Additional Comments to the Salt Diffusion Experiment

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The "derivation" included in the instruction manual of the electrolyte diffusion experiment is extremely unsatisfactory. This hand-out clears up some of the ambiguities.

Consider mass transfer due to diffusion in an isothermal, binary system of A and B. One way to write Fick's law is

$$\mathbf{J}_A^* = -cD_{AB}\nabla x_A \tag{1}$$

where $\mathbf{J}_A^*$ is the molar diffusive flux of component A. The asterisk indicates that the diffusive flux is measured relative to the molar-averaged velocity. The bold variable indicates that it is a vector. In equation (1), c is the molar concentration, D_{AB} is the diffusion coefficient of A in B, and x_A is the mole fraction of A. One can also write an expression for the molar diffusive flux of component B,

$$\mathbf{J}_B^* = -cD_{BA}\nabla x_B \tag{2}$$

where D_{BA} is the diffusion coefficient of B in A. It should be pointed out that in the general formulation, $D_{AB} \neq D_{BA}$. However, there are certain ways that one can formulate the diffusion process, so that the equality is observed. Our formulation here will satisfy the equality.

Because it is a binary mixture,

$$x_A + x_B = 1 . \tag{3}$$

As a result, the gradients of the mole fractions are related

$$\nabla x_A = -\nabla x_B . \tag{4}$$

It can also be shown for this particular choice of formulation that there is only one diffusivity,

$$D_{AB} = D_{BA} = D . \tag{5}$$

We can rewrite equations (1) and (2) as

$$\mathbf{J}_A^* = -cD\nabla x_A = -\mathbf{J}_B^* \tag{6}$$

As a result, there is no net molar flux due to diffusion.

$$\mathbf{J}_A^* + \mathbf{J}_B^* = 0 \tag{7}$$

We can write equation (6) in one dimension (the z-dimension) as

$$J_A^* = -cD\frac{\partial x_A}{\partial z}\,. \tag{8}$$

If we assume that the total molar concentration, *c*, is constant, then we can rewrite equation (8) as

$$J_A^* = -D\frac{\partial c_A}{\partial z}\,. \tag{9}$$

but this is only true if the total molar concentration is constant. If the total molar concentration is not constant, we cannot write equation (9). In this derivation, we will assume that the total molar concentration is constant. Thus, equation (9) is our starting point for the following derivation.

In this analysis, we are going to approximate the gradient as

$$\frac{\partial x_A}{\partial z} \approx \frac{c_{A,2} - c_{A,1}}{z_2 - z_1}\,. \tag{10}$$

where the subscript 1 indicates the position just on the salt-rich side of the membrane and the subscript 2 indicates the position just on the salt-lean side of the membrane. In that case, $z_2 - z_1$ is just the membrane thickness, L (which happens to unfortunately be labeled x in the lab manual). We assume that the mole fraction of salt on the salt-lean side is zero through-out our experiment. This is simply an assumption. As a result,

$$\frac{\partial x_A}{\partial z} \approx -\frac{c_{A,1}}{L}\,. \tag{11}$$

We specify $c_{A,1}$ (the default value is 2 moles/liter).

In equation (9), we also need to related the molar diffusive flux of A to measurable quantities. Recall that a molar flux has units of moles per area per time.

$$J_A^*[=]\frac{moles}{area \cdot time}\,. \tag{12}$$

The area of mass transfer in this problem is the cross-sectional area of the cylindrical capillary in the membrane multiplied by the number of capillaries.

$$area = \frac{\pi d^2}{4}N\,, \tag{13}$$

where *d* is the diameter of the capillary and *N* is the number of capillaries. What we now need is the molar flow rate [moles/time]. However, we measure the conductivity, *k*. We have to first assume that our measured conductivity is linearly proportional to the salt concentration,

$$k = C_M c_{salt} , \tag{14}$$

where C_M is a proportionality constant. Solving for the salt concentration, we have

$$c_{salt} = \frac{1}{C_M} k . \tag{15}$$

We need the molar flowrate. If we write a salt balance on the salt-lean side of the membrane, we have

$$accumulation = in - out + generation . \tag{16}$$

There is no generation term and there is no out term. Our in term is simply the moles/time entering the salt-lean side from the membrane. Our accumulation term is simply

$$accumulation = V \frac{\partial c_{salt}}{\partial t} . \tag{17}$$

Therefore our balance is simply

$$V \frac{\partial c_{salt}}{\partial t} = in . \tag{18}$$

We differentiate equation (15) and substitute it into equation (18).

$$V \frac{1}{C_M} \frac{\partial k}{\partial t} = in . \tag{19}$$

Our flux is thus

$$J_A^* = \frac{in}{area} = V \frac{1}{C_M} \frac{\partial k}{\partial t} \frac{4}{\pi d^2 N} . \tag{20}$$

We substitute equations (11) and (20) into equation (9).

$$V \frac{1}{C_M} \frac{\partial k}{\partial t} \frac{4}{\pi d^2 N} = -D \left(- \frac{c_{A,1}}{L} \right). \tag{21}$$

Solving for D, we have

$$D = \frac{4LV}{c_{A,1} C_M \pi d^2 N} \frac{\partial k}{\partial t} . \tag{22}$$

We estimate $\frac{\partial k}{\partial t}$ by computing the slope of a plot of conductivity versus time. Then we know everything on the right-hand-side of equation (22) and we use equation (22) to estimate the diffusivity. In using equation (22), I caution you to make sure that all your units cancel. Your diffusivity should have units of area per time, e.g. m^2/s. In order to do the calculation correctly, you will have to convert all quantities to, for example, SI units. This means that concentrations will have to be expressed in $moles/m^3$ rather than moles/liter.