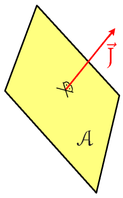
Transport phenomena

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



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

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

Diffusion—macroscopic view

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

$$\vec{J}_i = -D_i\vec{\nabla}c_i$$

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

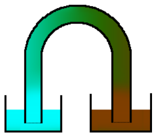
is proportional to the **concentration gradient**

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

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? $D_{\text{sucrose}}(25\,°\mathrm{C}) = 5.2\times10^{-6}\,\mathrm{cm^2\,s^{-1}}$.

0.74 mg



110 g sucrose in 1 L: $c_w = 110\,\mathrm{g\,dm^{-3}} = 110\,\mathrm{kg\,m^{-3}}$
$\operatorname{grad} c_w = c_w/l = 550\,\mathrm{kg\,m^{-4}}$
$D = 5.2\times10^{-6}\,\mathrm{cm^2\,s^{-1}} = 5.2\times10^{-10}\,\mathrm{m^2\,s^{-1}}$
$J = D\operatorname{grad} c_w = 2.56\times10^{-7}\,\mathrm{kg\,m^{-2}\,s^{-1}}$
$m = J\mathcal{A}t = 2.56\times10^{-7}\,\mathrm{kg\,m^{-2}\,s^{-1}}\times0.3\times10^{-4}\,\mathrm{m^2}\times24\times60^2\,\mathrm{s} = 7.4\times10^{-7}\,\mathrm{kg}$

Diffusion—microscopic view

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

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

Thermodynamic force = −grad of the chemical potential:

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

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

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

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

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

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

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

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

(also Einstein–Smoluchowski equation)

Einstein–Stokes equation

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

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

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

⇒ Einstein–Stokes equation:

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

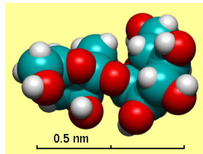
Opposite reasoning—hydrodynamic (Stokes) radius defined as:

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

≈ effective molecule size (incl. solvation shell)

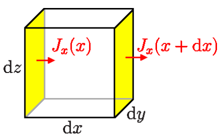
Example. Estimate the size of the sucrose molecule. Water viscosity is $0.891\times10^{-3}\ \mathrm{m^{-1}\,kg\,s^{-1}}$ at 25 °C.

$R = 0.47$ nm



Second Fick Law

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



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

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

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

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

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

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:

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

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

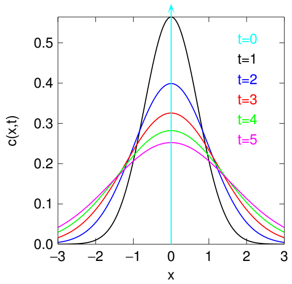
$$\left.-\frac{1}{3}\cos\left(\frac{3\pi x}{l}\right)\exp\left(-\frac{3^2\pi^2}{l^2}D\tau\right) + \frac{1}{5}\cos\left(\frac{5\pi x}{l}\right)\exp\left(-\frac{5^2\pi^2}{l^2}D\tau\right)\cdots\right]$$

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 ∝

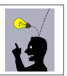
1D: $c(x,\tau) = (4\pi D\tau)^{-1/2}\exp\left(-\dfrac{x^2}{4D\tau}\right)$

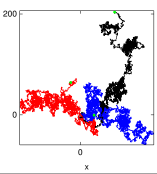
3D: $c(\vec{r},\tau) = (4\pi D\tau)^{-3/2}\exp\left(-\dfrac{r^2}{4D\tau}\right)$

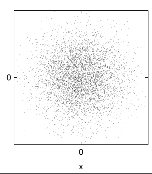


- 1D: $\langle x^2\rangle = 2D\tau$

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





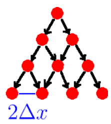


- 3D: $\langle r^2\rangle = 6D\tau$

Brownian motion as a random walk

(Smoluchowski, Einstein)

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



Using the central limit theorem:

- in one step: $\operatorname{Var}x = \langle x^2\rangle = \Delta x^2$
- in n steps (in time $\tau = n\Delta\tau$): $\operatorname{Var}x = n\Delta x^2$
  ⇒ 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: $\operatorname{Var}x \overset{\text{def.}}{=} \langle(x - \langle x\rangle)^2\rangle$, for $\langle x\rangle = 0$, then $\operatorname{Var}x = \langle x^2\rangle$

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

1/6

Electric conductivity

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

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

(Specific) conductivity (conductance) κ is 1/resistance of a unit cube

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

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

Molar conductivity

Strong electrolytes: conductivity proportional to concentration.

Molar conductivity λ:

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

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

Watch units—best convert c to mol m^{-3}!

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

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

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

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

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

$$j = j_A + j_C = (\lambda_A c_A + \lambda_C c_C)\mathcal{E} = (\lambda_A \nu_A + \lambda_C \nu_C) c\mathcal{E}$$

Mathematically

$$\lambda = \frac{\kappa}{c} = \sum_i \nu_i \lambda_i$$

Nothing is ideal

Limiting molar conductivity = molar conductivity at infinite dilution

$$\lambda_i^\infty = \lim_{c\to0}\lambda_i$$

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

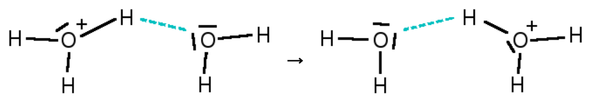
$$\lambda = \lambda(c) = \lambda^\infty - \text{const}\sqrt{c} \quad \text{nebo} \quad \lambda = \lambda^\infty - \text{const}\sqrt{I_c}$$

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



Conductivity of weak electrolytes

We count ions only, not unionized acid

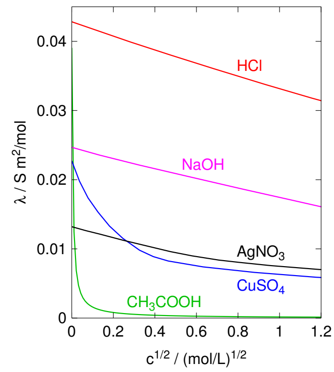
In the limiting concentration:

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

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

Ostwald's dilution law:

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



Conductivity and the diffusion coefficient

Einstein (Nernst–Einstein) equation:

$$D_i = \frac{k_B T}{f_i} = \frac{k_B T}{\mathcal{F}_i/v_i} = \frac{k_B T}{z_i e\mathcal{E}/(u_i\mathcal{E})} = \frac{k_B T}{z_i e/u_i} = \frac{RTu_i}{z_i F}$$

microscopically: $u_i = \frac{z_i e}{k_B T} D_i$ here z_i is with sign

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

- 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).

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

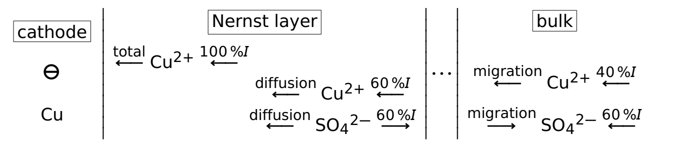
v = velocity
$\boldsymbol{\nu}$ = stechiom. coeff.

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

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

Properties: $t_\ominus + t_\oplus = 1$, $\frac{t_\ominus}{t_\oplus} = \frac{u_\ominus}{u_\oplus}$ $\quad v_i = u_i\mathcal{E},\ u_i = \frac{z_i e}{k_B T}D_i,\ \lambda_i = u_i z_i F$

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



Examples

Example. Calculate the specific conductivity of a uni-univalent electrolyte MA of concentration 0.01 mol dm^{-3}, assuming that both M and A are of the same size as the sucrose molecule ($D = 5.2\times10^{-6}$ cm^2 s^{-1} at 25 °C)?

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

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

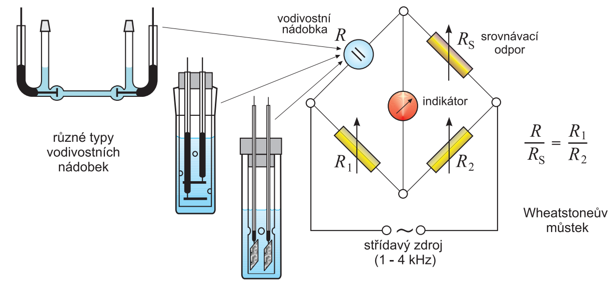
Example. Calculate the migration speeds of ions M$^+$, A$^-$ between electrodes 1 cm apart with applied voltage 2 V.

$v_{M^+} = -v_{A^-} = 4\times10^{-6}\,\mathrm{m\,s^{-1}} = 15\,\mathrm{mm\,h^{-1}}$

$$v_i = u_i\mathcal{E} \qquad u_i = \frac{z_i e}{k_B T} D_i \qquad \lambda_i = u_i z_i F$$

Conductivity measurements

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



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), $C = R_{\odot}\kappa_{\odot}$.