

So respiration is not a problem for long, rod-like or filamentary bacteria.

ions

The force on an ion of charge q in an electric field E is

$$F = qE.$$

A potential V_1 applied to one plate of metal separated by a distance l from a second metal plate kept at potential V_2 makes an electric field

$$E = \frac{V_2 - V_1}{l}$$

in the direction from plate 2 to plate 1.

If the ion is in a fluid or gas that has

viscosity, then the drift velocity v_d

will be given by Eq. (4.12) as

$$v_d = \frac{F}{\zeta} = \frac{qE}{\zeta}$$

where ζ is the viscous-friction coefficient of the ion in the fluid.

A concentration c moving at velocity v_d results in a flux

$$j = cv_d.$$

The present flux

$$j = \frac{cqE}{\zeta}$$

is called an electrophoretic flux of ions.

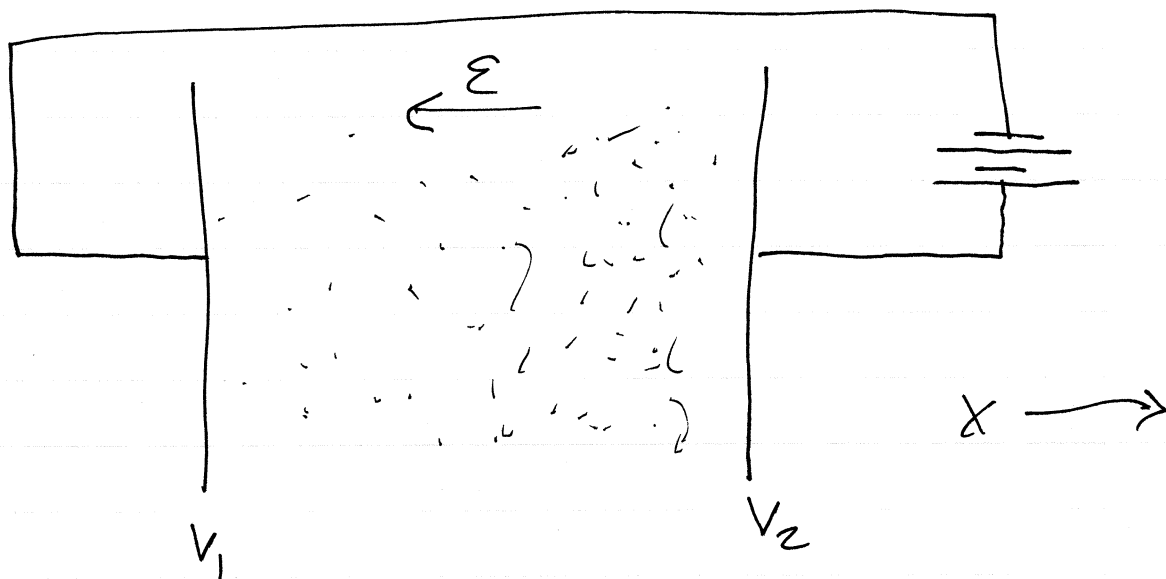
If the concentration c of ions is not uniform, then by Fick's law (4.19)

there will also be an entropic flux

$$j_e = -D dc/dx.$$

So the net flux of ions will be

$$j = \frac{q E(x) c(x)}{z} - D \frac{dc(x)}{dx}$$



in this example,

If $q > 0$, both components of the flux will be in the negative x -direction,

Now recall Einstein's relation (4.16)

$$z D = k T.$$

Then $z^{-1} = D / k T$ and so

$$j = D \left(- \frac{dc}{dx} + \frac{q}{k T} E c \right) \quad (4.24)$$

which is the Nernst-Planck formula.

What electric field E just cancels the entropic force and leads to zero flux, $j=0$? In the one-dimensional case with everything constant in the x - and y -directions, the condition for $j=0$ is

$$\frac{1}{c} \frac{dc}{dx} = \frac{q}{kT} E = \frac{d \ln c}{dx} \quad (4.25)$$

which we may integrate to

$$\begin{aligned} \ln \frac{c(x_2)}{c(x_1)} &= \frac{q}{kT} \int_{x_1}^{x_2} E(x) dx \\ &= -\frac{q}{kT} (V(x_2) - V(x_1)) \end{aligned} \quad (4.26a)$$

or

$$\frac{c(x_2)}{c(x_1)} = e^{-\frac{q}{kT} (V(x_2) - V(x_1))}$$

or

$$c(x) = c_0 e^{-\frac{qV(x)}{kT}}$$

where c_0 is some constant.

Now $qV(x) = U(x)$ is the potential energy of a charge q at the electrical potential — the voltage — $V(x)$. So our condition for equilibrium — no flux —

is the Boltzmann distribution

$$c(x) = c_0 e^{-\frac{U(x)}{kT}}$$

We may rewrite Eq. (4.26a) as

$$\ln c(x_2) - \ln c(x_1) = -q(V(x_2) - V(x_1)) / (kT)$$

or as

$$\Delta \ln c(x) = -q \Delta V_{eq}(x) / (kT), \quad (4.26b)$$

which is the Nernst relation. The subscript "eq" reminds us that this $\Delta V_{eq}(x)$ is what is needed to keep $\Delta c'$ in equilibrium.

How big a ΔV makes $c_2/c_1 = 10$?

$$\Delta \ln c = \ln c_2/c_1 = \ln 10 \approx 2.3, \text{ so}$$

Nernst's relation (4.26b) gives ΔV as

$$\Delta V = - \frac{\Delta \ln c}{q} kT$$

$$= - 2.3 \frac{kT}{e}$$

if $q = e$ the magnitude of the charge

of the electron. Now $kT \approx \frac{1}{40} \text{ eV}$, so

$$\Delta V = - \frac{2.3}{40} \text{ V} = -0.058 \text{ V} = -58 \text{ mV}.$$

If the solute is NaCl , then both Na^+ and Cl^- ions are present in the solution.

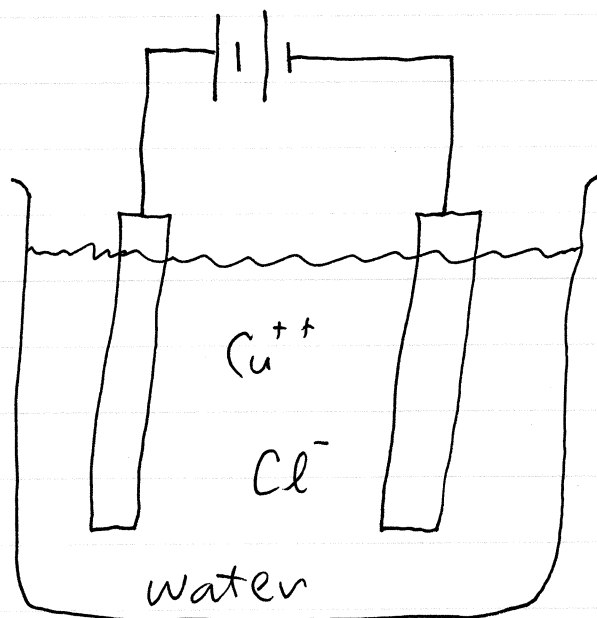
The Na^+ ions move to the plate of

lower voltage; the Cl^- ions go the

other way. Nerve and muscle cells

maintain potential differences ΔV
of a few tens of mV across their cell
membranes.

Electrolysis



Suppose we put the two plates in
a CuCl_2 solution. The CuCl_2 will
be present in the water as Cu^{++} ions
and as Cl^- ions. If the plates are
maintained at a potential difference ΔV ,

then the electric field \mathcal{E} between them will be $\Delta V = \mathcal{E}l$ if the distance between the plates is l .

We assume that the concentration of each kind of ion is uniform. Then by the Nernst-Planck formula (4.24) the field \mathcal{E} is (since $j = D \left(-\frac{dc}{dx} + \frac{qc}{kT} \mathcal{E} \right)$)

$$\mathcal{E} = \frac{kT}{Dq^2c} j.$$

If the plates have area A (each), then the current I is $I = qAj$ for ions of charge q . So ΔV is

$$\Delta V = \mathcal{E}l = \frac{kT}{Dq^2c} j = \frac{kT}{Dq^2c} \frac{l}{A} I$$

which is Ohm's law with $R = \frac{kT}{Dq^2c} \frac{l}{A}$.

The geometry of the galvanic cell is involved in R . To avoid mention of l and A , we define the electrical conductivity of the solution as

$$k = \sigma = \frac{l}{RA} = \frac{D q^2 c}{kT}$$

For each species of ion. Salt water conducts better than fresh water.

4 G (a) We try $c(x, z) = B e^{-x^2/(2At)}$

But is it normalized? Recall

$$\left(\int_{-\infty}^{\infty} dx e^{-x^2} \right)^2 = \int_0^{\infty} 2\pi r dr e^{-r^2} = -\pi \int_0^{\infty} du e^{-u} = \pi$$

So $\int_{-\infty}^{\infty} dx e^{-x^2} = \sqrt{\pi}$.

Let $x = y/\alpha$. Then

$$\int_{-\infty}^{\infty} \frac{dy}{\sqrt{\alpha}} e^{-y^2/\alpha} = \sqrt{\pi} \quad \text{so} \quad \int_{-\infty}^{\infty} dy e^{-\frac{y^2}{\alpha}} = \sqrt{\alpha\pi}.$$

$$S_0 \int_{-\infty}^{\infty} dx C(x,t) = B \int_{-\infty}^{\infty} e^{-\frac{x^2}{2At}} dx = B \sqrt{2\pi A t}$$

which cannot be normalized unless

$$B \text{ is a function of } t, \quad B = \frac{1}{\sqrt{2\pi A t}}$$

We now replace A by $2D$ and find

$$\text{that} \quad -\frac{x^2}{4Dt}$$

$$C(x,t) = \frac{e}{\sqrt{4\pi D t}}$$

is correctly normalized:

$$\int_{-\infty}^{\infty} C(x,t) dx = \frac{1}{\sqrt{4\pi D t}} \int_{-\infty}^{\infty} e^{-\frac{x^2}{4Dt}} dx = \frac{\sqrt{4\pi D t}}{\sqrt{4\pi D t}} = 1.$$

(b) Does $C(x,t)$ satisfy the diffusion equation

$$\frac{dC}{dt} = D \frac{d^2 C}{dx^2} \quad ?$$

$$C(x, t) = \frac{1}{\sqrt{4\pi Dt}} e^{-\frac{x^2}{4Dt}}$$

$$\frac{dc}{dx} = \frac{d}{dx} \left(-\frac{x^2}{4Dt} \right) C = -\frac{2x}{4Dt} C = -\frac{x}{2Dt} C$$

$$\frac{d^2c}{dx^2} = -\frac{C}{2Dt} + \left(-\frac{2x}{4Dt} \right)^2 C = \left(\frac{x^2}{4D^2t^2} - \frac{1}{2Dt} \right) C$$

$$\frac{dc}{dt} = \frac{d}{dt} \left(-\frac{x^2}{4Dt} \right) C + \frac{d}{dt} \left(\frac{1}{\sqrt{4\pi Dt}} \right) \sqrt{4\pi Dt} C$$

$$= \frac{x^2}{(4Dt)^2} 4D C - \frac{1}{2} \frac{4\pi D}{(4\pi Dt)^{3/2}} \sqrt{4\pi Dt} C$$

$$= \frac{x^2}{4D^2t^2} DC - \frac{2\pi}{4\pi Dt} DC$$

$$= D \left(\frac{x^2}{4D^2t^2} - \frac{1}{2Dt} \right) C$$

$$= D \frac{d^2c}{dx^2}$$

So $C(x, t)$ satisfies the diffusion equation

$$\frac{dc}{dt} = D \frac{d^2c}{dx^2}$$

(c)

$$\langle x^2 \rangle = \int_{-\infty}^{\infty} x^2 c(x,t) dx$$

$$= \int_{-\infty}^{\infty} x^2 \frac{1}{\sqrt{4\pi Dt}} e^{-\frac{x^2}{4Dt}} dx$$

$$= -\frac{d}{d\alpha} \int_{-\infty}^{\infty} \frac{4Dt}{\sqrt{4\pi Dt}} e^{-\frac{\alpha x^2}{4Dt}} dx \Big|_{\alpha=1}$$

$$= \sqrt{\frac{4Dt}{\pi}} \left(-\frac{d}{d\alpha}\right) \int_{-\infty}^{\infty} e^{-\frac{\alpha x^2}{4Dt}} dx \Big|_{\alpha=1}$$

$$= \sqrt{\frac{4\pi Dt}{\pi}} \left(-\frac{d}{d\alpha}\right) \sqrt{\frac{4Dt\pi}{\alpha}} \Big|_{\alpha=1}$$

$$= 4Dt \left(-\frac{d}{d\alpha}\right) \alpha^{-1/2} = 4Dt \frac{1}{2} \alpha^{-3/2} \Big|_{\alpha=1}$$

$$= 2Dt.$$

What about three dimensions?

The diffusions in y & z are independent of the diffusion in x , so

$$\begin{aligned}
 C(\vec{r}, t) &= C(x, t) C(y, t) C(z, t) \\
 &= \frac{1}{(4\pi Dt)^{3/2}} e^{-\frac{x^2 + y^2 + z^2}{4Dt}}
 \end{aligned}$$

for one particle — that is, for $\int C(\vec{r}, t) d\vec{r} = 1$.

For N particles,

$$C(\vec{r}, t) = \frac{N}{(4\pi Dt)^{3/2}} e^{-\frac{\vec{r}^2}{4Dt}} \quad (4.2)$$

where

$$\vec{r} = (x, y, z) \quad \text{and} \quad \vec{r}^2 = \vec{r} \cdot \vec{r} = x^2 + y^2 + z^2.$$

Recall that the mean displacement x_N after N steps of length L in one dimension obeys

$$\langle x_N^2 \rangle = NL^2. \quad (4.4)$$

So in three dimensions, $\langle \vec{r}_N^2 \rangle$ is

$$\langle \vec{r}_N^2 \rangle = 3NL^2,$$

which is true for the end of a model

polymer of N links, each of length $\sqrt{3}L$,

as we saw in section 4.3. To the extent

that polymers are random walks and that

random walks are gaussians, the probability

distribution for the end \vec{r}_N of a polymer

of N links of length $\sqrt{3}L$ is

$$P(\vec{r}_N) = \frac{1}{(2\pi NL^2)^{3/2}} e^{-\frac{r_N^2}{2NL^2}}$$

if the first link is stuck at $\vec{r}_0 = \vec{0}$.