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: \( J \text{ m}^{-2} \text{s}^{-1} = W \text{ m}^{-2} \),
  current density: \( A \text{ m}^{-2} \)

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

- Small forces—linearity
  \[ \vec{J} = \text{const} \cdot \vec{F} \]

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: mol m$^{-2}$ s$^{-1}$)

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

is proportional to the **concentration gradient**

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

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

**Example.** A U-shaped pipe of length $l = 20$ cm and cross section $A = 0.3$ 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?

$D_{\text{sucrose}}(25^\circ\text{C}) = 5.2 \times 10^{-6}$ cm$^2$ s$^{-1}$.
Flux is given by the mean velocity of molecules $\vec{v}_i$:

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

Thermodynamic force $= -\nabla$ of the chemical potential:

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

where formula $\mu_i = \mu_i^0 + RT \ln (c_i/c_{st})$ for infinity dilution was used.

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

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

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

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

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

\[ D_i = \frac{k_B T}{f_i} \]
(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)

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

$\Rightarrow$ Einstein–Stokes equation:

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

Opposite reasoning—hydrodynamic (Stokes) radius defined as:

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

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

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

$$R = 0.47 \text{ nm}$$
Second Fick Law

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

$$\sum_{x,y,z} [J_x(x) - J_x(x + dx)]dydz = -dV \nabla \cdot \vec{J}$$

$$\vec{J} = -D \nabla c \Rightarrow \frac{\partial c_i}{\partial \tau} = D_i \nabla^2 c_i$$

(equation of heat conduction)

**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?

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

$$c(x, 0) = \begin{cases} c_0 & x < l/2 \\ 0 & x > l/2 \end{cases}$$

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

4 months
Instead of for \( c(\vec{r}, \tau) \), let us solve the 2nd Fick law for the probability of finding a particle, provided that it sits at origin for \( \tau = 0 \). We get the **Gaussian distribution** with half-width \( \propto \tau^{1/2} \)

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

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

1D: \( \langle x^2 \rangle = 2D\tau \)

The previous example:
\( \tau \approx x^2/2D = 4 \text{ months} \) (\( x = 0.1 \text{ m} \))

3D: \( \langle \vec{r}^2 \rangle = 6D\tau \)
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

Using the central limit theorem:

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

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

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

$$R = \frac{V}{I}, \quad I = \frac{1}{R} V$$

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

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

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

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

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

<table>
<thead>
<tr>
<th>substance</th>
<th>(\kappa/(\text{S m}^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>silver</td>
<td>(63 \times 10^6)</td>
</tr>
<tr>
<td>sea water</td>
<td>5</td>
</tr>
<tr>
<td>tap water</td>
<td>(0.005) to (0.05)</td>
</tr>
<tr>
<td>Si</td>
<td>(1.6 \times 10^{-3})</td>
</tr>
<tr>
<td>distilled water (contains CO(_2))</td>
<td>(7.5 \times 10^{-5})</td>
</tr>
<tr>
<td>deionized water</td>
<td>(5.5 \times 10^{-6})</td>
</tr>
<tr>
<td>glass</td>
<td>(1 \times 10^{-15}) to (1 \times 10^{-11})</td>
</tr>
</tbody>
</table>
Molar conductivity

Strong electrolytes: conductivity proportional to concentration.

**Molar conductivity** \( \lambda \):

\[
\lambda = \frac{\kappa}{c}
\]

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

Watch units—best convert \(c\) to \(\text{mol m}^{-3}\)!

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

\[
\lambda = \frac{4 \text{ S m}^{-1}}{0.1 \text{ mol m}^{-3}} = 40 \text{ S m}^2\text{mol}^{-1}
\]
**Mobility and molar conductivity**

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

\[ u_i = \frac{v_i}{\xi} \quad \xi = U/l = \text{el. intensity, } U = \text{voltage} \]

Charges \( z_i e \) of velocity \( v_i \) and concentration \( c_i \) cause the current density \( \kappa_i \)

\[ j_i = v_i c_i z_i F = u_i \xi c_i z_i F = \lambda_i c_i \xi \quad \Rightarrow \quad \lambda_i = u_i z_i F = \text{molar conductivity of ion } i \]

Ions (in dilute solutions) migrate independently (**Kohlrausch law**), for electrolyte \( K^{z_\oplus+} A^{z_A -} \):

\[ j = j_A + j_K = (\lambda_A c_A + \lambda_K c_K) \xi = (\lambda_A \nu_A + \lambda_K \nu_K) c \xi \]

Mathematically

\[ \lambda = \frac{\kappa}{c} = \sum_i \nu_i \lambda_i \]

Deprecated (\( \lambda_i^e = \text{equivalent conductivity} \))

\[ \lambda = \sum_i \nu_i z_i \lambda_i^e \quad \lambda_i^e = u_i F = \frac{\lambda_i}{z_i} \]
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):

\[
\lambda = \lambda(c) = \lambda^\infty - \text{const} \sqrt{c}
\]

Typical values:

<table>
<thead>
<tr>
<th>cation</th>
<th>( \lambda^\infty / (\text{S m}^2 \text{mol}^{-1}) )</th>
<th>anion</th>
<th>( \lambda^\infty / (\text{S m}^2 \text{mol}^{-1}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{H}^+ )</td>
<td>0.035</td>
<td>( \text{OH}^- )</td>
<td>0.020</td>
</tr>
<tr>
<td>( \text{Na}^+ )</td>
<td>0.0050</td>
<td>( \text{Cl}^- )</td>
<td>0.0076</td>
</tr>
<tr>
<td>( \text{Ca}^{2+} )</td>
<td>0.012</td>
<td>( \text{SO}_4^{2-} )</td>
<td>0.016</td>
</tr>
</tbody>
</table>

Mobility and molar conductivity decreases with the ion size (\( \text{Cl}^- \) is slow), solvation (small \( \text{Li}^+ + 4 \text{H}_2\text{O} \) is slow)

\( \text{H}^+, \text{OH}^- \) are fast

movie credit: Matt K. Petersen, Wikipedia
Conductivity of weak electrolytes

We count ions only, not unionized acid

In the limiting concentration:

\[ \kappa = \lambda^\infty c_{\text{ions}} = \lambda^\infty \alpha c \quad \text{def.} \quad \lambda^\text{exptl} c \]

\[ \alpha = \frac{\lambda^\text{exptl}}{\lambda^\infty} \]

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:

$$D_i = \frac{k_B T}{f_i} = \frac{k_B T}{F_i / \nu_i} = \frac{k_B T}{z_i e \mathcal{E} / (u_i \mathcal{E})} = \frac{k_B T}{z_i e / u_i} = \frac{RT u_i}{z_i F}$$

here $z_i$ is with sign

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

Diffusion: caused by a gradient of concentration/chemical potential

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

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

Migration: caused by el. field

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

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 electrolysis.

\[ t_\Theta = \frac{I_\Theta}{I} = \frac{I_\Theta}{I_\Theta + I_\oplus} \]

Different ions carry different fractions of the current because different ions move at different speeds under the same potential gradient.

For \( K^{z_\Theta +} A^{z_\Theta -} \) (electroneutrality: \( z_\Theta c_\Theta = z_\Theta c_\oplus \)): here \( z_\Theta > 0 \)

\[ t_\Theta = \frac{v_\Theta c_\Theta z_\Theta}{v_\Theta c_\Theta z_\Theta + v_\oplus c_\oplus z_\oplus} = \frac{v_\Theta}{v_\Theta + v_\oplus} = \frac{u_\Theta}{u_\Theta + u_\oplus} = \frac{z_\Theta D_\Theta}{z_\Theta D_\Theta + z_\Theta D_\oplus} = \frac{v_\Theta \lambda_\Theta}{v_\Theta \lambda_\Theta + v_\oplus \lambda_\oplus} \]

**Properties:**

\[ t_\Theta + t_\oplus = 1 \quad \frac{t_\Theta}{t_\oplus} = \frac{u_\Theta}{u_\oplus} \]

**Example.** Electrolysis of \( \text{CuSO}_4 \): \( t_{\text{Cu}^{2+}} = 40 \% \), \( t_{\text{SO}_4^{2-}} = 60 \% \).

<table>
<thead>
<tr>
<th>cathode</th>
<th>Nernst layer</th>
<th>bulk</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \Theta )</td>
<td>( \text{total} \text{ Cu}^{2+} 100 % )</td>
<td>migration ( \text{Cu}^{2+} 40 % )</td>
</tr>
<tr>
<td>Cu</td>
<td>diffusion ( \text{Cu}^{2+} 60 % )</td>
<td>migration ( \text{SO}_4^{2-} 60 % )</td>
</tr>
<tr>
<td></td>
<td>diffusion ( \text{SO}_4^{2-} 60 % )</td>
<td></td>
</tr>
</tbody>
</table>
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 (\(D = 5.2 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}\) at 25 °C)?

\[
\kappa = 0.04 \text{ S m}^{-1} (\lambda = 0.002 \text{ S m}^{-2} \text{ mol}^{-1})
\]

Note: 0.01 M of KCl has \(\kappa = 0.14 \text{ S m}^{-1} > 0.04 \text{ S m}^{-1}\), 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.

\[
v = 4 \times 10^{-6} \text{ m s}^{-1} = 15 \text{ mm h}^{-1}
\]
Conductivity measurements

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

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

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

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