in the water, with a concentration $c_0$. But the oxygen nearby gets depleted, as the bacterium uses it up.

The lake is huge, so the bacterium won't affect its overall oxygen level; instead the envronment near the bacterium will come to a quasi-steady state, in which the oxygen concentration $c$ doesn't depend on time. In this state the oxygen concentration $c(r)$ will depend on the distance $r$ from the center of the bacterium. Very far away, we know $c(\infty) = c_0$. We'll assume that every oxygen molecule that reaches the bacterium's surface gets immediately gobbled up. Hence at the surface $c(R) = 0$. From Fick's law there then must be a flux $j$ of oxygen molecules inward.

**Example**    Find the full concentration profile $c(r)$ and the maximum number of oxygen molecules per time that the bacterium can consume.

*Solution:*   Imagine drawing a series of concentric spherical shells around the bacterium with radii $r_1$, $r_2$,.... Oxygen is moving across each shell on its way to the center. Because we're in a quasi-steady state, oxygen does not pile up anywhere: The number of molecules per time crossing each shell equals the number per time crossing the next shell. This condition means that $j(r)$ times the surface area of the shell must be a constant, independent of $r$. Call this constant $I$. So now we know $j(r)$ in terms of $I$ (but we don't know $I$ yet).

Next, Fick's law says $j = D\frac{\mathrm{d}c}{\mathrm{d}r}$, but we also know $j = \frac{I}{4\pi r^2}$. Solving for $c(r)$ gives $c(r) = A - \frac{1}{r}\frac{I}{4\pi D}$, where $A$ is some constant. We can fix both $I$ and $A$ by imposing $c(\infty) = c_0$ and $c(R) = 0$, finding $A = c_0$ and $I = 4\pi DRc_0$. Along the way, we also find that the concentration profile itself is $c(r) = c_0(1 - (R/r))$.

Remarkably, *we have just computed the maximum rate at which oxygen molecules can be consumed by any bacterium whatsoever!* We didn't need to use any biochemistry at all, just the fact that living organisms are subject to constraints from the physical world. Notice that the oxygen uptake $I$ increases with increasing bacterial size, but only as the first power of $R$. We might expect the oxygen *consumption*, however, to increase roughly with an organism's *volume.* Together, these statements imply an upper limit to the size of a bacterium: If $R$ gets too large, the bacterium would literally suffocate.

―――――――――――**Your Turn 4f**―――――――――――
a. Evaluate the above expression for $I$, using the illustrative values $R = 1\,\mu\mathrm{m}$ and $c_0 \approx 0.2\,\mathrm{mole/m}^3$.
b. A convenient measure of an organism's overall metabolic activity is its rate of $O_2$ consumption divided by its mass. Find the maximum possible metabolic activity of a bacterium of arbitrary radius $R$, again using $c_0 \approx 0.2\,\mathrm{mole\,m}^{-3}$.
c. The actual metabolic activity of a bacterium is about $0.02\,\mathrm{mole\,kg}^{-1}\mathrm{s}^{-1}$. What limit do you then get on the size $R$ of a bacterium? Compare to the size of real bacteria. Can you think of some way for a bacterium to evade this limit?

$\boxed{T_2}$ *Section 4.6.2′ on page 134 mentions the concept of allometric exponents.*

### 4.6.3   The Nernst relation sets the scale of membrane potentials

Many of the molecules floating in water carry net electric charge, unlike the alcohol studied in the Example on page 122. For example, when ordinary salt dissolves, the individual sodium and
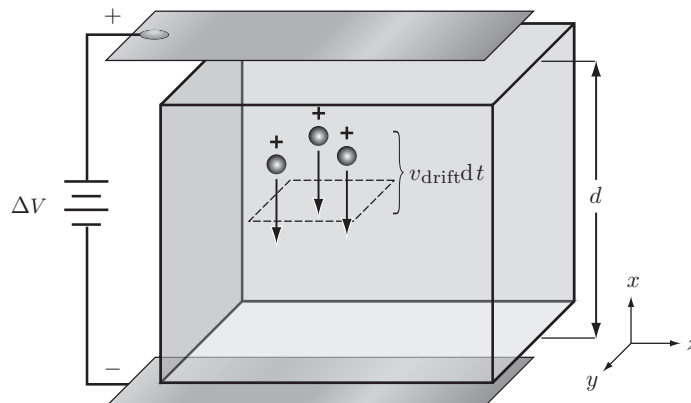
Figure 4.14: (Sketch.) Origin of the Nernst relation. An electric field pointing downward drives positively charged ions down. The system comes to equilibrium with a downward concentration gradient of positive ions and an upward gradient of negative ions. The flux through the surface element shown (dashed square) equals the number density $c$ times $v_{\mathrm{drift}}$.

chlorine atoms separate, but the chlorine atom grabs one extra electron from sodium, becoming a negatively charged chloride ion, $Cl^-$, and leaving the sodium as a positive ion, $Na^+$. Any electric field $\mathcal{E}$ present in the solution will then exert forces on the individual ions, dragging them just as gravity drags colloidal particles to the bottom of a test tube.

Suppose first that we have a uniform-density solution of charged particles, each of charge $q$, in a region with electric field $\mathcal{E}$. For example, we could place two parallel plates just outside the solution's container, a distance $d$ apart, and connect them to a battery that maintains constant potential difference $\Delta V$ across them. We know from first-year physics that then $\mathcal{E} = \Delta V/d$, and each charged particle feels a force $q\mathcal{E}$, so it drifts with the net speed we found in Equation 4.12: $v_{\mathrm{drift}} = q\mathcal{E}/\zeta$, where $\zeta$ is the viscous friction coefficient.

Imagine a small net of area $A$ stretched out perpendicular to the electric field (that is, parallel to the plates); see Figure 4.14. To find the flux of ions induced by the field, we ask how many ions get caught in the net each second. The average ion drifts a distance $v_{\mathrm{drift}}\mathrm{d}t$ in time $\mathrm{d}t$, so in this time all the ions contained in a slab of volume $Av_{\mathrm{drift}}\mathrm{d}t$ get caught in the net. The number of ions caught equals this volume times the concentration $c$. The flux $j$ is then the number crossing per area per time, or $cv_{\mathrm{drift}}$. Check to make sure this formula has the proper units. Substituting the drift velocity gives $j = q\mathcal{E}c/\zeta$, the **electrophoretic flux** of ions.

Now suppose that the density of ions is *not* uniform. For this case, we add the driven (electrophoretic) flux just found to the probabilistic (Fick's law) flux, Equation 4.18, obtaining

$$j(x) = \frac{q\mathcal{E}(x)c(x)}{\zeta} - D\frac{\mathrm{d}c}{\mathrm{d}x}.$$

We next rewrite the viscous friction coefficient in terms of $D$ using the Einstein relation (Equa-

tion 4.15 on page 108), to get[9]

$$\boxed{j = D\Big(-\frac{\mathrm{d}c}{\mathrm{d}x} + \frac{q}{k_{\mathrm{B}}T}\mathcal{E}c\Big). \qquad \textbf{Nernst–Planck formula}} \tag{4.23}$$

The Nernst–Planck formula helps us to answer a fundamental question: What electric field would be needed to get *zero* net flux, canceling out the diffusive tendency to erase nonuniformity? To answer the question, we set $j = 0$ in Equation 4.23. In a planar geometry, where everything is constant in the $y, z$ directions, we get the **flux matching condition**:

$$\frac{1}{c}\frac{\mathrm{d}c}{\mathrm{d}x} = \frac{q}{k_{\mathrm{B}}T}\mathcal{E}. \tag{4.24}$$

The left side of this formula can be written as $\frac{\mathrm{d}}{\mathrm{d}x}(\ln c)$.

To use Equation 4.24, we now integrate both sides over the region between the plates in Figure 4.14. The left side is $\int_0^d \mathrm{d}x \frac{\mathrm{d}}{\mathrm{d}x}\ln c = \ln c_{\mathrm{top}} - \ln c_{\mathrm{bot}}$, the difference in $\ln c$ from one plate to the other. To understand the right side, we first note that $q\mathcal{E}$ is the force acting on a charged particle, so that $q\mathcal{E}\mathrm{d}x$ is the *work* expended moving it a distance $\mathrm{d}x$. The integral of this quantity is the total work needed to move a charge all the way from the $-$ plate to the $+$ plate. But the work per charge, $\mathcal{E}\Delta x$, is called the **potential difference** $\Delta V$ between the plates. Thus the condition for equilibrium, obtained from Equation 4.24, becomes

$$\boxed{\Delta(\ln c) \equiv \ln c_{\mathrm{top}} - \ln c_{\mathrm{bot}} = -q\Delta V_{\mathrm{eq}}/k_{\mathrm{B}}T. \qquad \textbf{Nernst relation}} \tag{4.25}$$

The subscript on $\Delta V_{\mathrm{eq}}$ reminds us that this is the voltage needed to maintain a concentration jump *in equilibrium.* (Chapter 11 will consider nonequilibrium situations, where the actual potential difference differs from $\Delta V_{\mathrm{eq}}$, driving a net flux of ions.)

The Nernst relation is not exact. We have neglected the force on each ion from its neighboring ions, that is, the interactions between ions. At very low concentration $c$, this mutual interaction is indeed small relative to the attraction of the charged plates, but at higher concentration, corrections will be needed.

Equation 4.25 predicts that positive charges will pile up at $x = 0$ in Figure 4.14: They're attracted to the negative plate. We have so far been ignoring the corresponding negative charges (for example the chloride ions in salt), but the same formula applies to them as well. Because they carry negative charge ($q < 0$), Equation 4.25 says they pile up at $x = d$: They're attracted to the positive plate.

Substituting some real numbers into Equation 4.25 yields a suggestive result. Consider a singly charged ion like Na$^+$, for which $q = e$. Suppose we have a moderately big concentration jump, $c_{\mathrm{bot}}/c_{\mathrm{top}} = 10$. Using the fact that $\frac{k_{\mathrm{B}}T_{\mathrm{r}}}{e} = \frac{1}{40}$volt (see Appendix B), we find $\Delta V = 58\,\mathrm{mV}$. What's suggestive about this result is that many living cells, particularly nerve and muscle cells, really do maintain a potential difference across their membranes of a few tens of millivolts! We haven't proven that these potentials are equilibrium Nernst potentials, and indeed Chapter 11 will show that they're not. But the observation *does* show that simple dimensional arguments successfully predict the scale of membrane potentials with almost no hard work at all.

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[9] $\boxed{T_2}$ In the three-dimensional language introduced in Section 4.4.2$'$ on page 133, the Nernst–Planck formula becomes $\mathbf{j} = D\Big(-\boldsymbol{\nabla}c + (q/k_{\mathrm{B}}T)\boldsymbol{\mathcal{E}}c\Big)$. The gradient $\boldsymbol{\nabla}c$ points in the direction of most steeply increasing concentration.

Something interesting happened on the way from Equation 4.23 to Equation 4.25: When we consider equilibrium only, the value of $D$ drops out. That's reasonable: $D$ controls how *fast* things move in response to a field; its units involve time. But equilibrium is an eternal state; it can't depend on time. In fact, exponentiating the Nernst relation gives that $c(x)$ is a constant times $\mathrm{e}^{-qV(x)/k_\mathrm{B}T}$. But this result is an old friend: It says that the spatial distribution of ions follows Boltzmann's law (Equation 3.26 on page 78). A charge $q$ in an electric field has electrostatic potential energy $qV(x)$ at $x$; its probability to be there is proportional to the exponential of minus its energy, measured in units of the thermal energy $k_\mathrm{B}T$. Thus, a positive charge doesn't like to be in a region of large positive potential, and vice versa for negative charges. Our formulas are mutually consistent.[10]

### 4.6.4 The electrical resistance of a solution reflects frictional dissipation

Suppose we actually place the metal plates in Figure 4.14 *inside* the container of salt water, so that they become electrodes. Then the ions in solution won't pile up: The positive ones get electrons from the $-$ electrode, while the negative ones hand their excess electrons over to the $+$ electrode. The resulting neutral atoms leave the solution; for example, they can electroplate onto the attracting electrode or bubble away as gas.[11] Then, instead of establishing equilibrium, our system continuously *conducts* electricity, at a rate controlled by the steady-state ion fluxes.

The potential drop across our cell is $\Delta V = \mathcal{E}d$, where $d$ is the separation of the plates. According to the Nernst–Planck formula (Equation 4.23), this time with uniform $c$, the electric field is $\mathcal{E} = \frac{k_\mathrm{B}T}{Dqc}j$. Recall that $j$ is the number of ions passing per area per time. To convert this expression to the total electric current $I$, note that each ion deposits charge $q$ when it lands on a plate; thus, $I = qAj$, where $A$ is the plate area. Putting it together, we find

$$\Delta V = \left( \frac{k_\mathrm{B}T}{Dq^2 c} \frac{d}{A} \right) I. \tag{4.26}$$

But this is a familiar looking equation: It's **Ohm's law**, $\Delta V = IR$. Equation 4.26 gives the **electrical resistance** $R$ of the cell as the constant of proportionality between voltage and current. To use this formula, we must remember that each type of ion contributes to the total current; for ordinary salt, we'd need to add separately the contributions from $Na^+$ with $q = e$ and $Cl^-$ with $q = -e$, or in other words, double the right-hand side of the formula.

The resistance depends on the solution, but also on the geometry of the cell. It's customary to eliminate the geometry dependence by defining the **electrical conductivity** of the solution as $\kappa = d/(RA)$. Then our result is that $\kappa = Dq^2 c/k_\mathrm{B}T$. It makes sense—saltier water conducts better.

Actually, *any* conserved quantity carried by random walkers will have a diffusive, and hence dissipative, transport law. We've studied the *number* of particles, and the closely related quantity electric charge. But particles also carry *energy*, another conserved quantity. So it shouldn't surprise us that there's also a flux of thermal *energy* whenever this energy is not uniform to begin with, that is, when the temperature is nonuniform. And indeed, the law of heat conduction reads just like another Fick-type law: The flux $j_\mathrm{Q}$ of thermal energy is a constant (the "thermal conductivity")

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[10] $T_2$ Einstein's original derivation of his relation inverted the logic here. Instead of starting with Equation 4.15 and rediscovering the Boltzmann distribution, as we just did, he began with Boltzmann and arrived at Equation 4.15.

[11] $T_2$ This is not what actually happens with a solution of ordinary salt, since sodium metal and chlorine gas are so strongly reactive with water. Nevertheless, the discussion below is valid for the *alternating-current* conductivity of NaCl.