Transport (kinetic) phenomena:
diffusion, electric conductivity, viscosity, heat conduction . . .

- Flux of mass, charge, momentum, heat, . . . . . .
  $\vec{J}$ = amount (of quantity) transported per unit area (perpendicular to the vector of flux) within time unit
  Units: energy/heat flux: $\mathrm{J\,m^{-2}\,s^{-1}} = \mathrm{W\,m^{-2}}$,
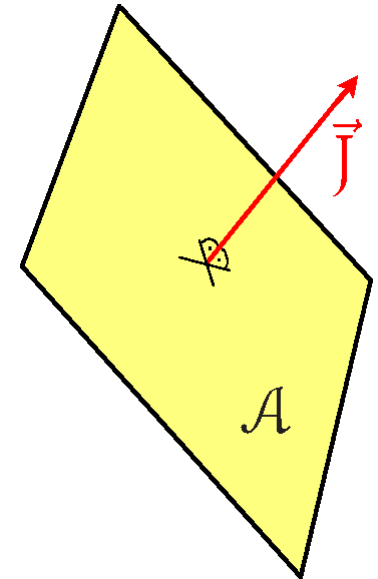  current density: $\mathrm{A\,m^{-2}}$

- Cause = (generalized, thermodynamic) force
  $\vec{\mathcal{F}} = -$ gradient of a potential
  (chemical potential/concentration, electric potential, temperature)

- Small forces—linearity

$$\vec{J} = \mathrm{const} \cdot \vec{\mathcal{F}}$$

In gases we use the **kinetic theory**: molecules (simplest: hard spheres) fly through space and sometimes collide

**First Fick Law**: Flux $\vec{J}_i$ of compound $i$ (units: $\mathrm{mol\,m^{-2}\,s^{-1}}$)
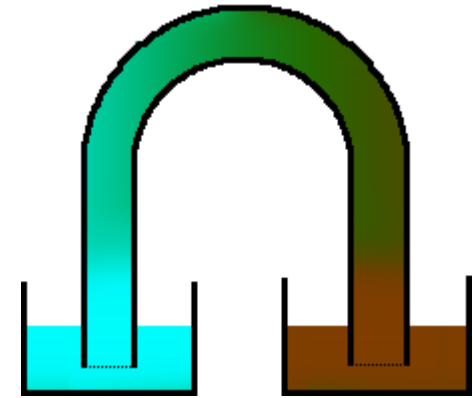
$$\vec{J}_i = -D_i \vec{\nabla} c_i$$

is proportional to the **concentration gradient**

$$\vec{\nabla} c_i = \mathrm{grad}\, c_i = \left(\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z}\right) c_i = \left(\frac{\partial c_i}{\partial x}, \frac{\partial c_i}{\partial y}, \frac{\partial c_i}{\partial z}\right)$$

For mass concentration in $\mathrm{kg\,m^{-3}}$, the flux is in $\mathrm{kg\,m^{-2}\,s^{-1}}$

$D_i$ = diffusion coefficient (diffusivity) of molecules $i$, unit: $\mathrm{m^2\,s^{-1}}$

**Example.** A U-shaped pipe of lenght $l = 20$ cm and cross section $\mathcal{A} = 0.3\,\mathrm{cm^2}$. One end is in Coca-Cola (11 wt.% of sugar), other end in pure water. How much sugar is transported by diffusion in one day? $D_{\mathrm{sucrose}}(25\,°C) = 5.2 \times 10^{-6}\,\mathrm{cm^2\,s^{-1}}$.

0.74 mg

$m = \int J \mathcal{A} t = 2.56 \times 10^{-7}\,\mathrm{kg\,m^{-2}\,s^{-1}} \times 0.3 \times 10^{-4}\,\mathrm{m^2} \times 24 \times 60^2\,\mathrm{s} = 7.4 \times 10^{-7}\,\mathrm{kg}$

$J = D\,\mathrm{grad}\,c_w = 2.56 \times 10^{-7}\,\mathrm{kg\,m^{-2}\,s^{-1}}$

$D = 5.2 \times 10^{-6}\,\mathrm{cm^2\,s^{-1}} = 5.2 \times 10^{-10}\,\mathrm{m^2\,s^{-1}}$

$\mathrm{grad}\,c_w = c_w/l = 550\,\mathrm{kg\,m^{-4}}$

110 g sucrose in 1 L: $c_w = 110\,\mathrm{g\,dm^{-3}} = 110\,\mathrm{kg\,m^{-3}}$

Flux is given by the mean velocity of molecules $\vec{v}_i$:

$$\vec{J}_i = \vec{v}_i c_i$$

Thermodynamic force = $-\text{grad}$
of the chemical potential:

$$\vec{\mathcal{F}}_i = -\vec{\nabla}\left(\frac{\mu_i}{N_A}\right) = -\frac{k_B T}{c_i}\vec{\nabla}c_i$$

Difference of chemical potentials = reversible work needed to move a particle (mole) from one state to another

where formula $\mu_i = \mu_i^{\ominus} + RT\ln(c_i/c^{st})$ for infinity dillution was used.

Friction force acting against molecule moving by velocity $\vec{v}_i$ through a medium is:

$$\vec{\mathcal{F}}_i^{fr} = -f_i\vec{v}_i$$

where $f_i$ is the friction coeficient. Both forces are in equilibrium:

$$\vec{\mathcal{F}}_i^{fr} + \mathcal{F}_i = 0 \quad \text{i.e.} \quad -\vec{\mathcal{F}}_i^{fr} = f_i\vec{v}_i = f_i\frac{\vec{J}_i}{c_i} = \mathcal{F}_i = -\frac{k_B T}{c_i}\vec{\nabla}c_i$$

On comparing with $\vec{J}_i = -D_i\vec{\nabla}c_i$ we get the **Einstein equation**: $\boxed{D_i = \dfrac{k_B T}{f_i}}$

(also Einstein–Smoluchowski equation)

# Einstein–Stokes equation

Colloid particles or large spherical molecules of radius $R_i$ in a solvent of viscosity $\eta$ it holds (Stokes formula)

$$\vec{\mathcal{F}}_i = 6\pi\eta R_i \vec{v}_i$$

$f_i$ ↗

$\Rightarrow$ Einstein–Stokes equation:

$$D_i = \frac{k_B T}{f_i} \quad \Rightarrow \quad D_i = \frac{k_B T}{6\pi\eta R_i}$$

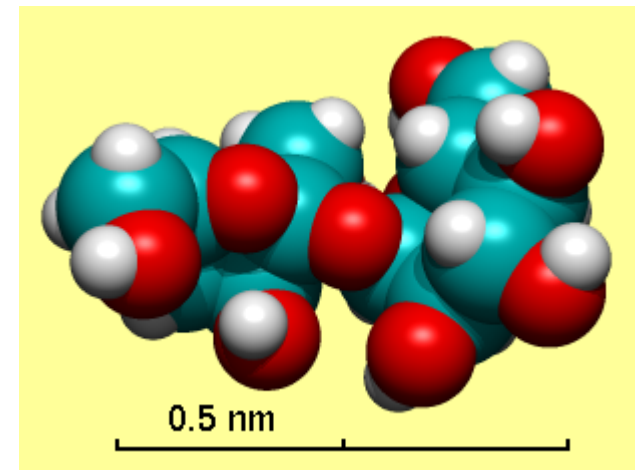Arrhenius law for viscosity (decreases with increasing $T$), diffusivity (increases with increasing $T$

Opposite reasoning—hydrodynamic (Stokes) radius defined as:
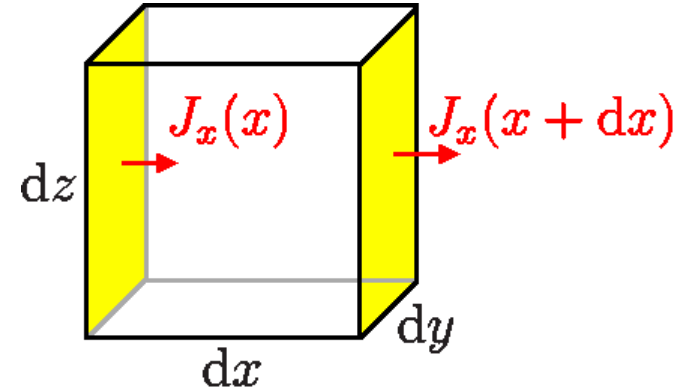
$$R_i = \frac{k_B T}{6\pi\eta D_i}$$

$\approx$ effective molecule size (incl. solvation shell)

**Example.** Estimate the size of the sucrose molecule. Water viscosity is $0.891 \times 10^{-3}\ \mathrm{m^{-1}\,kg\,s^{-1}}$ at $25\,°\mathrm{C}$.

$R = 0.47$ nm



0.5 nm

Non-stationary phenomenon ($c$ changes with time).
The amount of substance increases within
time $d\tau$ in volume $dV = dxdydz$:

$$\sum_{x,y,z} [J_x(x) - J_x(x + dx)]\, dydz$$

$$= \sum_{x,y,z} [J_x(x) - \{J_x(x) + \frac{\partial J_x}{\partial x}dx\})]\, dydz$$

$$= -\sum_{x,y,z} \frac{\partial J_x}{\partial x} dxdydz = -\vec{\nabla} \cdot \vec{J} dV = -\vec{\nabla} \cdot (-D\vec{\nabla}c)\, dV$$

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

$$\frac{\partial c_i}{\partial \tau} = D_i\nabla^2 c_i$$

This type of equation is called "equation of heat conduction". It is a parrabolic partial differential equation

# Second Fick Law

**Example.** Coca-Cola in a cylinder (height 10 cm) + pure water (10 cm). What time is needed until the surface concentration = half of bottom concentration?

4 months

Fourier method:

$$\frac{\partial c}{\partial \tau} = D\frac{\partial^2 c}{\partial x^2} \qquad c(x, 0) = \begin{cases} c_0 & x < l/2 \\ 0 & x > l/2 \end{cases}$$

$$c(x, \tau) = \frac{c_0}{2} + \frac{2c_0}{\pi}\left[\cos\left(\frac{\pi x}{l}\right)\exp\left(-\frac{\pi^2}{l^2}D\tau\right)\right.$$
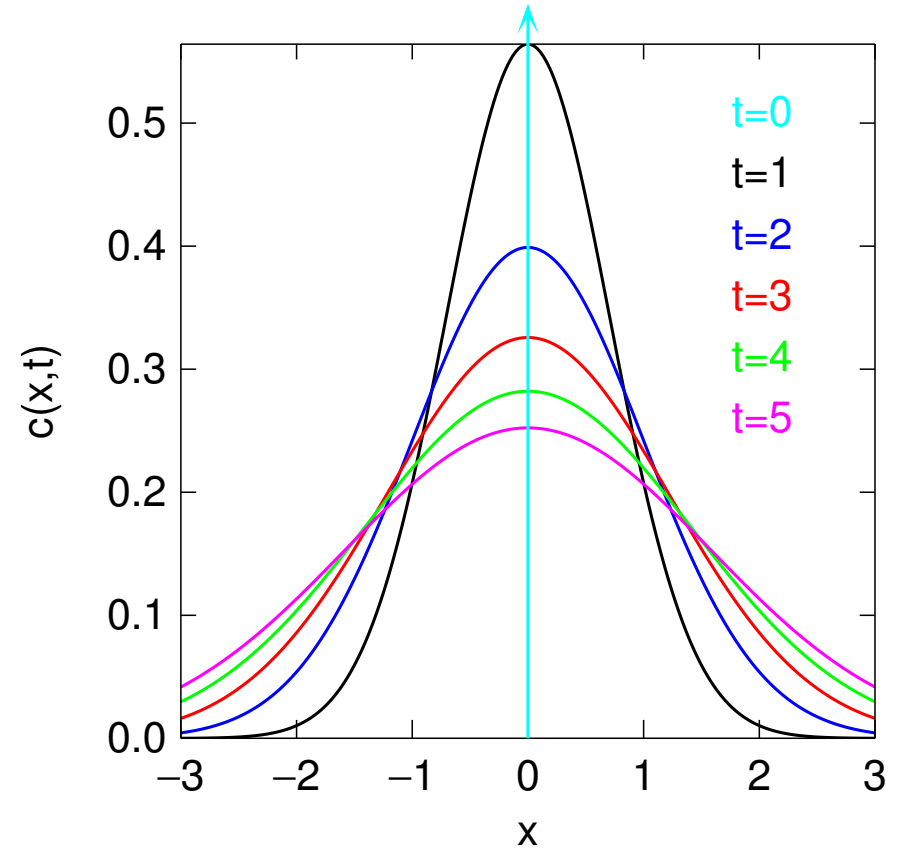
$$\left. -\frac{1}{3}\cos\left(\frac{3\pi x}{l}\right)\exp\left(-\frac{3^2\pi^2}{l^2}D\tau\right) + \frac{1}{5}\cos\left(\frac{5\pi x}{l}\right)\exp\left(-\frac{5^2\pi^2}{l^2}D\tau\right)\cdots\right]$$

# Diffusion and the Brownian motion

Instead of for $c(\vec{r}, \tau)$, let us solve the 2nd Fick law for the probability of finding a particle, starting from origin at $\tau = 0$. We get the **Gaussian distribution** with half-width $\propto$
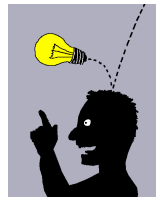
1D:   $c(x, \tau) = (4\pi D\tau)^{-1/2} \exp\left(-\dfrac{x^2}{4D\tau}\right)$

3D:   $c(\vec{r}, \tau) = (4\pi D\tau)^{-3/2} \exp\left(-\dfrac{r^2}{4D\tau}\right)$
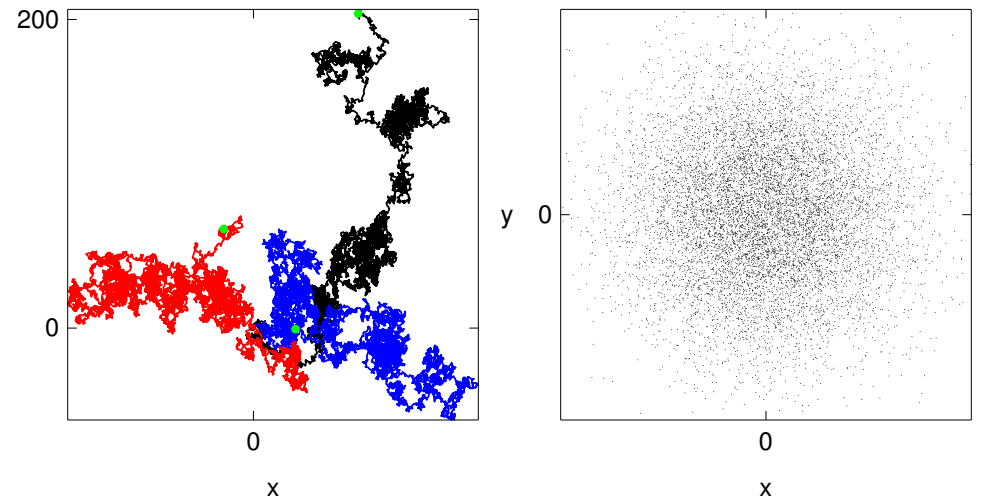


● 1D:  $\langle x^2 \rangle = 2D\tau$

Last example – order-of-magnintude
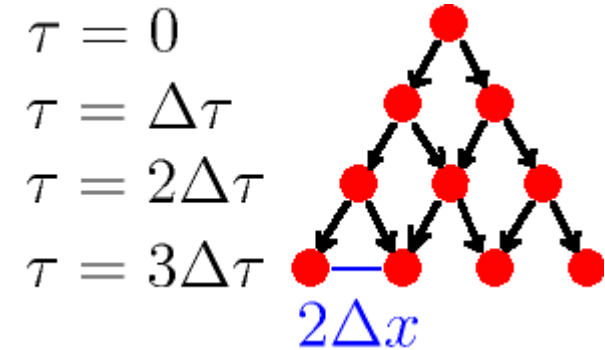$\tau \approx x^2/2D = 4$ months
(for $x = 0.1\,\mathrm{m}$)

● 3D:  $\langle r^2 \rangle = 6D\tau$

# Brownian motion as a random walk

(Smoluchowski, Einstein)

● within time $\Delta\tau$, a particle moves randomly
  – by $\Delta x$ with probability 1/2
  – by $-\Delta x$ with probability 1/2

$\tau = 0$

$\tau = \Delta\tau$

$\tau = 2\Delta\tau$

$\tau = 3\Delta\tau$

$2\Delta x$

Using the central limit theorem:

● in one step: $\mathrm{Var}\,x = \langle x^2 \rangle = \Delta x^2$

● in $n$ steps (in time $\tau = n\Delta\tau$): $\mathrm{Var}\,x = n\Delta x^2$
  $\Rightarrow$ Gaussian normal distribution with $\sigma = \sqrt{n\Delta x^2} = \sqrt{\tau/\Delta\tau}\,\Delta x$:

$$\frac{1}{\sqrt{2\pi}\sigma} e^{-x^2/2\sigma^2} = \frac{1}{\sqrt{2\pi\tau}}\frac{\sqrt{\Delta\tau}}{\Delta x}\exp\left[-\frac{-x^2}{2\tau}\frac{\Delta\tau}{\Delta x^2}\right]$$

which is for $2D = \Delta x^2/\Delta\tau$ the same as $c(x, \tau)$

NB: $\mathrm{Var}\,x \overset{\text{def.}}{=} \langle(x - \langle x\rangle)^2\rangle$, for $\langle x\rangle = 0$, then $\mathrm{Var}\,x = \langle x^2\rangle$

**Example.** Calculate $\mathrm{Var}\,u$, where $u$ is a random number from interval $(-1, 1)$

# Electric conductivity

Ohm Law (here: $U$ = voltage, $U = \phi_2 - \phi_1$):

$$R = \frac{U}{I} \qquad I = \frac{1}{R}U \qquad 1/R = \text{conductivity, } [1/R] = 1/\Omega = S = \text{Siemens}$$

**(Specific) conductivity (conductance)** $\kappa$ is 1/resistance of a unit cube

$$\frac{1}{R} = \kappa\frac{\mathcal{A}}{l} \qquad \mathcal{A} = \text{area, } l = \text{layer thickness, } [\kappa] = S\,m^{-1}$$

Vector notation: $\vec{j} = \kappa\vec{\mathcal{E}} = -\kappa\vec{\nabla}\phi$

$\vec{j}$ = el. current density, $j = I/\mathcal{A}$, $\vec{\mathcal{E}}$ = el. field intensity, $\mathcal{E} = U/l$

# Electric conductivity

| substance | $\kappa/(\mathrm{S\,m^{-1}})$ |
|---|---|
| graphene | $1 \times 10^8$ |
| silver | $63 \times 10^6$ |
| sea water | 5 |
| Ge | 2.2 |
| tap water | 0.005 to 0.05 |
| Si | $1.6 \times 10^{-3}$ |
| distilled water (contains $CO_2$) | $7.5 \times 10^{-5}$ |
| deionized water | $5.5 \times 10^{-6}$ |
| glass | $1 \times 10^{-15}$–$1 \times 10^{-11}$ |
| teflon | $1 \times 10^{-25}$–$1 \times 10^{-23}$ |

Strong electrolytes: conductivity proportional to concentration.

**Molar conductivity** $\lambda$:

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

Units: $[\kappa] = \mathrm{S\,m^{-1}}$, $[\lambda] = \mathrm{S\,m^2\,mol^{-1}}$.

Watch units—best convert $c$ to $\mathrm{mol\,m^{-3}}$!

**Example.** Conductivity of a 0.1 M solution of HCl o is $4\,\mathrm{S\,m^{-1}}$. Calculate the molar conductivity.

$0.04\,\mathrm{S\,m^2\,mol^{-1}}$

# Mobility and molar conductivity

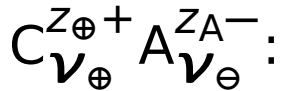**Mobility** of an ion = averaged velocity in a unit electric field:

$$u_i = \frac{v_i}{\mathcal{E}} \qquad \mathcal{E} = U/l = \text{el. intensity}, \ U = \text{voltage}$$

Charges $z_i e$ of velocity $v_i$ and concentration $c_i$ cause the current density

$$\overset{\text{``}\kappa_i\text{''}}{\swarrow}$$

$$j_i = v_i c_i z_i F = u_i \mathcal{E} c_i z_i F \overset{!}{=} \lambda_i c_i \mathcal{E} \quad \Rightarrow \quad \boxed{\lambda_i = u_i z_i F} = \text{molar conductivity of ion } i$$

Ions (in dilute solutions) migrate independently (**Kohlrausch law**), for electrolyte
$C_{\boldsymbol{\nu}_\oplus}^{z_\oplus +} A_{\boldsymbol{\nu}_\ominus}^{z_A -}$: $\qquad\qquad\qquad\qquad\qquad$ here we define $z_A > 0$

$$j = j_A + j_C = (\lambda_A c_A + \lambda_C c_C)\mathcal{E} = (\lambda_A \boldsymbol{\nu}_A + \lambda_C \boldsymbol{\nu}_C) c\mathcal{E}$$

Mathematically

$$\lambda = \frac{\kappa}{c} = \sum_i \boldsymbol{\nu}_i \lambda_i$$

# Nothing is ideal

**Limiting molar conductivity** = molar conductivity at infinite dilution

$$\lambda_i^\infty = \lim_{c \to 0} \lambda_i$$

Departure from the limiting linear behavior (cf. Debye–Hückel theory):

$$\lambda = \lambda(c) = \lambda^\infty - \text{const}\sqrt{c} \quad \text{nebo} \quad \lambda = \lambda^\infty - \text{const}\sqrt{I_c}$$
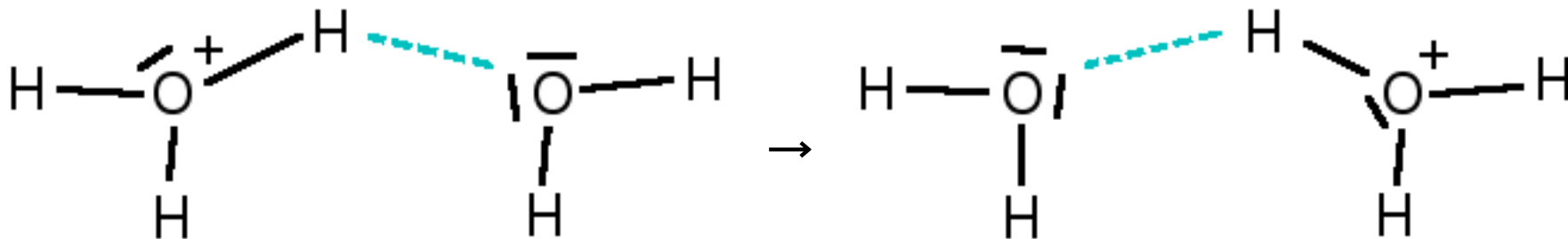
Typical values:

| cation | $\lambda^\infty/(\text{S m}^2\,\text{mol}^{-1})$ | anion | $\lambda^\infty/(\text{S m}^2\,\text{mol}^{-1})$ |
|--------|------|--------|------|
| $H^+$ | 0.035 | $OH^-$ | 0.020 |
| $Na^+$ | 0.0050 | $Cl^-$ | 0.0076 |
| $Ca^{2+}$ | 0.012 | $SO_4^{2-}$ | 0.016 |

⬤ Mobility and molar conductivity decreases with the ion size ($Cl^-$ is slow), solvation (small $Li^+ + 4\,H_2O$ is slow)

⬤ $H^+$, $OH^-$ are fast

*movie credit: Matt K. Petersen, Wikipedia*
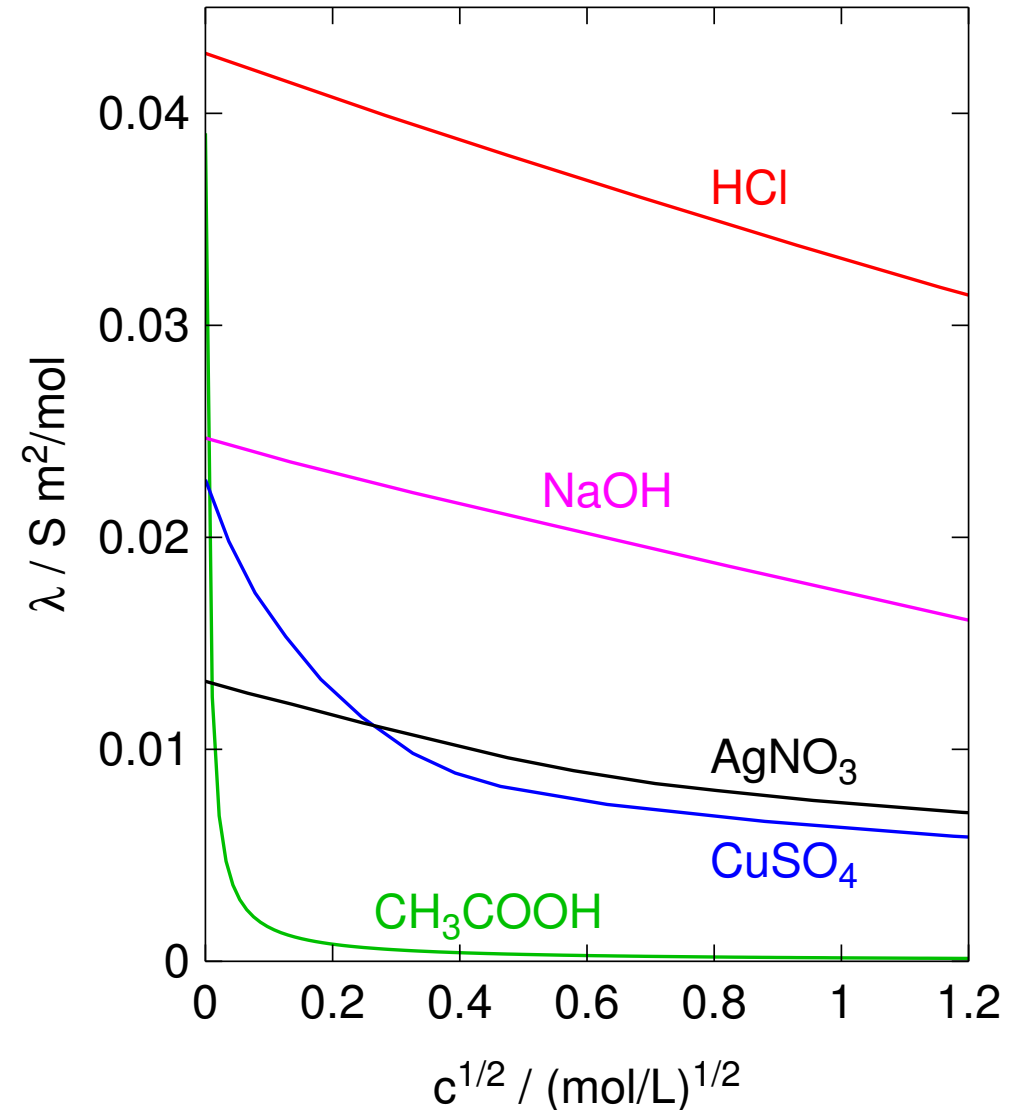
We count ions only, not unionized acid

In the limiting concentration:

$$\kappa = \lambda^\infty c_{\text{ions}} = \lambda^\infty \alpha c \overset{\text{def.}}{=} \lambda^{\text{exptl}} c$$

$$\alpha = \frac{\lambda^{\text{exptl}}}{\lambda^\infty}$$

**Ostwald's dilution law**:

$$K = \frac{c}{c^{\text{st}}} \frac{\alpha^2}{1-\alpha} = \frac{c}{c^{\text{st}}} \frac{(\lambda^{\text{exptl}})^2}{\lambda^\infty (\lambda^\infty - \lambda^{\text{exptl}})}$$

Einstein (Nernst–Einstein) equation:

$$D_i = \frac{k_\mathrm{B}T}{f_i} = \frac{k_\mathrm{B}T}{\mathcal{F}_i/v_i} = \frac{k_\mathrm{B}T}{z_i e \mathcal{E}/(u_i \mathcal{E})} = \frac{k_\mathrm{B}T}{z_i e/u_i} = \frac{RT u_i}{z_i F}$$

microscopically:

$$u_i = \frac{z_i e}{k_\mathrm{B}T} D_i$$

here $z_i$ is with sign

$$z_i F D_i = RT u_i \quad \Rightarrow \quad \lambda_i = u_i z_i F = \frac{z_i^2 F^2}{RT} D_i$$

🟣 diffusion: caused by a gradient of concentration/chemical potential

$$\vec{J}_i \;=\; -D_i \vec{\nabla} c_i = -c_i \frac{D_i}{RT} \vec{\nabla} \mu_i$$

$$\vec{J}_i \;=\; -c_i \frac{z_i F D_i}{RT} \vec{\nabla} \mu_i = -c_i u_i \vec{\nabla} \mu_i$$

🟣 migration: caused by el. field

$$\vec{J}_i = -\kappa_i \vec{\nabla} \phi = -c_i \lambda_i \vec{\nabla} \phi = -c_i u_i z_i F \vec{\nabla} \phi$$

Let us define the **electrochemical potential** $\tilde{\mu}_i = \mu_i + z_i F \phi$, then

$$\vec{J}_i = -c_i u_i \vec{\nabla} \tilde{\mu}_i = -c_i \frac{D_i z_i F}{RT} \vec{\nabla} \tilde{\mu}_i = -c_i \frac{\lambda_i}{z_i F} \vec{\nabla} \tilde{\mu}_i$$

# Transference numbers

**Transference number** (transport number) of an ion is the fraction of the total current that is carried by that ion during migration (electrolysis).

$$t_\ominus = \frac{I_\ominus}{I} = \frac{I_\ominus}{I_\ominus + I_\oplus}$$

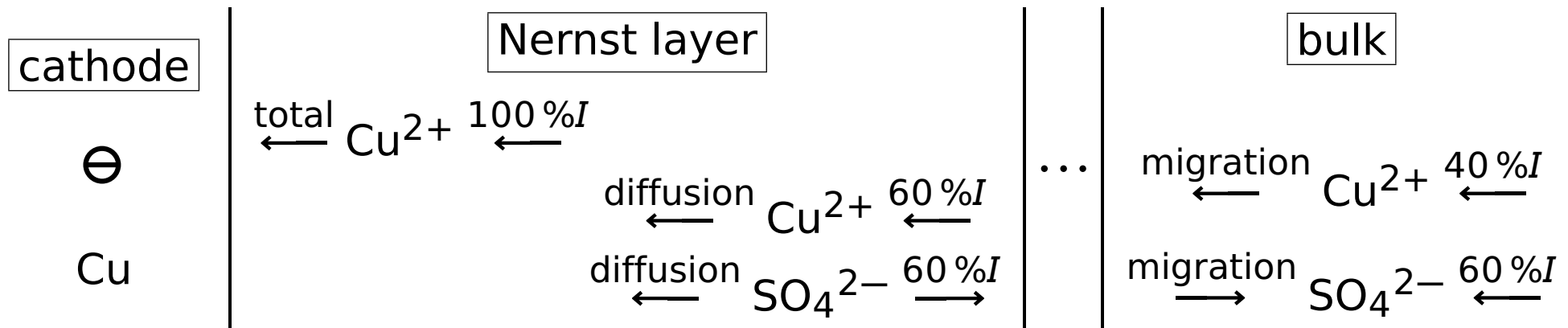$\nu$ = velocity
$\boldsymbol{\nu}$ = stechiom. coeff.

Ions move at different speeds under the same field. For $K_{\boldsymbol{\nu}_\oplus}^{z_\oplus+} A_{\boldsymbol{\nu}_\ominus}^{z_\ominus-}$ (electroneutrality: $z_\ominus c_\ominus = z_\oplus c_\oplus$; here $z_\ominus > 0$)

$$t_\ominus = \frac{v_\ominus c_\ominus z_\ominus}{v_\ominus c_\ominus z_\ominus + v_\oplus c_\oplus z_\oplus} = \frac{v_\ominus}{v_\ominus + v_\oplus} = \frac{u_\ominus}{u_\ominus + u_\oplus} = \frac{z_\ominus D_\ominus}{z_\ominus D_\ominus + z_\oplus D_\oplus} = \frac{\boldsymbol{\nu}_\ominus \lambda_\ominus}{\boldsymbol{\nu}_\ominus \lambda_\ominus + \boldsymbol{\nu}_\oplus \lambda_\oplus}$$

**Properties:** $\qquad t_\ominus + t_\oplus = 1, \quad \dfrac{t_\ominus}{t_\oplus} = \dfrac{u_\ominus}{u_\oplus}$

$v_i = u_i \mathcal{E}, \; u_i = \dfrac{z_i e}{k_B T} D_i, \; \lambda_i = u_i z_i F$

**Example.** Electrolysis of $CuSO_4$: $t_{Cu^{2+}} = 40\,\%$, $t_{SO_4^{2-}} = 60\,\%$.

**Example.** Calculate the specific conductivity of a uni-univalent electrolyte MA of concentration $0.01\,\text{mol}\,\text{dm}^{-3}$, assuming that both M and A are of the same size as the sucrose molecule ($D = 5.2 \times 10^{-6}\,\text{cm}^2\,\text{s}^{-1}$ at $25\,°\text{C}$)?

$$\kappa = 0.04\,\text{S}\,\text{m}^{-1} \quad (\lambda_\pm = 0.002\,\text{S}\,\text{m}^{-2}\,\text{mol}^{-1})$$

Note: $0.01\,\text{M}\odot$ of KCl has $\kappa = 0.14\,\text{S}\,\text{m}^{-1} > 0.04\,\text{S}\,\text{m}^{-1}$, because the ions are smaller than sucrose

**Example.** Calculate the migration speeds of ions $\text{M}^+$, $\text{A}^-$ between electrodes 1 cm apart with applied voltage 2 V.

$$v_{\text{M}^+} = -v_{\text{A}^-} = 4 \times 10^{-6}\,\text{m}\,\text{s}^{-1} = 15\,\text{mm}\,\text{h}^{-1}$$

$$v_i = u_i \mathcal{E} \quad u_i = \frac{z_i e}{k_\text{B} T} D_i \quad \lambda_i = u_i z_i F$$

# Conductivity measurements

**Usage:** determination of ion concentrations (usually small)
⇒ solubility, dissociation constants, conductometric titration…



vodivostní nádobka

$R$

$R_\mathrm{S}$ srovnávací odpor

indikátor

$R_1$

$R_2$

$$\frac{R}{R_\mathrm{S}} = \frac{R_1}{R_2}$$

různé typy vodivostních nádobek

Wheatstoneův můstek

střídavý zdroj (1 - 4 kHz)
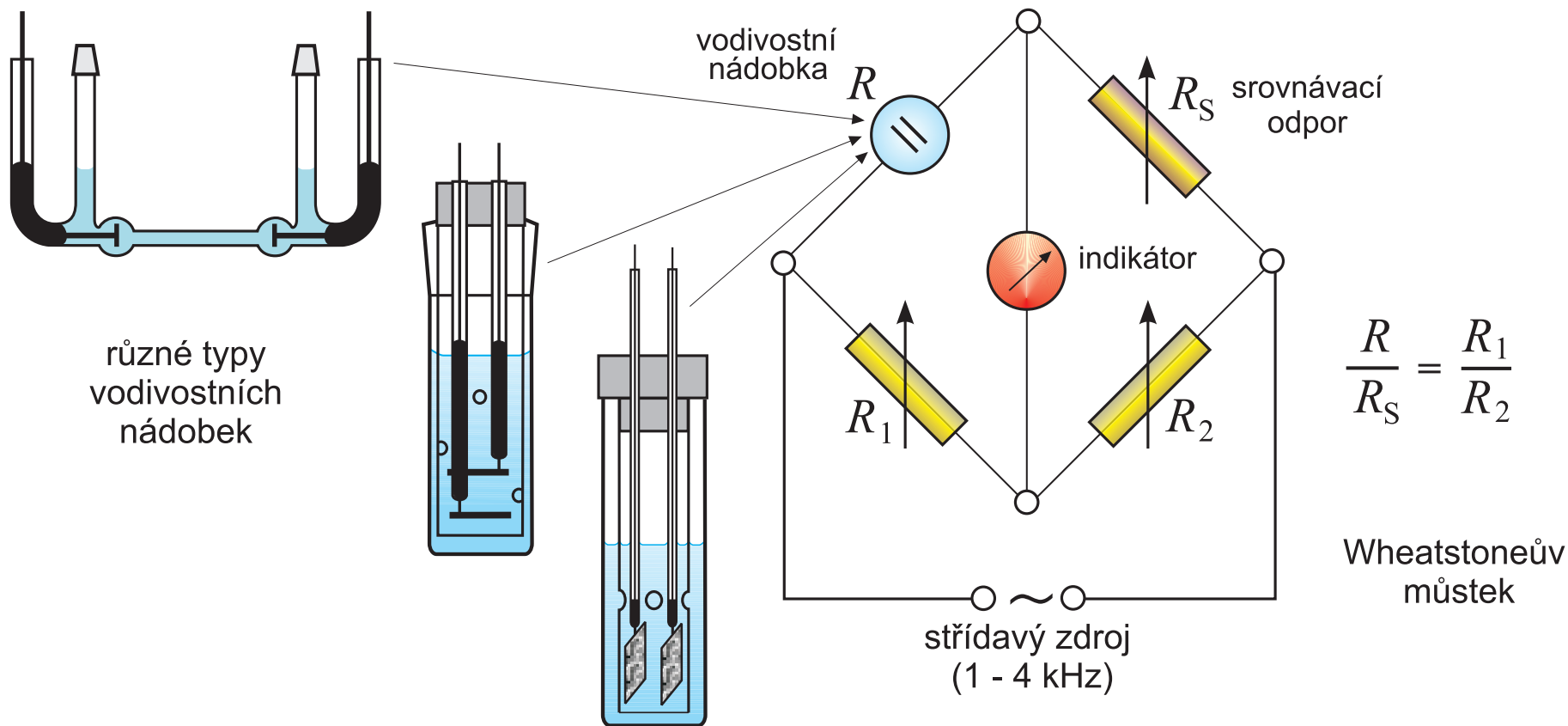
Resistance constant of conductance cell (probe) $C$ (dimension = $m^{-1}$):

$$\frac{1}{R} = \kappa \cdot \frac{\mathcal{A}}{l} \qquad \Rightarrow \qquad R\kappa = \frac{l}{\mathcal{A}} = C$$

$C$ determined from a solution of known conductivity (e.g., KCl), $C = R_\odot \kappa_\odot$.