p^2}{\mathrm{d}x} = -\frac{1}{kT}\frac{\pi R_0^4}{16\eta}\frac{p_2^2 - p_1^2}{x_2 - x_1}}$$

Poiseuille Equation
for ideal gases

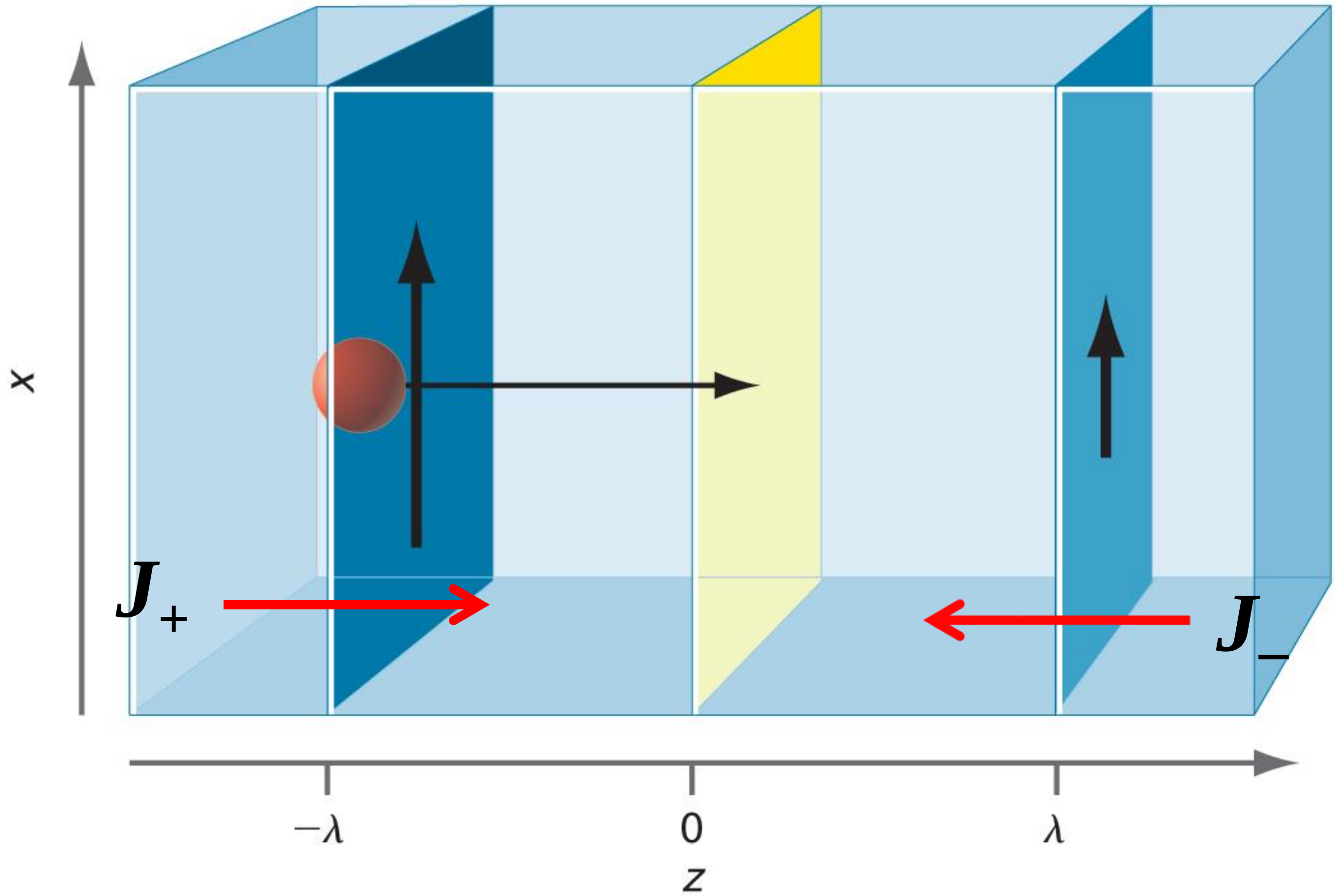
Section 17.6 Kinetic Theory of Gas Viscosity



Molecules jumping back and forth produce friction between layers of gas flowing at different speeds.

Slower molecules jumping into the faster layer slow it down. Faster molecules jumping into the slower layer speed it up.

Kinetic Theory of Gas Viscosity



$$\boxed{J_+ = C\frac{<v>}{4}\left[mv(z=0) - \lambda\frac{\partial(mv)}{\partial z}\right]}$$

$$\boxed{J_- = C\frac{<v>}{4}\left[mv(z=0) + \lambda\frac{\partial(mv)}{\partial z}\right]}$$

Kinetic Theory of Gas Viscosity

Total momentum flux across the plane at $z = 0$:

$$J_z = J_+ - J_- = -C\frac{<v>}{2}\lambda\frac{\partial(mv)}{\partial z} = -C\frac{<v>}{2}m\lambda\frac{\partial v}{\partial z}$$

Comparison with Newton's law

$$J_z = -\eta\frac{\partial v}{\partial z}$$

shows the viscosity is approximately

$$\eta_\mathrm{a} = C\frac{<v>}{2}m\lambda = \sqrt{\frac{kT}{\pi m}}\;\frac{1}{\sigma}\;m$$

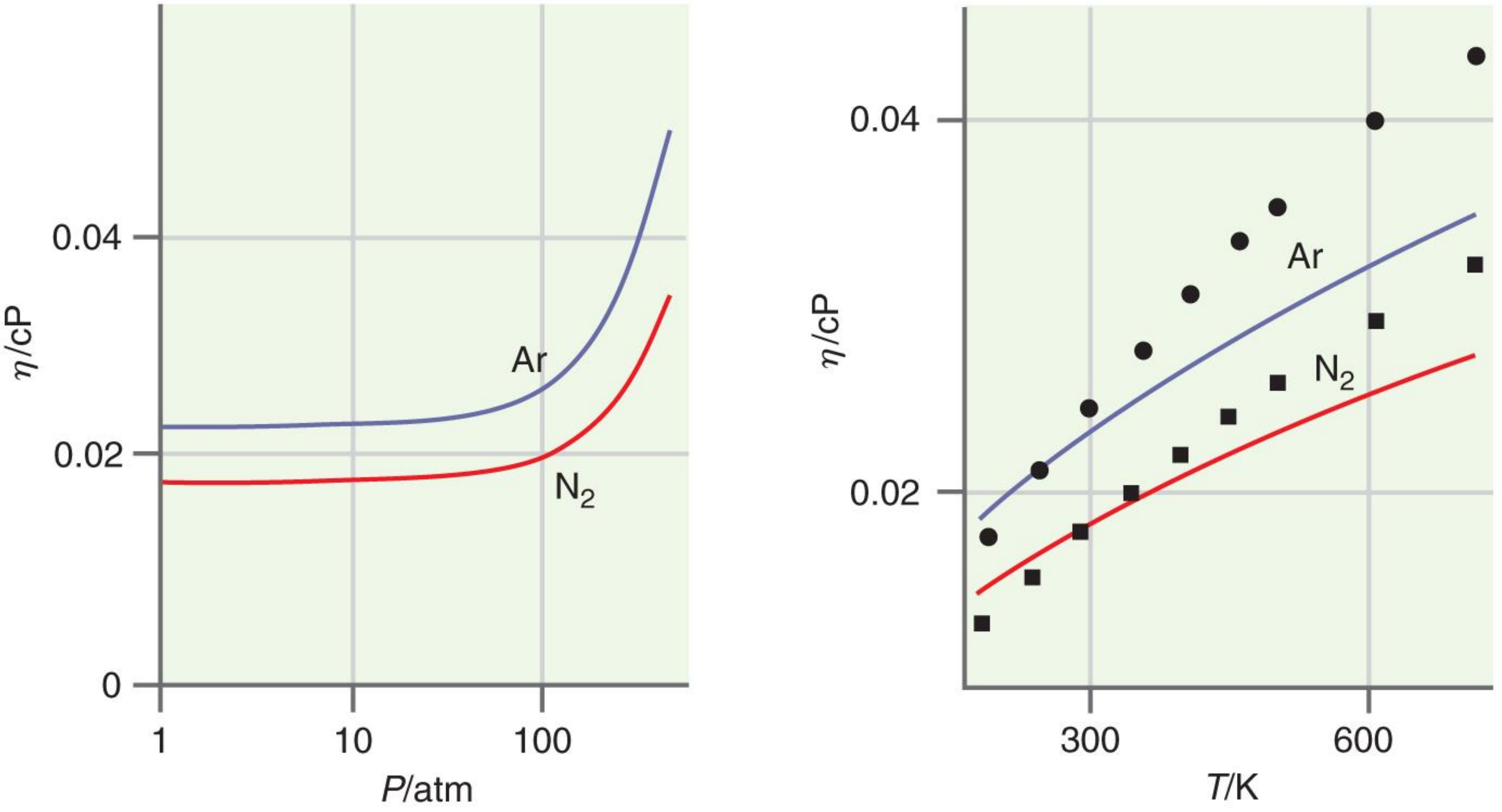
Kinetic Theory of Gas Viscosity

Exact viscosity for a gas of hard-sphere molecules (allowing for collisions over a mean free path):

$$\boxed{\eta = \frac{5\pi}{16}\eta_\mathrm{a} = \frac{5\pi}{16}\sqrt{\frac{kT}{\pi m}}\,\frac{1}{\sigma}\,m}$$

Points to ponder. The predicted viscosity:

- is independent of the pressure!
- increases with temperature!
- increases with molecular mass


η/cP
0.04
0.02
0
1
10
100
P/atm
Ar
N2
η/cP
0.04
0.02
300
600
T/K
Ar
N2

Section 17.7 Viscosity Measurements

Many methods are used for viscosity measurements. Techniques based on **flow rates through capillary tubes** are frequently used.

Example Carbon dioxide gas flows at 293 K through a 1.00-m-long tube (inner diameter 0.75 mm) with an inlet pressure of 1.05 atm and an outlet pressure of 1.00 atm. The flow rate is 2.76 cm^3 per second measured at 1.00 atm. Calculate the viscosity.

Flow rate (molecules per second) from dV/dt measured at tube outlet (1.00 atm):

$$\frac{\mathrm{d}N}{\mathrm{d}t} = \frac{\mathrm{d}(pV/kT)}{\mathrm{d}t} = \frac{p}{kT}\frac{\mathrm{d}V}{\mathrm{d}t} = \frac{101325\ \mathrm{Pa}}{(1.381\times10^{-23}\ \mathrm{J\,K^{-1}})\ (293\ \mathrm{K})}\ (2.76\times10^{-6}\ \mathrm{m^3\,s^{-1}})$$

$$\frac{\mathrm{d}N}{\mathrm{d}t} = 6.91\times10^{19}\ \mathrm{s^{-1}}$$

Example (*cont.*)

Rearrange $$\frac{\mathrm{d}N}{\mathrm{d}t} = -\frac{1}{kT}\frac{\pi R_0^4}{16\eta}\frac{\mathrm{d}p^2}{\mathrm{d}x}$$ (for <u>gases</u>)

to get $$\eta = -\frac{1}{kT}\frac{\pi R_0^4}{16}\frac{\mathrm{d}p^2}{\mathrm{d}x}\frac{1}{\mathrm{d}N/\mathrm{d}t} = -\frac{1}{kT}\frac{\pi R_0^4}{16}\frac{p_2^2 - p_1^2}{x_2 - x_1}\frac{1}{\mathrm{d}N/\mathrm{d}t}$$

$$\eta = -\frac{1}{(1.381\times10^{-23})(293)}\frac{\pi(0.00075/2)^4}{16}\frac{[101325^2 - (1.05\times101325)^2]}{1.00}\frac{1}{6.91\times10^{19}}$$

(*all SI units*)

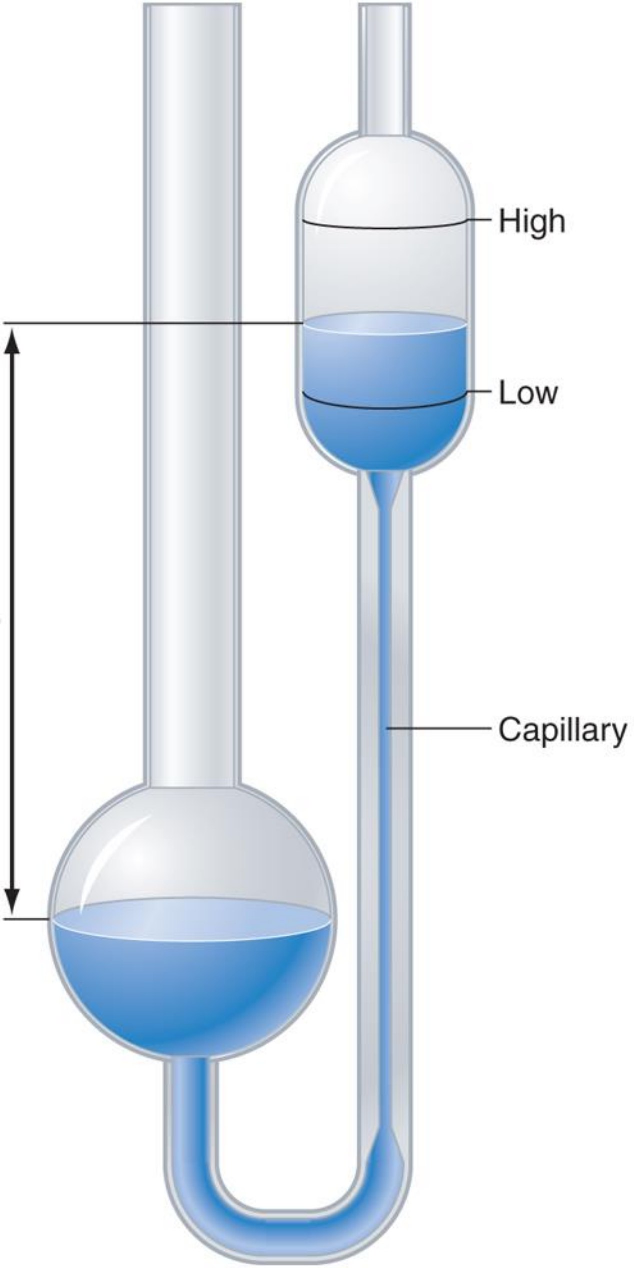
$$\eta = 1.46 \times 10^{-5}\ \mathrm{Pa\ s}$$

Capillary Viscometer for Liquids

A column of liquid of density ρ and height h exerts pressure $\rho g h$.

The gravitational acceleration is $g = 9.81 \text{ m s}^{-2}$.

The time t required for a fixed volume of liquid (in the bulb) to drain through a vertical capillary is proportional to the liquid density and inversely proportional to the viscosity.

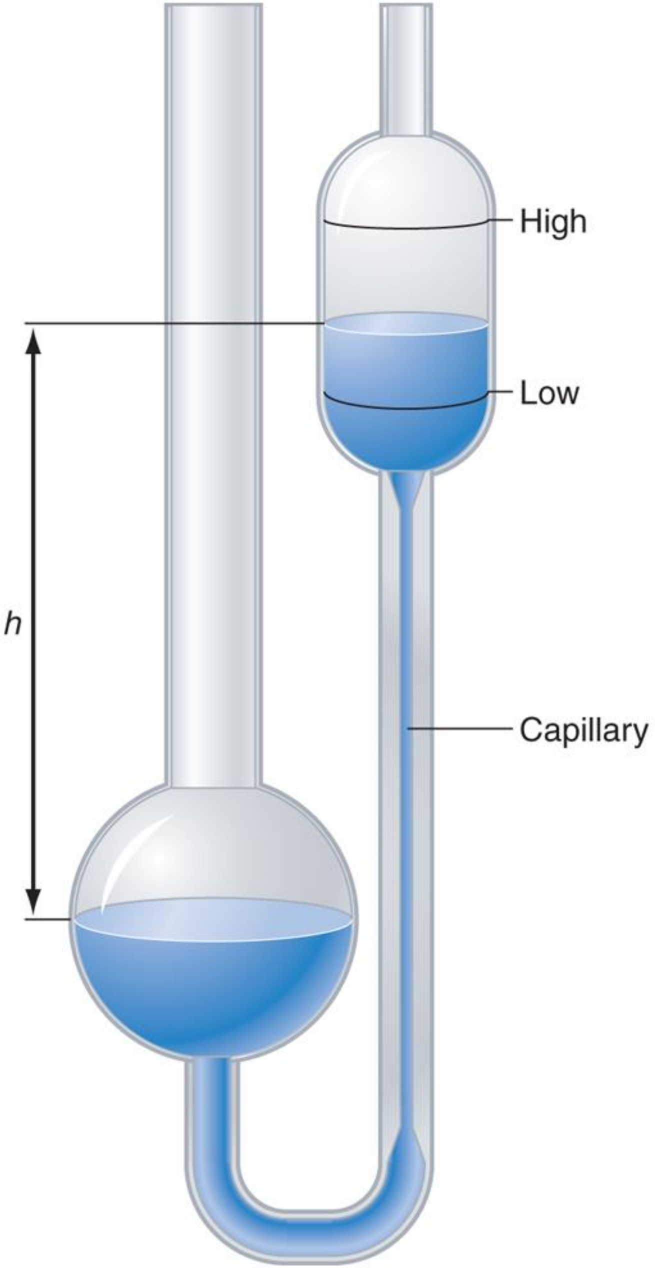


Capillary Viscometer for Liquids

drainage time $t \propto \eta\rho^{-1}$

$$\boxed{\eta = K_{\text{viscometer}}\,\rho\, t}$$

The proportionality constant $K_{\text{viscometer}}$ is determined for each viscometer by calibration with a liquid of known viscosity and density, such as pure water.



! Warnings !

Non-Newtonian Fluids

Some fluids (certain polymer solutions, thick syrups, slurries, …) do not obey Newton’s viscosity equation: the momentum flux is not proportional the velocity gradient.

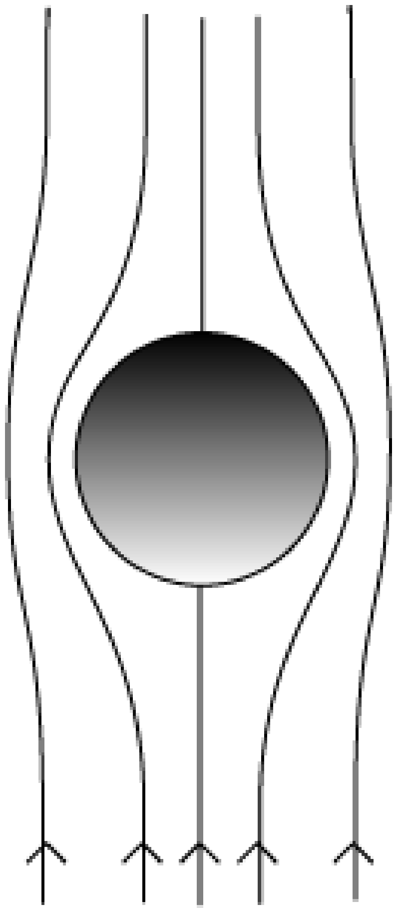
Turbulent Flow

We’ve assumed laminar flow of gases and liquids through tubes. This assumption is valid at low flow rates satisfying

$$\boxed{\text{Reynolds number } \frac{2R_0\rho v_{\text{average}}}{\eta} < 2000 \text{ for laminar flow}}$$

At higher flow rates, the fluid motion is turbulent and much more difficult to describe.

Sections 17.8 and 17.9 Sedimentation and Diffusion in Liquids



Sedimentation Experiment

Drop a steel ball bearing into a jar of honey.

The gravitational force on the ball bearing is balanced by an equal frictional force acting in the opposite direction (upward).

The ball bearing soon reaches a constant “terminal velocity” as it drops.

Stokes Law

terminal velocity = (mobility coefficient) × (applied force)

$$v_{\text{terminal}} = \Lambda F$$

The **mobility coefficient** Λ of an object depends on

- the size of the object
- the shape of the object
- flow pattern around the object (laminar? turbulent?)
- viscosity of the liquid

mobility coefficient for
a sphere of radius r

$$\Lambda = \frac{1}{6\pi\eta r}$$

(laminar flow)

Example A spherical particle (diameter 20 μm, density 1750 kg m^{-3}) settles from a suspension in water (density 1000 kg m^{-3}, viscosity 0.00089 Pa s). Calculate the terminal sedimentation velocity.

$$v_{\text{terminal}} = (\text{mobility coefficient}) \times (\text{applied force}) = \mathit{\Lambda} F$$

$$= \mathit{\Lambda} \times (\text{gravity force} - \text{buoyancy force}) = -\mathit{\Lambda} m_{\text{effective}}\, g$$

$$= -\frac{1}{6\pi\eta r}\left[\left(\frac{4}{3}\pi r^{3}\right)\left(\rho_{\text{particle}} - \rho_{\text{water}}\right)\right] g$$

(*all SI units*)

$$= -\frac{1}{6\pi\,(0.00089)\,(10\times10^{-6})}\left[\left(\frac{4}{3}\pi\,(10\times10^{-6})^{3}(1750-1000\right)\right]9.81$$

$$\boxed{v_{\text{terminal}} = -0.000734\ \text{m s}^{-1}}$$

$= -0.734$ mm s^{-1}

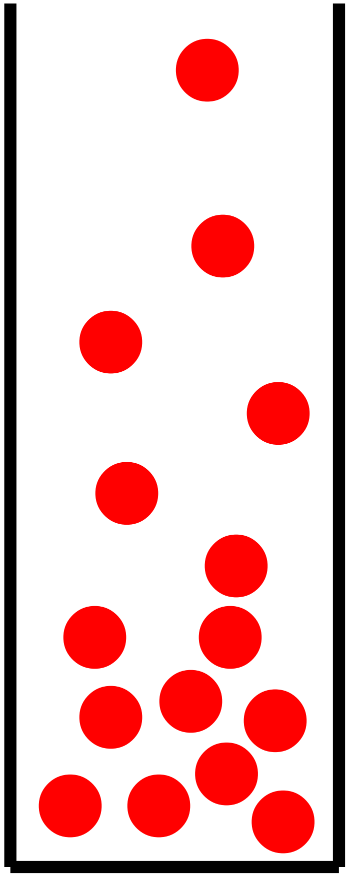
(minus sign indicates downward velocity)

terminal velocity proportional to:

$\boldsymbol{r^2}$ $\boldsymbol{\eta^{-1}}$ $\boldsymbol{\rho_{\text{particle}} - \rho_{\text{liquid}}}$ $\boldsymbol{g}$

- another way to measure viscosity – the **falling ball method** – calculate η from v_{terminal}
- **bubbles *rise*!** $(\rho_{\text{particle}} - \rho_{\text{liquid}} < 0$, so $\boldsymbol{v_{\text{terminal}} > 0})$
- **small particles settle <u>slowly</u>** – can be a problem
- **sedimentation coefficient** s defined as the terminal velocity divided by the acceleration: $\boldsymbol{s = v_{\text{terminal}} / g}$
- use a **centrifuge** for larger acceleration and faster sedimentation - replace gravity acceleration g with angular acceleration $\omega^2 R_{\text{rotor}}$

Sedimentation Equilibrium



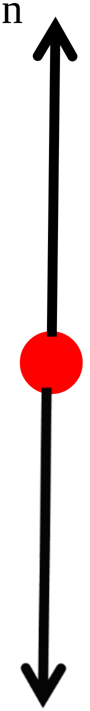
Sedimentation causes the particle concentration to increase in the lower end of the suspension.

At equilibrium:

The downward sedimentation velocity equals the upward diffusion velocity at each point along the column.

Sedimentation Equilibrium

$$v_{\text{diffusion}} = -\Lambda \mathrm{d}\mu/\mathrm{d}x$$



$$v_{\text{terminal}} = -\Lambda m_{\text{eff}} g$$

force balance:

gravitational force + diffusion force = 0

$$-m_{\text{eff}}\,g \quad - \quad \frac{\mathrm{d}\mu}{\mathrm{d}x} \quad = \quad 0$$

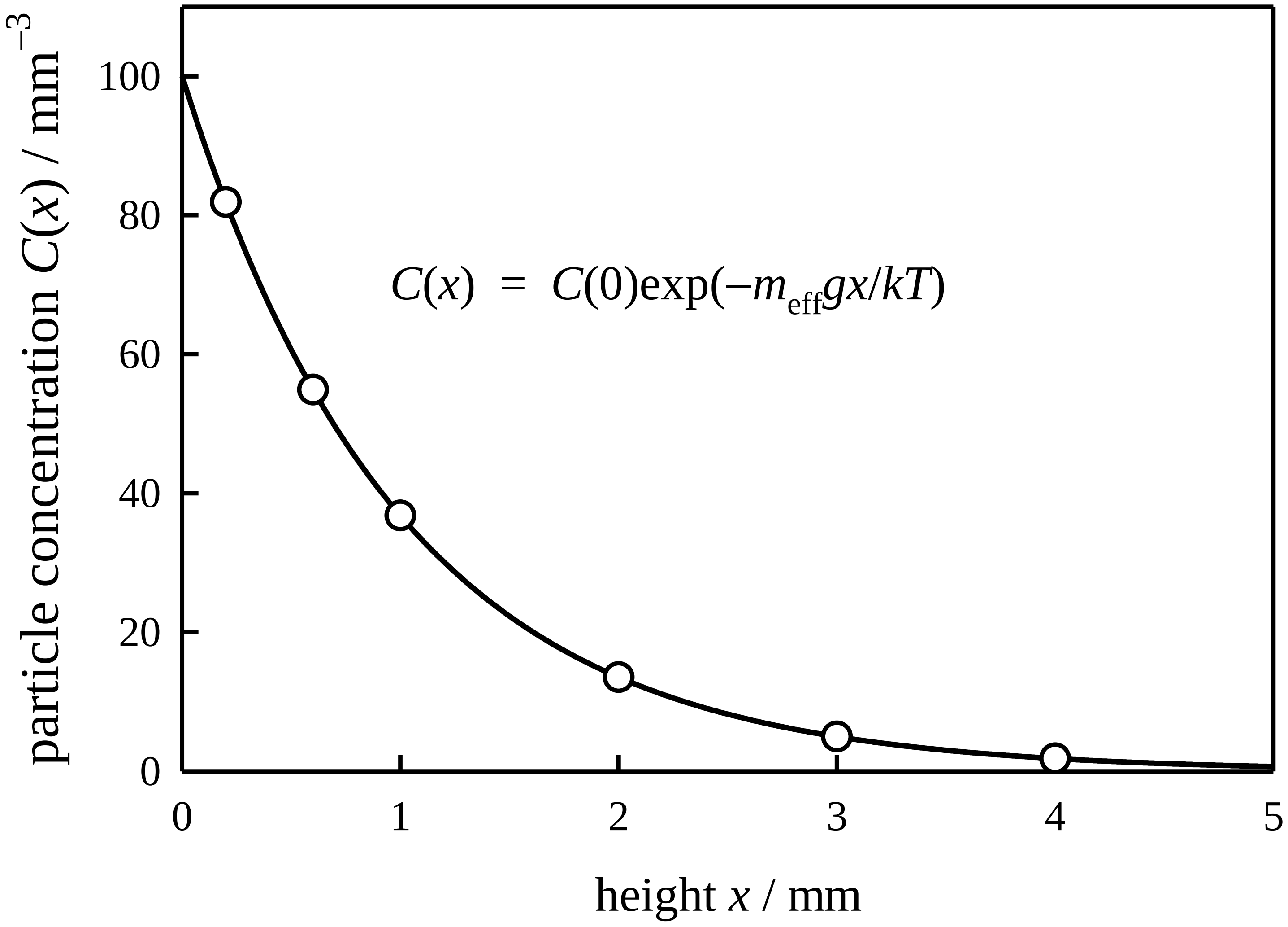
$$-m_{\text{eff}}\,g \quad - \quad \frac{\mathrm{d}}{\mathrm{d}x}\left(\mu^{\mathrm{o}} + kT\ln C\right) \quad = \quad 0$$

$$-m_{\text{eff}}\,g \quad - \quad kT\,\frac{\mathrm{d}\ln C}{\mathrm{d}x} \quad = \quad 0$$

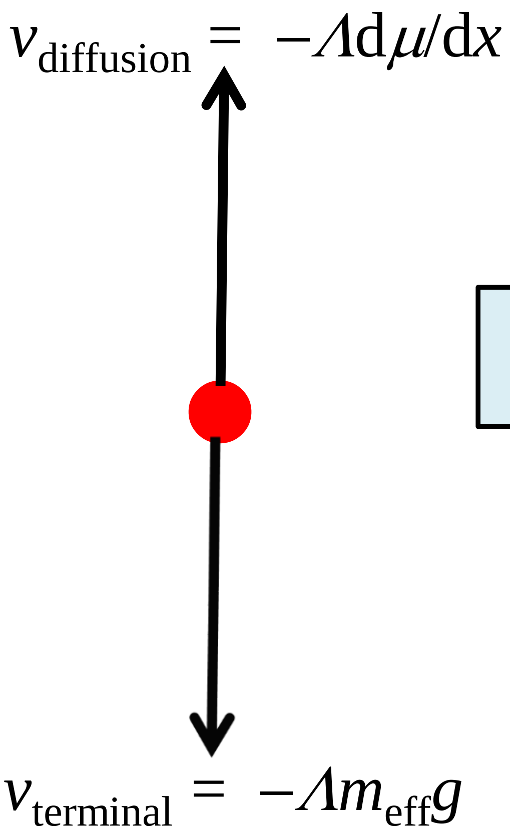
$$\mathrm{d}\ln C \quad = \quad -\frac{m_{\text{eff}}\,g}{kT}\,\mathrm{d}x$$

$$\ln C(x) \quad - \quad \ln C(x=0) \quad = \quad -\frac{m_{\text{eff}}\,g}{kT}\,x$$

Sedimentation Equilibrium



Sedimentation Equilibrium



$v_{\text{diffusion}} = -\Lambda \mathrm{d}\mu/\mathrm{d}x$

$v_{\text{terminal}} = -\Lambda m_{\text{eff}}g$

Boltzmann distribution of particles over gravitational **energy levels** $\boldsymbol{m_{\text{eff}}\,gx}$ in a vertical column of solution:

$$\boxed{C(x) = C(\text{at } x = 0)\mathrm{e}^{-m_{\text{eff}}\,g\,x/kT}}$$

- helped confirm the existence of molecules

  (*seeing is believing*!)

- provided one of the first estimates k, Avogadro number = R/k and hence the sizes and masses of molecules

- 1926 Nobel Prize in Physics for Jean Perrin for the discovery of “the discontinuous structure of matter” **(*atoms and molecules*!)**

Centrifuge Rotate Samples at High Speeds

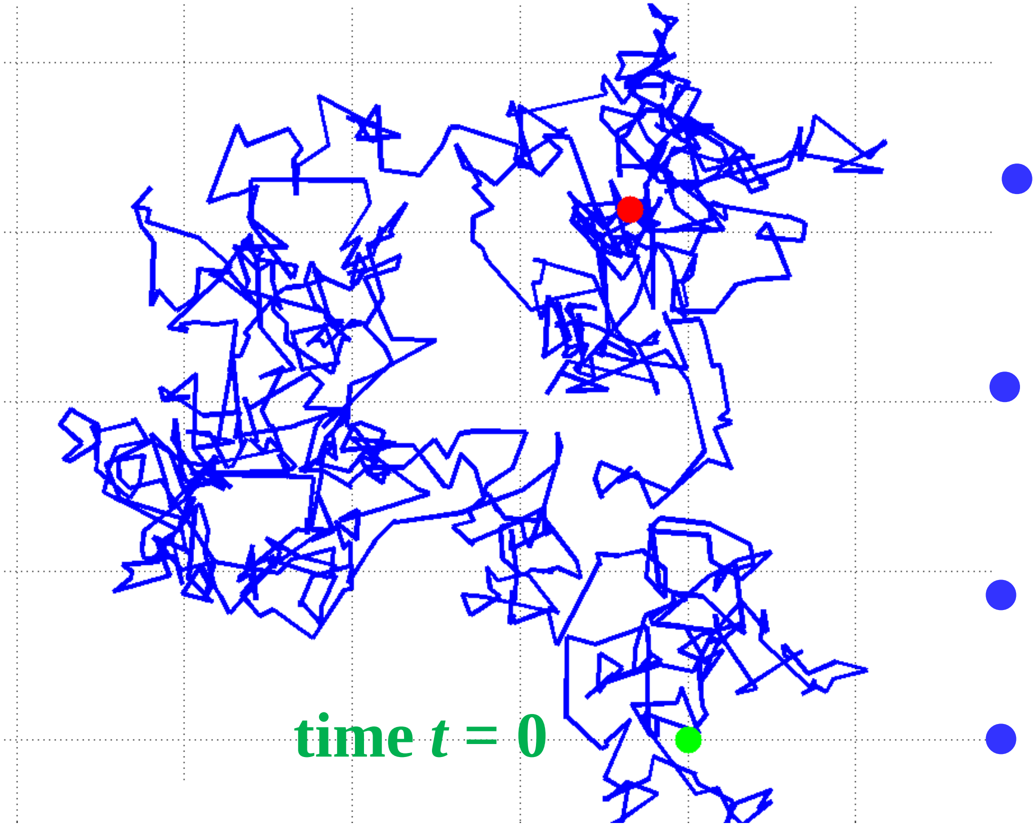
separates materials based on density differences

replaces g = 9.8 m s^{-1} from the earth's gravity with angular acceleration $\omega^2 R_{\text{rotor}}$

much faster than gravity sedimentation

ultracentrifuges are commercially available operating at **150,000 rpm (supersonic rotors!) and 1,000,000 g !**

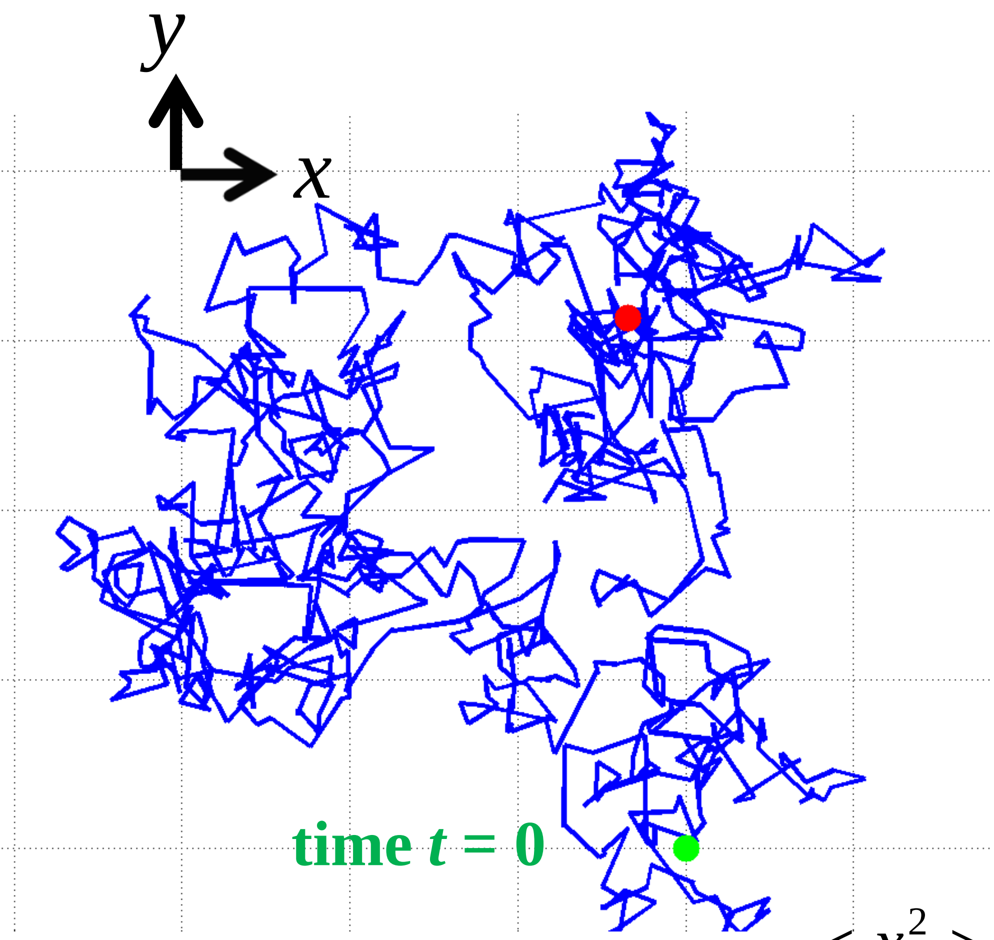
Brownian Motion



- small particles suspended in a liquid undergo ceaseless jittery motion
- studied by Brown (a botanist) in the 1820s
- observed pollen grains in water under a microscope
- **perpetual motion?**
- **a "vital force"?**

No, it's *diffusion!*

Brownian Motion



Stokes-Einstein equation

$$\boxed{D = kT\Lambda}$$

For spherical particles, **calculate**

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

then **confirm by experiment** (Perrin again!):

$$<x^2> + <y^2> = 4Dt = 4\frac{kT}{6\pi\eta r}t$$

single-molecule dynamics *circa* 1910!

Section 17.10 Transport of Electric Charge

- flow of electrons, ions and other charged particles
- driven by a gradient in electric potential

Ohm's Law

$$\boxed{J_x = -\kappa \frac{\partial \phi}{\partial x} = \kappa E_x}$$

J_x = flux density of electric charge [coulomb s^{-1} m^{-2} = ampere m^{-2}]

$\boldsymbol{\kappa}$ = **electrical conductivity** [coulomb s^{-1} volt^{-1} m^{-1} = S m^{-1}]

$\dfrac{\partial \phi}{\partial x}$ = gradient in the electric potential [volt m^{-1}]

$E_x = -\dfrac{\partial \phi}{\partial x}$ = electric field [volt m^{-1}]

also written as:

$$\boxed{J_x = -\rho^{-1} \frac{\partial \phi}{\partial x}}$$

$\boldsymbol{\rho}$ = **electrical resistivity** = κ^{-1} [S^{-1} m = ohm m]

SI conductance unit = S = siemens

1 S = 1 ohm^{-1}
= 1 ampere volt^{-1}
= 1 coulomb volt^{-1} second^{-1}

Units

electric charge Q

1 coulomb = 1 C = electric charge of 6.022×10^{23} (1 mol) protons

electric current I (= $J_x \times$ area)

1 ampere = 1 C s^{-1}

electric conductance Λ (= $|I/\Delta\phi|$)

1 siemens = 1 S = 1 C s^{-1} volt^{-1} = 1 ohm^{-1}

electric resistance R (= $|\Delta\phi/I|$)

1 ohm = 1 volt s C^{-1} = 1 S^{-1}

Conductivities and Resistivities at 293 K (20 ºC)

	conductivity **κ / S m^{-1}**	**resistivity** **ρ / S^{-1} m**
Teflon	10^{-20}	10^{20}
quartz	10^{-18}	10^{18}
diamond	10^{-12}	10^{12}
glass	10^{-15} to 10^{-11}	10^{11} to 10^{15}
water (deionized)	5.5×10^{-6}	1.8×10^{5}
seawater	≈ 5	≈ 0.2
mercury	1.0×10^{6}	9.8×10^{-7}
aluminum	3.6×10^{7}	2.8×10^{-8}
copper	5.8×10^{7}	1.7×10^{-8}
silver	6.3×10^{7}	1.5×10^{-8}
superconductor	**∞**	**0**

Electrical Conductivity

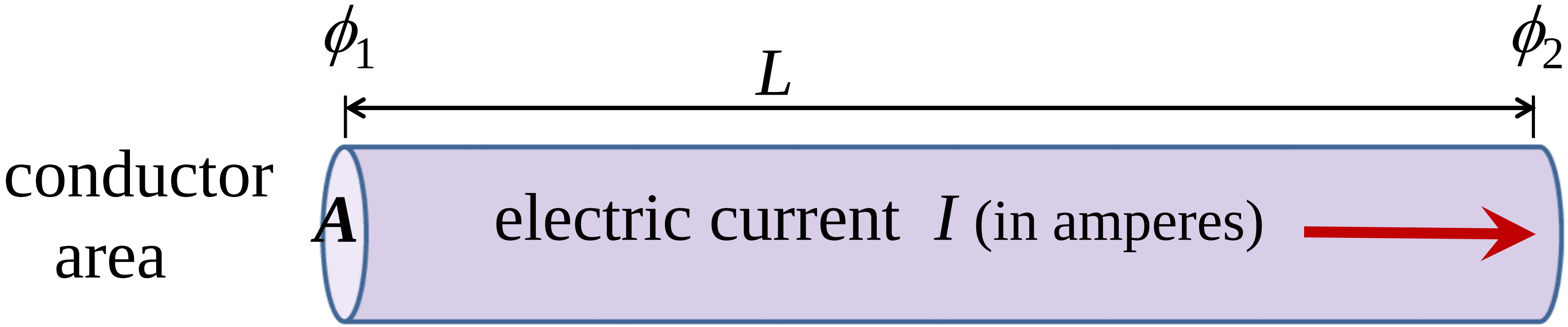
Why important?

Because circuits pumping electric charges are everywhere!

- computers, radios, cell phones, electric motors, lighting, …
- resistive heating
- ionic conduction in electrochemical cells
- plasma (gases composed of charged particles) processes
- static electricity and lightning
- conductivity detectors for ion analysis using HPLC
- transmission of nerve impulses and ***brain waves***

a more familiar version of Ohm’s law:

Apply the voltage difference $V = \phi_2 - \phi_1$ to the ends of a electrical conductor of length L and area A.



$$I = J_x A = -\kappa A \frac{\partial \phi}{\partial x} = -\kappa A \frac{\phi_2 - \phi_1}{L} = -\frac{\kappa A}{L} V$$

a more familiar version of Ohm's law:

Apply the voltage difference $V = \phi_2 - \phi_1$ to the ends of a electrical conductor of length L and area A.

Compare $I = -\frac{\kappa A}{L} V$ and $\boxed{I = -\frac{1}{R} V = -\frac{\text{voltage difference}}{\text{resistance}}}$

electric resistance $R = \frac{L}{\kappa A}$

units: ohm = volt ampere^{-1}

R

- proportional to the length L
- inversely proportional to the area A and conductivity κ.

(*does this make sense*?)

another version of Ohm's law:

Apply the voltage difference $V = \phi_2 - \phi_1$ to the ends of a electrical conductor of length L and area A.

$$\boxed{I \;=\; -\Lambda V \;=\; -(\text{conductance}) \times (\text{voltage})}$$

electric conductance $$\Lambda = \frac{\kappa A}{L}$$

$$\boxed{\text{units:}\quad \mathrm{S} = \text{ohm}^{-1} = \text{ampere volt}^{-1}}$$

S = Siemens (SI conductance unit)

Λ

- proportional to the area A and conductivity κ
- inversely proportional to the length L

Example A 1.50 V voltage difference is applied to a 5.00-m length of copper wire (diameter 0.250 mm) at 20 ^{o}C. Calculate the electric current. *Data*: copper conductivity κ = 5.8 × 10^7 ohm^{-1} m^{-1}

$$R = \frac{L}{A\kappa} = \frac{5.00\ \mathrm{m}}{\pi\,(0.000125\ \mathrm{m})^2\ (5.8\times 10^7\,\mathrm{ohm}^{-1}\ \mathrm{m}^{-1})}$$

resistance $R = 1.76\ \mathrm{ohm} = 1.76\ \mathrm{S}^{-1}$

conductance $\Lambda = 1/R = 0.57\ \mathrm{ohm}^{-1} = 0.57\ \mathrm{S}$

electric current $$I = \frac{\Delta\phi}{R} = \frac{1.50\ \mathrm{volt}}{1.76\ \mathrm{ohm}} = 0.85\ \mathrm{C\,s}^{-1} = 0.85\ \mathrm{ampere}$$

power $$I\Delta\phi = (0.85\ \mathrm{ampere})(1.50\ \mathrm{volt})$$

$$= 1.28\ \mathrm{J\,s}^{-1} = 1.28\ \mathrm{Watt}$$

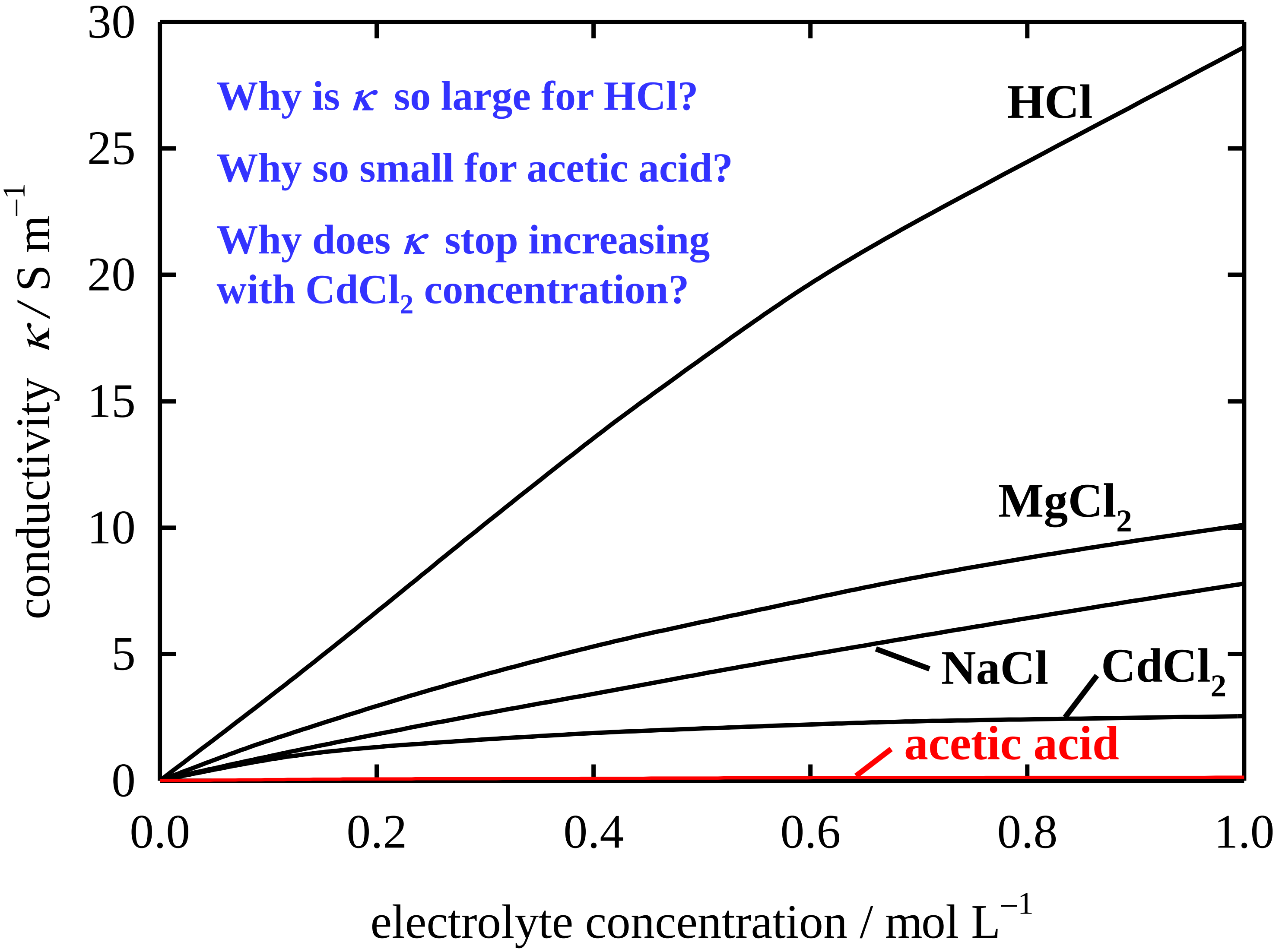
Metals

- **electronic conductors**: electrons carry the current
- fixed number of charge carriers for each metal
- fixed conductivity at a given temperature

Electrolytes (*e.g.*, aqueous NaCl)

- **ionic conductors**: ions (*e.g.*, Na^+, Cl^-) carry the current
- number of charge carriers increases with electrolyte concentration
- conductivity increases with electrolyte concentration

Ionic Conductivities κ of Aqueous Electrolyte Solutions at 20 °C

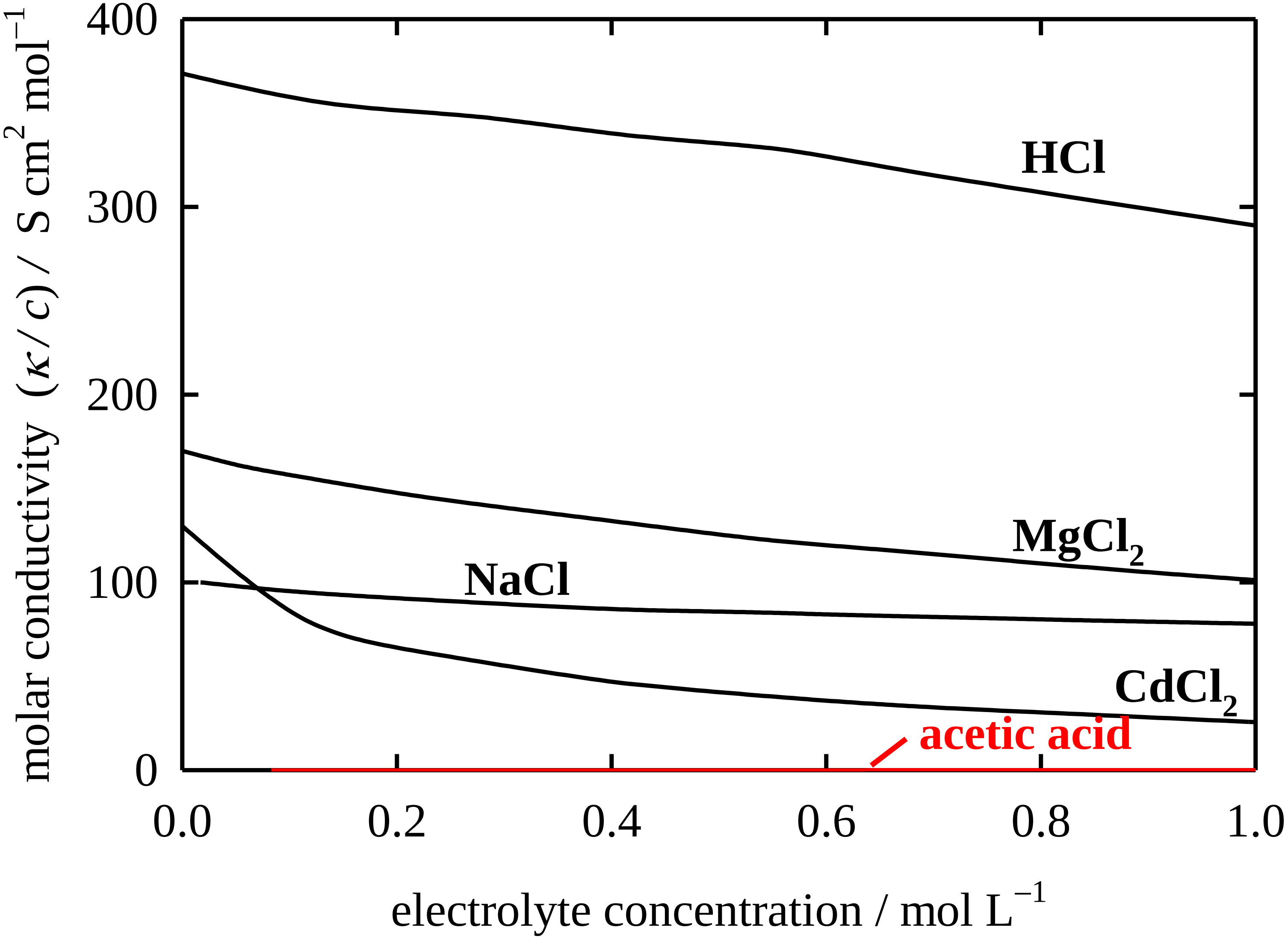


Why is κ so large for HCl?

Why so small for acetic acid?

Why does κ stop increasing with $CdCl_2$ concentration?

Molar Conductivities κ / c of Aqueous Electrolyte Solutions



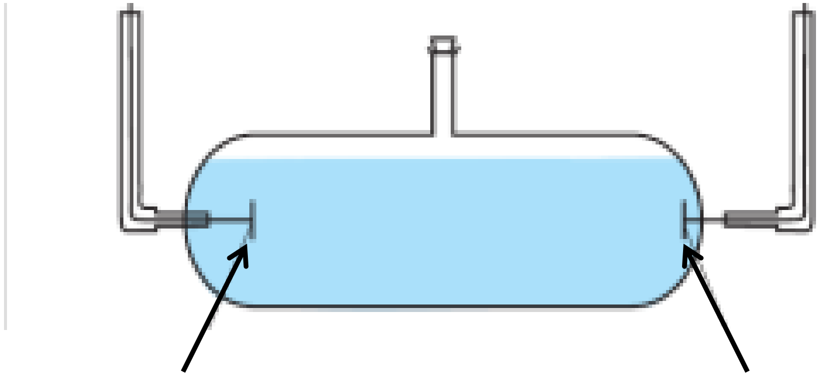
Useful feature:

Dividing the conductivity by the molar electrolyte concentration allows for changes in the number of charge carriers:

so κ / c is less variable than κ

Electrolyte Conductivity Cell

- inert metal electrodes, area *A* and distance *L* apart
- *A* and *L* are not known precisely for most cells



platinum electrode **platinum electrode**

- but *A* and *L* are constant for each cell
- cell conductance (1/*R*) is therefore proportional to conductivity κ
- measure conductivities by calibrating each cell with a solution of accurately known conductivity

Example A conductivity cell is calibrated at 25 ^{o}C with a 0.1000 mol L^{-1} KCl solution (κ = 1.2896 S m^{-1}). The measured cell resistance is 45.67 ohms. Determine the cell constant L/A.

$$R = \frac{L}{A\kappa}$$

$$\frac{L}{A} = R\kappa = (45.67\ \mathrm{S})\,(1.2896\ \mathrm{S\ m^{-1}}) = 58.89\ \mathrm{m^{-1}}$$

When filled with 0.0500 mol L^{-1} $LaCl_3$ solution, the cell resistance is 41.35 ohm. Calculate the conductivity (κ) and the **molar conductivity** ($\Lambda_m = \kappa/c$) of the $LaCl_3$ solution.

$$\kappa = \frac{L}{A}\frac{1}{R} = (58.89\ \mathrm{m^{-1}})\,\frac{1}{41.35\ \mathrm{ohm}} = 1.424\ \mathrm{S\ m^{-1}}$$

$$\Lambda_m = \frac{\kappa}{c} = \frac{1.424\ \mathrm{S\ m^{-1}}}{0.0500\ \mathrm{mol\ L^{-1}}}\ \frac{0.001\ \mathrm{m^3}}{\mathrm{L}} = 0.02848\ \ \mathrm{S\ m^2\ mol^{-1}}$$

Strong Electrolytes

Why "strong"? Completely dissociated to ionic species.

Example: $\Lambda_m(CaCl_2) = \Lambda_m(Ca^{2+}) + 2\Lambda_m(Cl^-)$

! Warning !

Many "strong" electrolytes are incompletely dissociated, especially for polyvalent ions (why?) or concentrated solutions (why?).

Examples:

Aqueous $MgSO_4$ solutions contain Mg^{2+} ions, SO_4^{2-} ions, and neutral $MgSO_4$ **ion pairs**.

Aqueous $CdCl_2$ solutions contain Cd^{2+} ions, Cl^- ions, and $CdCl^+$, $CdCl_2$, $CdCl_3^-$ and $CdCl_4^{2-}$ **ion complexes**.

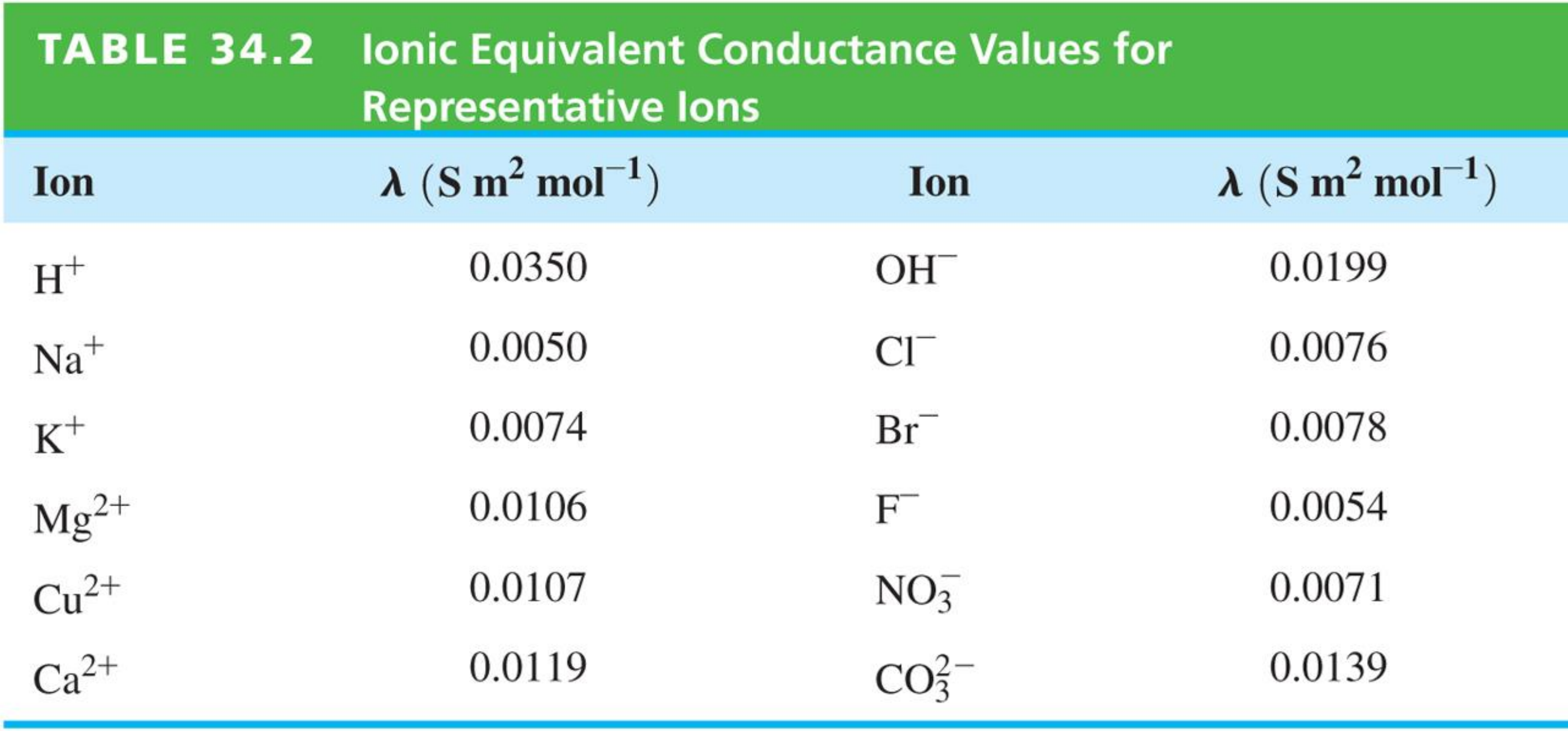
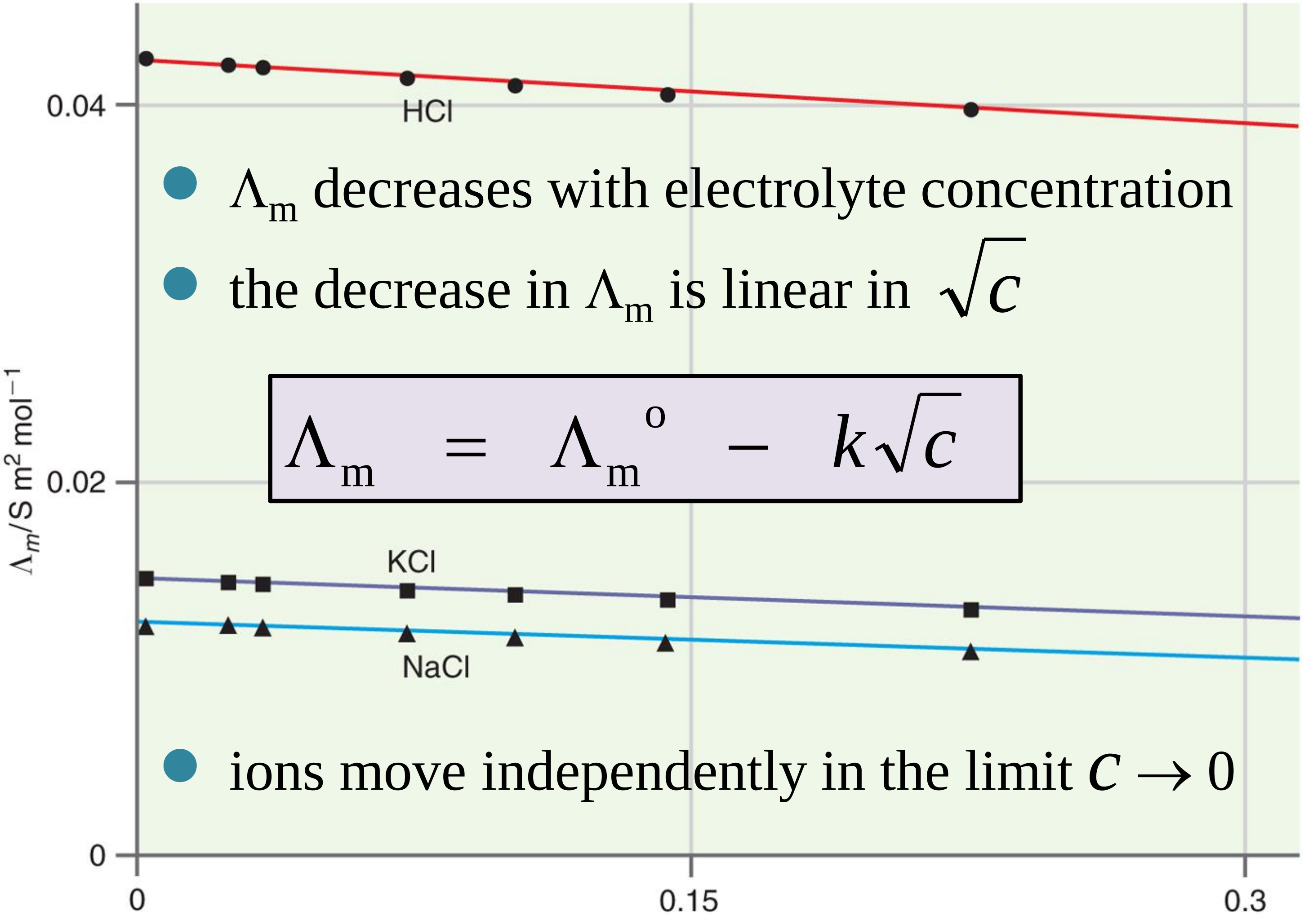


TABLE 34.2 Ionic Equivalent Conductance Values for Representative Ions

Ion	λ (S m^2 mol^{-1})	Ion	λ (S m^2 mol^{-1})
H^+	0.0350	OH^-	0.0199
Na^+	0.0050	Cl^-	0.0076
K^+	0.0074	Br^-	0.0078
Mg^{2+}	0.0106	F^-	0.0054
Cu^{2+}	0.0107	NO_3^-	0.0071
Ca^{2+}	0.0119	CO_3^{2-}	0.0139

Single-Ion Properties !

Molar Conductivities of **Dilute** Strong Electrolytes



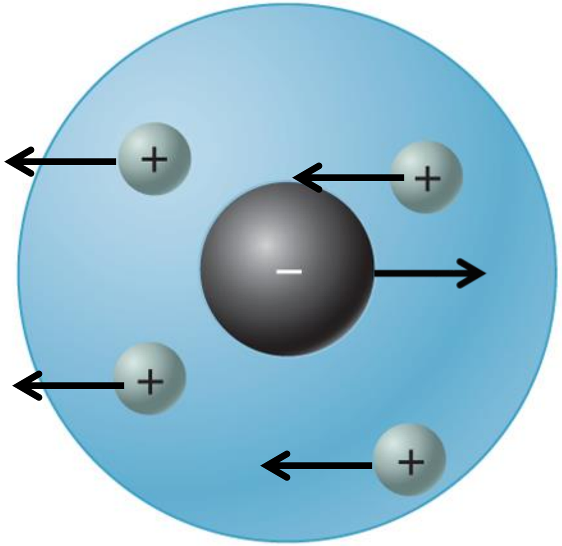
- Λ_m decreases with electrolyte concentration
- the decrease in Λ_m is linear in $\sqrt{c}$

$$\boxed{\Lambda_\mathrm{m} = \Lambda_\mathrm{m}^\mathrm{o} - k\sqrt{c}}$$

- ions move independently in the limit $c \rightarrow 0$

$\sqrt{c}$

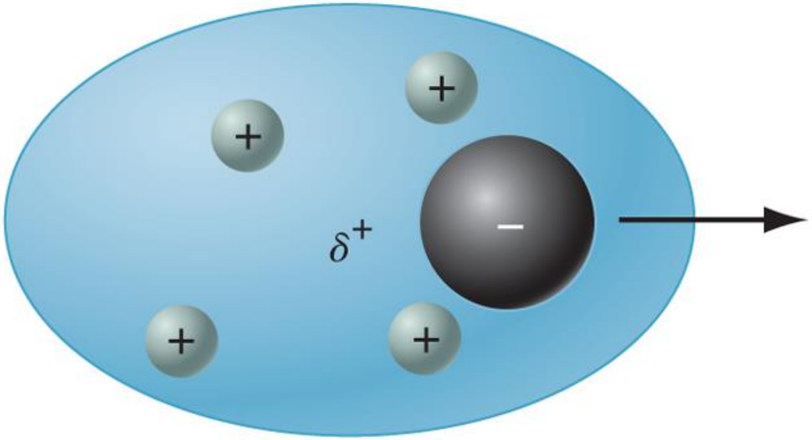
Why does the molar conductivity decrease with ion concentration?



1. Electrophoretic Effect

Each ion is "swimming upstream" against the flow of solvent molecules carried along by the ions of opposite charge moving in the opposite direction.

2. Relaxation Effect



During ionic conduction, the the oppositely charged ion atmosphere lags behind each ion.

The resulting electric forces slow down the ions, reducing the molar conductivity.

Weak Electrolytes

Why "weak"? **Incompletely dissociated** to ionic species.

Example aqueous acetic acid solutions contain undissociated molecular acetic acid, hydrogen ions, and acetate ions.

(molecular)

$$\boxed{\mathbf{CH_3COOH \quad = \quad H^+ \quad + \quad CH_3COO^-}}$$

concentrations: $(1-\alpha)c \qquad \alpha c \qquad \alpha c$

extent of dissociation

$$\alpha = \frac{[\text{dissociated acid}]}{[\text{total acid}]} = \frac{c_{\mathrm{CH3OO-}}}{c} = \frac{c_{\mathrm{H+}}}{c}$$

equilibrium constant

$$K = \frac{a_{\mathrm{H+}} \; a_{\mathrm{CH3OO-}}}{a_{\mathrm{CH3COOH}}} \approx \frac{c_{\mathrm{H+}} \; c_{\mathrm{CH3OO-}}}{c_{\mathrm{CH3COOH}}} = \frac{\alpha c \;\; \alpha c}{(1-\alpha)c}$$

Weak Electrolytes

Use non-equilibrium ionic conductivity measurements
to determine equilibrium constants for weak acid dissociation.

$$\mathrm{CH_3COOH} \quad = \quad \mathrm{H^+} \quad + \quad \mathrm{CH_3COO^-}$$

(non–conducting)

extent of dissociation

$$\alpha = \frac{[\text{dissociated acid}]}{[\text{total acid}]} \approx \frac{\Lambda_\mathrm{m}}{\Lambda_\mathrm{m}^\mathrm{o}}$$

Why? Acetic acid is completely dissociated in the limit $c \to 0$.

$$\boxed{\mathbf{CH_3COOH \quad = \quad H^+ \quad + \quad CH_3COO^-}} \qquad \boldsymbol{K}\,?$$

Measure:

- the molar conductivity Λ_m of aqueous acetic acid solutions at different acetic acid concentrations c
- limiting molar conductivities of the **strong electrolytes** hydrochloric acid, sodium acetate, sodium chloride

Calculate the molar conductivity of completely dissociated acetic acid:

$$\Lambda_m{}^o(CH_3COOH) = \Lambda_m{}^o(HCl) + \Lambda_m{}^o(CH_3COONa) - \Lambda_m{}^o(NaCl)$$

$$= 0.042616 + 0.009100 - 0.012645 \text{ S m}^2 \text{ mol}^{-1}$$

$$= 0.039071 \text{ S m}^2 \text{ mol}^{-1} \quad (\text{at } 25\ ^o\text{C})$$

$$\boxed{\mathbf{CH_3COOH \quad = \quad H^+ \quad + \quad CH_3COO^-}} \qquad \boldsymbol{K}\,?$$

At each acetic acid concentration, use measured conductivities to calculate the approximate equilibrium constant:

$$K_\mathrm{a} \approx \frac{\alpha^2 c}{(1-\alpha)} \approx \frac{(\Lambda/\Lambda_\mathrm{m}{}^\mathrm{o})^2 c}{[1-(\Lambda/\Lambda_\mathrm{m}{}^\mathrm{o})]}$$

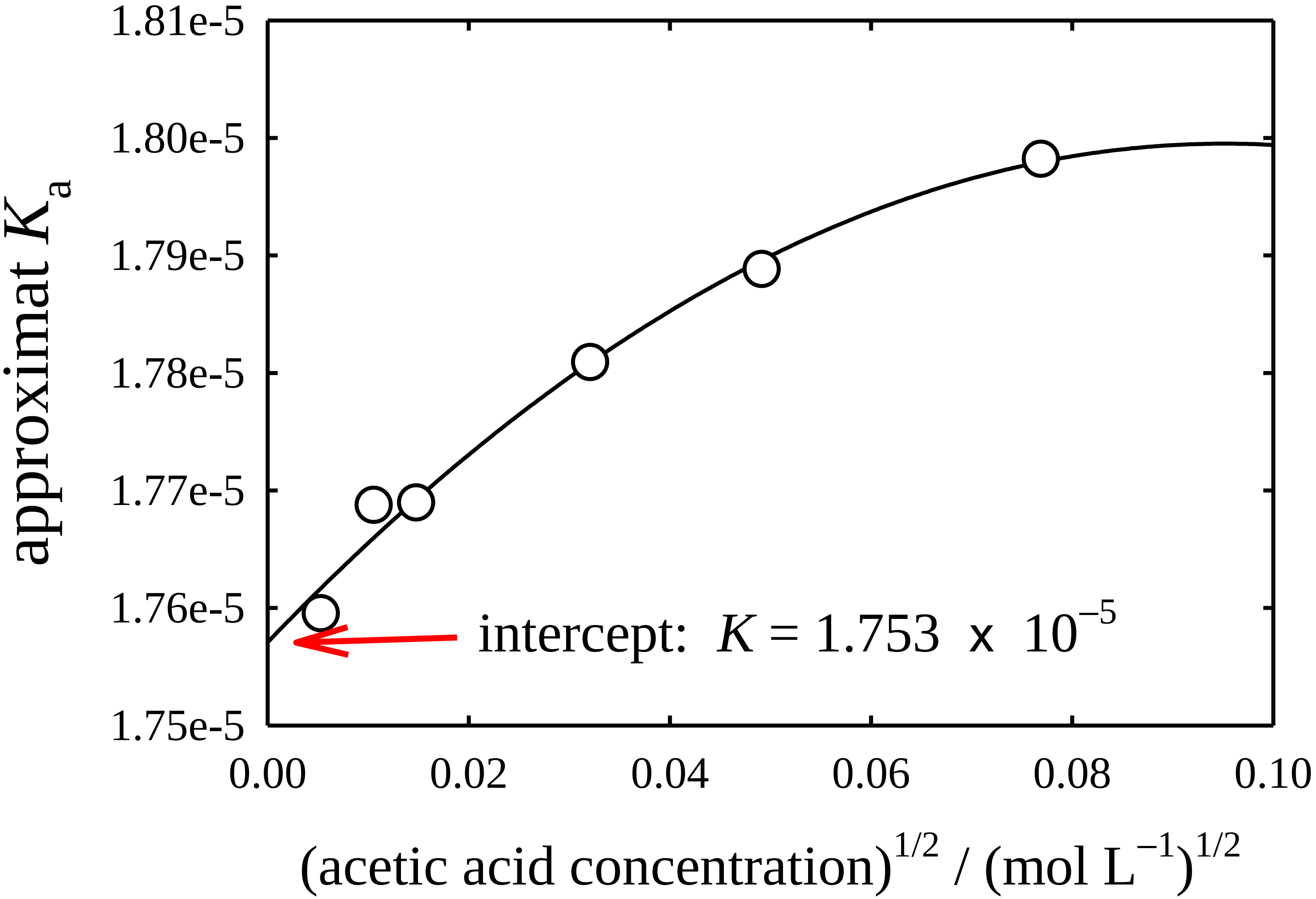
(Why approximate? Ideal solutions and independent ion migration assumed.)

Exact K value obtained by extrapolation of K_a to infinite dilution.

$$\boxed{\text{In the limit } c \to 0, \text{ find } K_\mathrm{a} = K = 1.753 \times 10^{-5}}$$

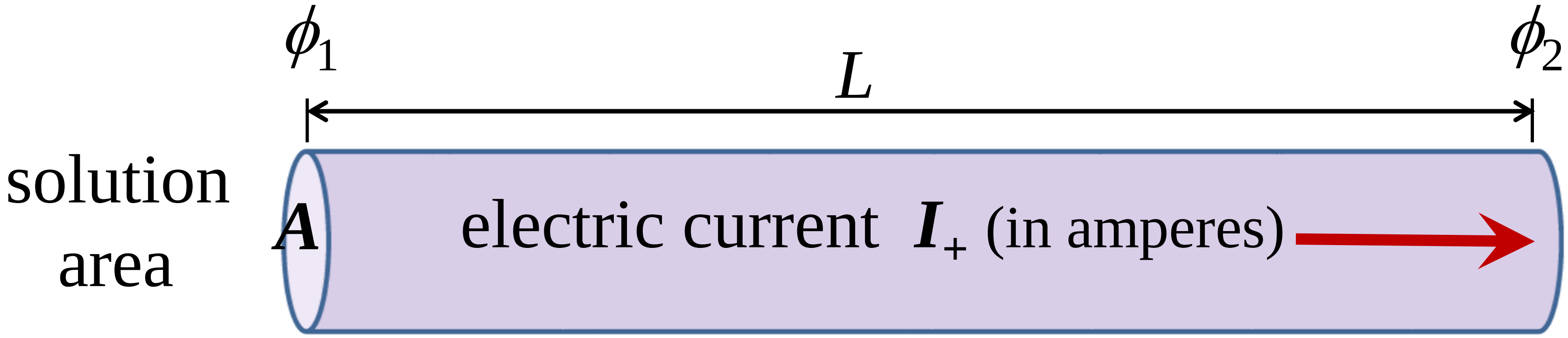
In agreement with K measurements using electrochemical cells.

Conductometric Measurement of the Equilibrium Constant for the Dissociation of Aqueous Acetic Acid



What are the <u>speeds</u> of ions moving in an electric field?

Apply the voltage difference $V = \phi_2 - \phi_1$ to the ends of a solution column of length L and area A.



ϕ_1 L ϕ_2

solution area **A**

electric current $\boldsymbol{I_+}$ (in amperes)

Cation "+" at molar concentration $c_{+\mathrm{m}}$ with molar conductivity $\lambda_{+\mathrm{m}}$ produces the electric current (in units of coulombs per second):

$$I_+ = J_{+Q} A = -\kappa_+ \frac{\partial \phi}{\partial x} A = -c_{+\mathrm{m}} \lambda_{+\mathrm{m}} \frac{\phi_2 - \phi_1}{L} A$$

Each mole of cations carries electric charge z_+F.

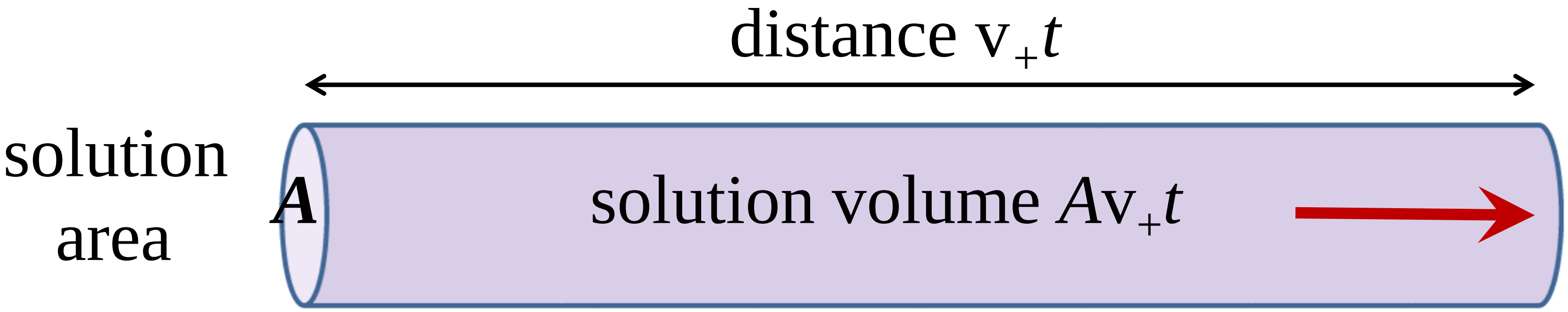
For example, charge $2F$ for one mole of Ca^{2+} ions.

The molar flux $J_{+\mathrm{m}}A$ of cations (units: mol s^{-1}) and the electric current $J_{+Q}A$ carried by the cations (units: C s^{-1}) through area A are therefore related by

$$J_{+\mathrm{m}}A = \frac{J_{+Q}}{z_+F}A = -\frac{c_{+\mathrm{m}}\lambda_{+\mathrm{m}}}{z_+F}\frac{\partial\phi}{\partial x}A$$

Cations drift toward the negative electrode at average speed v_+.

In time t, each cation moves the distance $\mathrm{v}_+ t$. The number of moles of cations passing through area A is $J_{+\mathrm{m}} A t = c_+ A \mathrm{v}_+ t$.


distance $\mathrm{v}_+ t$

solution area A

solution volume $A\mathrm{v}_+ t$

Useful relations between the cation molar flux and drift speed

$$J_{+\mathrm{m}} A = c_{+\mathrm{m}} \mathrm{v}_{+\mathrm{m}} A$$

and cation molar flux density and drift speed:

$$J_{+\mathrm{m}} = c_{+\mathrm{m}} \mathrm{v}_{+\mathrm{m}}$$

cation molar flux density (mol m^{-2} s^{-1}):

$$J_{+\mathrm{m}} = c_{+\mathrm{m}} \mathrm{v}_{+\mathrm{m}} = \frac{1}{z_+ F}\left(J_{+Q}\right) = \frac{1}{z_+ F}\left(-c_{+\mathrm{m}}\lambda_{+\mathrm{m}}\frac{\partial\phi}{\partial x}\right)$$

cation drift speed (m s^{-1}) in electric field $-\partial\phi/\partial x$ (V m^{-1}):

$$\mathrm{v}_+ = \frac{\lambda_{+\mathrm{m}}}{z_+ F}\left(-\frac{\partial\phi}{\partial x}\right)$$

cation electric mobility (cation drift speed per unit electric field):

$$\boxed{u_+ = \frac{\lambda_{+\mathrm{m}}}{z_+ F}}$$

Example Calculate the **drift speed of aqueous Na$^+$ ions** (molar conductivity $\lambda_{+\mathrm{m}} = 0.0050\ \mathrm{S\ m^2\ mol^{-1}}$) in a 10 V/cm electric field.

electric mobility of the Na$^+$ ions:

$$u_+ = \frac{\lambda_{+\mathrm{m}}}{z_+ F} = \frac{0.0050\ \mathrm{S\,m^2\ mol^{-1}}}{(1)\ 96485\ \mathrm{C\ mol^{-1}}} = 5.2\times10^{-8}\ \mathrm{m^2\ s^{-1}\ V^{-1}}$$

drift speed of the Na$^+$ ions:

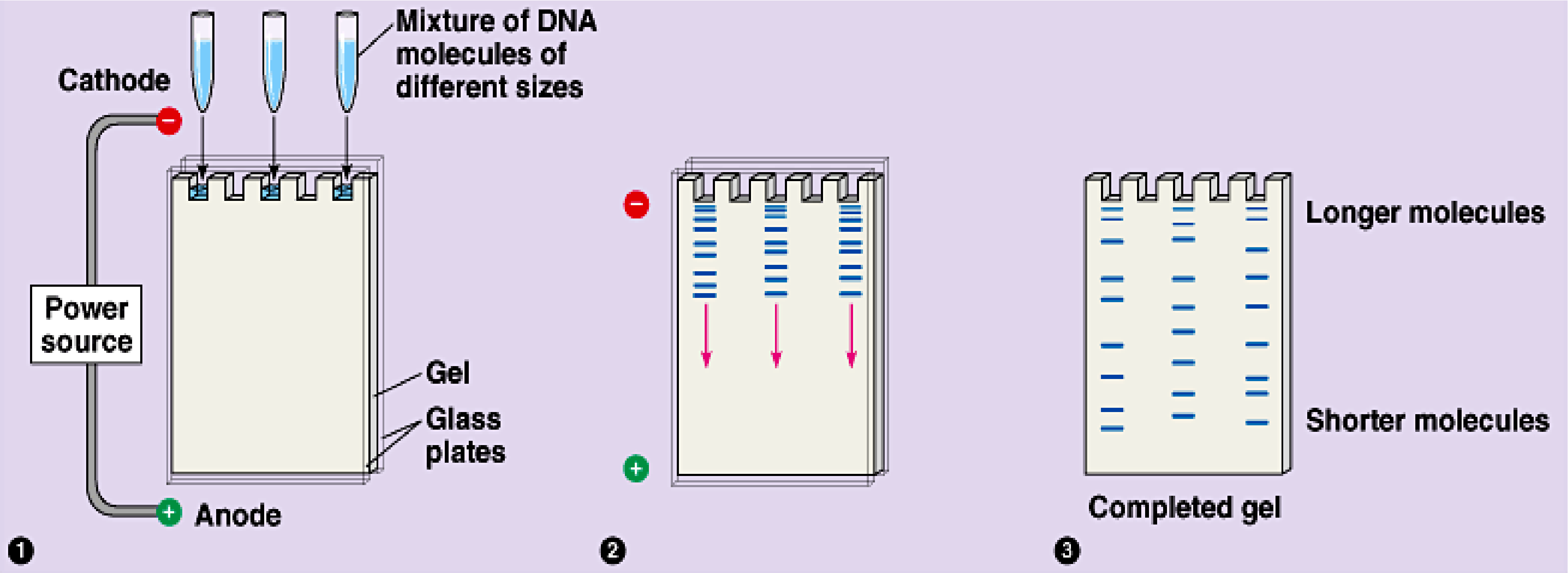
$$\mathrm{v}_+ = u_+ \frac{\partial\phi}{\partial x} = (5.2\times10^{-8}\ \mathrm{m^2\ s^{-1}\ V^{-1}})\ (10\ \mathrm{V\ cm^{-1}})\ (100\ \mathrm{cm\ m^{-1}})$$

$$= 5.2\times10^{-5}\ \mathrm{m\ s^{-1}}$$

$$= 19\ \mathrm{cm\ hour^{-1}}$$

Application: Gel Electrophoresis

separate ions from a mixture based on ionic mobility



related: capillary electrophoresis

What are the mobilities of ions in electrolyte solutions?

mobility ≡ drift speed per unit applied force

The electric force acting on one mole of cations of charge z_+F is

$$f_\mathrm{m} = -z_+F\,\frac{\partial \phi}{\partial x}$$

Find:

$$\mathrm{v}_+ = \frac{\lambda_{+\mathrm{m}}}{z_+F}\left(-\frac{\partial \phi}{\partial x}\right) = \frac{\lambda_{+\mathrm{m}}}{(z_+F)^2}\left(-z_+F\,\frac{\partial \phi}{\partial x}\right) = \frac{\lambda_{+\mathrm{m}}}{(z_+F)^2}\,f_\mathrm{m}$$

What are the <u>mobilities</u> of ions in electrolyte solutions?

cation molar mobility (Drift speed per unit force per mole of cations):

$$\boxed{\Lambda_{+\mathrm{m}} = \frac{\lambda_{+\mathrm{m}}}{(z_+F)^2}}$$

cation mobility (Drift speed per unit force per cation, larger than $\Lambda_{+\mathrm{m}}$ by a factor of 6.022×10^{23} mol^{-1}. *Why*?):

$$\boxed{\Lambda_+ = N_{\mathrm{Avogadro}}\Lambda_{+\mathrm{m}} = \frac{N_{\mathrm{Avogadro}}\lambda_{+\mathrm{m}}}{(z_+F)^2}} \approx \frac{1}{6\pi\eta r}$$