9.09J/7.29J - Cellular Neurobiology, Spring 2005
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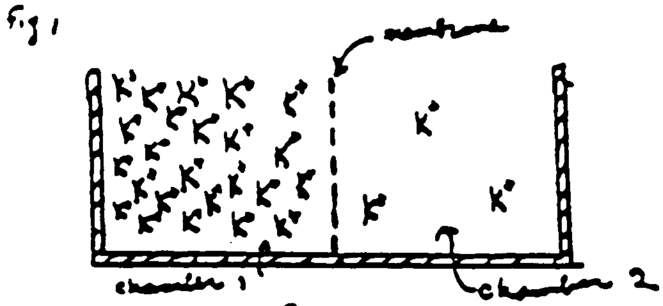
9.09J Cellular Neurobiology

HANDOUT

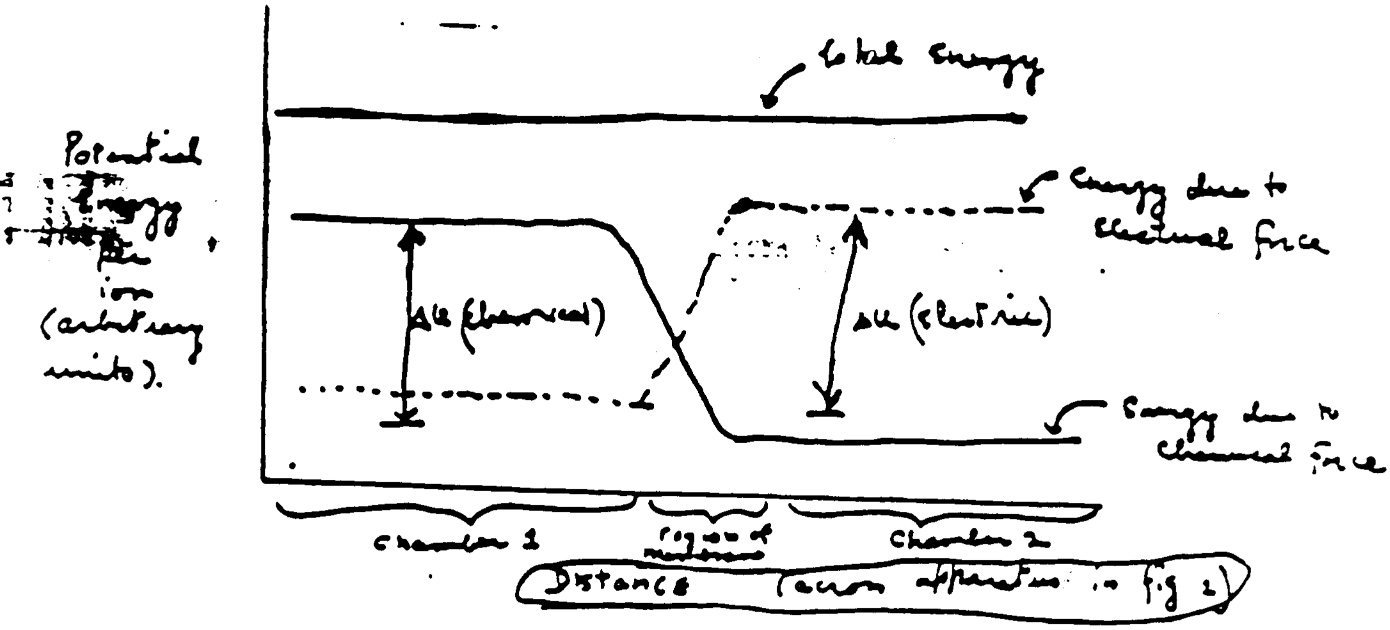
Quickie derivation of the Nernst equation (Weird, but solid as a rock)

First, let's consider conditions. We have two chambers separated by a membrane. The chambers have different concentrations of an ion (say, potassium, K^+). The membrane is permeable only to K^+ ions. (It has special holes hat only K^+ ions fit through.)



$\{[K^+]_1$ = potassium ion concentration in chamber 1

Under these conditions, there will be a voltage AV across the membrane. How does it arise? There is a net diffusion of K^+ ions from high concentration (chamber 1) to low concentration (chamber 2). If no other force were present this would continue until the concentration in both chambers were equal (makes sense, huh?). However, this process never goes that far. When a few K^+ ions diffuse from chamber 1 to chamber 2, they create an excess of (+) charge in chamber 2. This creates the voltage difference and an equilibrium will be reached when the tendency of the ions to diffuse down the concentration gradient is exactly counterbalanced by the tendency of the voltage gradient to push them back. Maybe a potential energy diagram will help:



At equilibrium (rate of ion flow from 1 to 2 = rate of ion flow from 2 to 1), the potential energy per ion must be equal in both chambers - (otherwise ions would flow down the "energy hill" and there would be net diffusion). You can see from the diagram that equilibrium occurs when ΔU (chemical) = ΔU (electrical), i.e., when an ion going across the membrane from chamber 1 to chamber 2 loses exactly as much energy going up the voltage "hill" as it gains going down the concentration hill. So the big equation is:

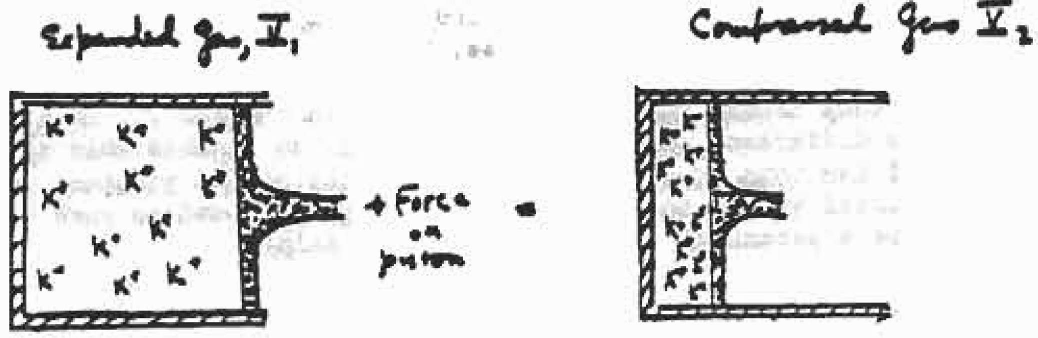
$$\Delta U \text{ (electric)} = \Delta U \text{ chem} \quad (1).$$

What we have to do now is calculate the ΔU's and plug them in. Let's start with the hardest, ΔU (chem). It's very difficult to decide how much work it would take to concentrate a bunch of ions in solution: if you try to squash them together mechanically, the water gets in the way. Let's try an easier problem (which will turn out to be equivalent) concentrating ions in a gas.

Let us imagine a gas of K^+ ions. Impossible, you grumble. No matter, I wittily reply. A gas is a gas; they all behave the gas law PV = nRT, and impossible ones will obey it too. This gas is particularly strange, since all the particles are electric charged, but we will worry about electric charges separately, in the ΔU (electric) part of the deviation.

O.K., we have n moles of this gas in a piston, we're going to concentrate it by squashing it from an initial volume V_1 to a final volume V_2.

Fig 3



We want to find out the change in potential energy involved in the squashing. We know from early on that:

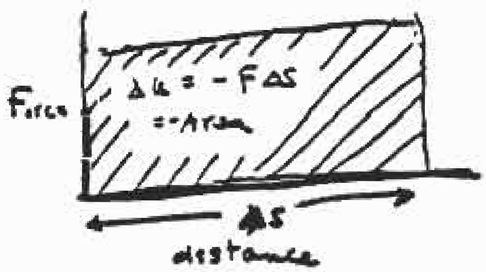
$$W = \Delta U = -F\ S \qquad (2)$$

W = work
ΔU = change in potential energy
F = force
ΔS = distance through which the force acts.

Th[illegible] like a step in the right direction, since we're applying a force through a distance. There are, however, two complications.

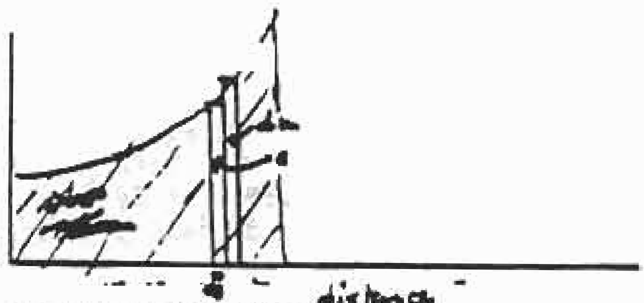
(a): Equation 2 is for a <u>uniform</u> force. Note that as we squash the gas its pressure will increase and it will be harder and harder to squash it further, so F is not a constant, it's a <u>function</u> of distance. We could get around this problem by chopping up ΔS into a lot of little lengths, ds, finding the force $F(s)$ at each of them, multiplying the force there by the little piece, ds giving a small increment dU, and adding up all the little dU's to get the total change ΔU.

Fig. 4 old rule $\Delta u = -F.\Delta S$



new rule: $\Delta U = -\Sigma du = -\Sigma F(s) \cdot ds = -\int F(s)\ ds$

Fig 5



We know that the easy way to sum up such little pieces is to integrate, so the new rule (for non-constant forces) is

$$\Delta U = \int_{s_1}^{s_2} F(s)\ ds \qquad (3)$$

So far so good. The other complication is (b): We've talked in terms of force F and distance. But the gas law is written in terms of pressures and volumes, i.e. :

$$PV = nRT \qquad (4)$$

- P = Pressure
- V = Volume
- n = number of moles of gas
- R = a constant, the "gas law constant" =
- T = Temperature, in °Kelvin

How do we get from forces to pressures and so forth? By cleverly noting that pressure (in newtons/dm^2) = Force/Area and Volume =(distance) x area (of piston). If we <u>divide</u> force by the area (of the piston) and multiply distance S by area (of the piston) the product remains the same:

$$\Delta U = -F \cdot \Delta S = -F/A \cdot A^{*}\Delta S = -P\Delta V$$

Similarly for our integral expression:

$$\Delta U = \quad F\ ds = \int_{s_1}^{s_2} F/A \cdot A ds = \int_{V_1}^{V_2} P \cdot dV \qquad (5)$$

The hard part is over. The rest is a matter of arithmetic. We want to express the change in potential energy in terms of the initial and final volume. Let's solve for Pressure using the gas law and plug the expression into the equation.

$$PV = nRT \qquad (6)$$
$$P = \frac{nRT}{V}$$

Substituting (6) into (5)

$$\Delta U = -\int_{V_1}^{V_2} P\,dV = -\int_{V_1}^{V_2} \frac{nRT}{V}\,dV = -nRT\int_{V_1}^{V_2} \frac{dV}{V}$$

Now the integral $\int \frac{1}{x}\,dx$ is $\ln x$, so the integral $\int \frac{1}{V}\,dV = \ln V$, so the expression in (7) is $\Delta U = -nRT\int \frac{dV}{V} = -nRT[\ln V]_{V_1}^{V_2} = -nRT\,(\ln V_2 - \ln V_1)$

$$-nRT \ln \frac{V_2}{V_1}$$

Note that this is beginning to look like the Nernst equation, with R and T and ln. It looks like we're on the right track. Next we have to go from volumes to concentrations. That's not hard. If we have N moles of gas in a liter of volume and we squash it to half a liter, we double the concentration. In fact, in general

$$V = \frac{const}{[K^+]} \qquad (9)$$

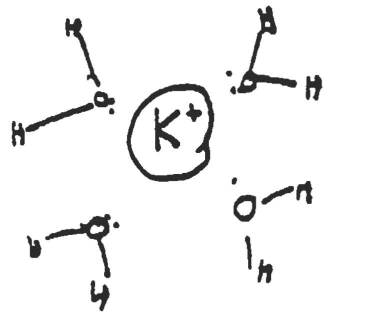
$[K^+]$ = concentration of potassium ions in moles/liter

Substituting (9) into (8)

$$\Delta U = -RT \ln \frac{const/[K^+]_2}{const/[K^+]_1} = -RT \ln \frac{[K^+]_1}{[K^+]_2} \qquad (10$$

Next we go from a gas to a solution. Let's dissolve n moles of K^+ ions at concentration $[K^+]_1$ into water. There will be a change of potential energy ΔU solution (very negative - the naked K^+ ions would be extremely happy to get into the water). You need to know one thing (definition) about an ideal solution which is that <u>the solute (K^+) ions interact only with the solvent (H_2O) molecules, not with each other.</u> Dilute solutions of ions are nearly ideal solutions, so the rule above is a good approximation. (Each ion is surrounded and "clothed" by a hydration shell of water molecules, as you learned in Chem 101-102.)

Fig 6

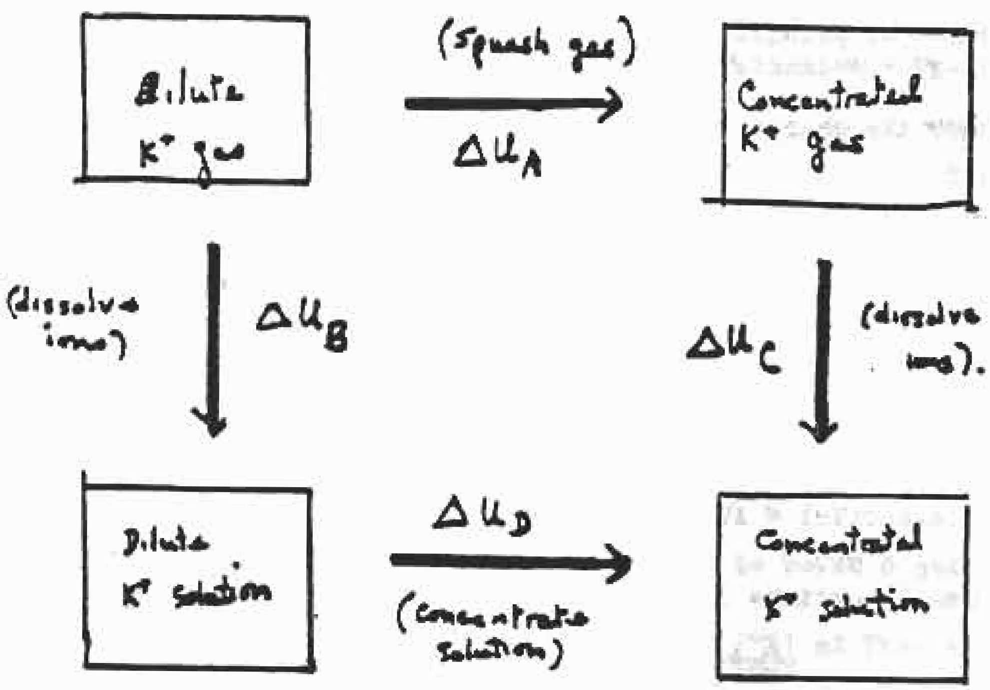


a K^+ ion (drawn oversize) in solution, surrounded by water molecules. The more positively charged oxygen molecules are electrostatically attracted toward the ion, hence they point inward.

What the rule allows us to say is that ΔU for dissolving n moles of K^+ ion is a function only of the number of ions dissolved, not of the concentration. (ΔU is just the sum of a lot of small ΔU's corresponding to the energy of hydration of each K^+ ion. The value of the little ΔU is concentration independent, since the K^{+2} ions don't talk to each other. Therefore <u>ΔU for dissolving a concentrated K^+ gas in water, forming a concentrated solution = ΔU for dissolving a dilute K^+ gas to form a dilute solution.</u>

What this means is that ΔU (chem) for concentrating an ideal gas is the same as ΔU (chem) for concentrating an ideal solution. To illustrate this, we need a path diagram for the four states with various ΔU's in between.

Fig 7



What we just said above is that $\Delta U_B = \Delta U_C$ (concentration - independent). It follows that $\Delta U_A = \Delta U_D$ because changes in potential energy ΔU to get from one state to another is the same regardless of the path one takes. One can go from a dilute gas to a concentrated solution either by concentrating the gas and then dissolving it:

$$\Delta U = \Delta U_A + \Delta U_C$$

or by dissolving the dilute gas and then concentrating the solution

$$\Delta U = \Delta U_B + \Delta U_D$$

Since U is the same in each case

$$\Delta U_A + \Delta U_C = \Delta U_B + \Delta U_D \qquad (11).$$

We already showed that $\Delta U_B = \Delta U_C$. Subtracting these equal quantities from both sides of eq. (11) gives

$$\Delta U_A = \Delta U_D$$

as I asserted above. Now we have already calculated the magnitude of ΔU_A, the energy expended in squashing a gas (see equation 10). Therefore we know the energy involved in concentrating n moles of a solution

$$\Delta U \text{ (chem)} = \Delta U_D = -nRT \ln \frac{[K^+]_1}{[K^+]_2} \quad (13)$$

So much for the chemical energy part of the Nernst equation. How about the electrical part? From the definition of electrical potential (and voltage) in lecture 1,

$$\Delta U \text{ (electric)} = q\,\Delta\varphi = q \cdot V \quad (14)$$

- q = charge transported across voltage
- φ = electrical potential
- V = voltage = potential difference.

We need to know the charge on n moles of K^+ ions.

$$q = n\,z\,F$$

- n = number of moles of ions
- z = charge per ion ($z = +1$ for K^+).
- F = Faraday's constant = charge (in couloumbs) on 1 mole of electrons.

so $\Delta U \text{ (electric)} = n\,z\,F \cdot V$ (15)

The simple equation we started with was

$$\Delta U \text{ (electric)} = \Delta U \text{ (chem)} \quad (1)$$

for transporting n moles of ions from chamber 1 to chamber 2. Now we know both terms [equations (13) and (15)] let's plug them in

$$n\,z\,F \cdot V = -nRT \ln \frac{[K^+]_1}{[K^+]_2} \quad (16)$$

Solving (16) for the voltage:

$$V = \frac{-RT}{zF} \ln \frac{[K^+]_1}{[K^+]_2}$$

Hot damn! The Nernst equation.

Note A. We did it here for K^+ ions, but that was just to give you a concrete (and familiar) example. The ~~equation~~ derivation is general for any ion (provided the membrane is permeable to that ion only) and to chambers of any configuration (in the squid axon chamber 1 is the inside of the nerve and chamber 1 is the outside).

Note B. $\frac{-RT}{zF} \ln X \simeq -58 \text{ mV} \cdot \log X$

for $z = 1$ and $T \simeq 25°C$. (Dr. Gelperin already announced this.)

Note C. There is often a problem in the sign of the voltage (measured from where to where?). You can get around this by memorizing conventions, or by reviewing the initial consideration which led us to expect the voltage. The region of concentrated (+) ions will be negative because uncompensated ions will diffuse down the concentration gradient creating a region of net (+) charge someplace else.