How do I know if the use of quasi-steady state is valid?

One of the most confusing aspects in introductory mass transfer is the use of the quasi-steady state (also called pseudo-steady state) approximation. We obviously have a problem that is transient in nature, but with a slight of hand, we throw the time dependence away from part of the problem. The question is whether we can have a more quantitative assessment of this quasi-steady state approximation. The answer is yes. And we'll take the closed diffusion cell as an example. Such a configuration is not uncommon in bench-top dialysis or membrane testers.

Consider a thin membrane separating two compartments in a closed container. The two compartments have volumes \( V_1 \) and \( V_2 \). The membrane has cross section \( A \) and thickness \( \delta \). We consider a solute in dilute solution, and with concentrations, \( C_1 \) and \( C_2 \) in the two compartments. We also consider that the concentration in the lower compartment \( V_1 \) is higher at the beginning of the experiment. Thus this is a transient experiment in which the solute will diffuse from the lower to the upper compartment until the concentration is equilibrated in the container. The complete problem statement requires the following mass balances.

In the membrane, we have the transient diffusion problem

\[
\frac{\partial C_m}{\partial t} = D \frac{\partial^2 C_m}{\partial x^2} \tag{1}
\]

where \( C_m \) denotes the concentration of the diffusing solute within the membrane. At \( t = 0 \), the initial condition is \( C_m(x,0) = C_o \), and the boundary conditions are \( C_m(0,t) = \alpha C_1 \), and \( C_m(\delta,t) = \alpha C_2 \), where \( \alpha \) is some(!) partition coefficient between the fluid (say, water) and the membrane phase (some polymer). We have defined the coordinate \( x \) in the membrane such that the underside is \( x = 0 \), while the upper side facing \( V_2 \) is \( x = \delta \). While the notation is not explicit, we should note that the concentrations in the compartments are functions of time, \( C_1 = C_1(t) \), and \( C_2 = C_2(t) \).

So, of course, we have to write down the mass balances of the solute in the two compartments: \( C_1 \) and \( C_2 \). We assume that the concentrations are uniform in the two compartments. Hence, we can write the loss of the solute from compartment 1 as

\[
V_1 \frac{dC_1}{dt} = -A \left( -D \frac{\partial C_m}{\partial x} \right) \bigg|_{x=0} \tag{2}
\]

and the gain in compartment 2 as

\[
V_2 \frac{dC_2}{dt} = A \left( -D \frac{\partial C_m}{\partial x} \right) \bigg|_{x=\delta} \tag{3}
\]

with initial conditions \( C_1(0) = C_{1o} \), and \( C_2(0) = C_{2o} \). With all the necessary initial and boundary conditions defined, we now have a well-posed, but also very imposing, problem.

Next, we want to make the assertion that the transient diffusion problem in Eq. (1) can be replaced by the quasi-steady state solution \(^1\)

\[
C_m = \alpha \left[ C_1 - \frac{C_1 - C_2}{\delta} x \right] \tag{4}
\]

\(^1\) This is the solution to \( \frac{\partial^2 C_m}{\partial x^2} = 0 \) with the two membrane boundary conditions.
and the corresponding quasi-steady diffusive flux is

\[ -D \frac{\partial C_m}{\partial x} \bigg|_{x=0} = \frac{D\alpha}{\delta} (C_1 - C_2) \]  

(5)

This model is quasi-steady state because we still have \( C_1 = C_1(t) \), and \( C_2 = C_2(t) \). The mass balances in Eqs. (2) and (3) can now be written as

\[ V_1 \frac{dC_1}{dt} = -A \frac{D\alpha}{\delta} (C_1 - C_2) \]  

(2a)

and

\[ V_2 \frac{dC_2}{dt} = A \frac{D\alpha}{\delta} (C_1 - C_2) \]  

(3a)

This is obviously a trivial problem compared with the original statement. But under what circumstance can we make such a bold assertion? The key is in the comparison of relative time scales. You'd find that while scaling analysis is not presented formally in any text, it is one of the most important skills that we must master in the construction of mathematical models.

In the present problem, the rough idea is that the time dependence in the solution of Eq. (1) is in form of exponential functions (you'll see that when we get to Chapter 4). So are the solutions to (2a) and (3a). (We'll show that below with Eq. 8.) The smaller, or shorter, the time scale, the quicker the exponential terms vanish. Thus if the membrane diffusion problem has a much smaller time scale than the compartment problem, its exponential terms decay away quickly, and the membrane diffusion solution appears as if it were a steady state problem compared to the slower, larger time scale compartment problem.

Now we have to find the respective time scales. For diffusion, it is easy. The diffusion time scale is

\[ t_D = \frac{\delta^2}{D} \]  

(6)

where we use the subscript D to denote a diffusion time scale.

To find the time scale with respect to the rate of change in compartment concentrations, let's make the simplification of \( C_2 = 0 \). [You will see many problems that fit into this scenario later in the text.] Thus Eq. (2a) becomes

\[ V_1 \frac{dC_1}{dt} = -A \frac{D\alpha}{\delta} C_1 \]

or

\[ \frac{\partial C}{\partial t} = \frac{\partial^2 C}{\partial z^2} \]

Even as we state the flux in Eq. (5) at \( x = 0 \), we could have omitted the location. Recall our notes in differential balance: the flux is constant with respect to \( x \) in this problem.

We can do this easily without Chapter 4. We normalize \( x \) by the obvious reference length scale \( \delta \) and define \( z = x/\delta \). Eq. (1) then appears as

\[ \frac{\delta^2 C_m}{D} \frac{\partial C_m}{\partial t} = \frac{\partial^2 C_m}{\partial z^2} \]

from which it should be apparent that if we want dimensionless time in the equation, the choice is to define \( \tau = tD/\delta^2 \), meaning that the reference time scale is \( t_D = \delta^2/D \). It's a poor style and habit to leave an equation half-normalized. So let's also define \( c = C_m/C_{1o} \), based on the initial concentration in the lower compartment. The entirely dimensionless equation is

\[ \frac{\partial c}{\partial \tau} = \frac{\partial^2 c}{\partial z^2} \]
\[ t_c \frac{dC_1}{dt} = -C_1 , \quad t_c = \frac{V_1 \delta}{AD_A} \]  
\[ C_1 = C_{1o} e^{-t/t_c} \]  
\[ \alpha \frac{A \delta}{V_1} \ll 1 \]  
\[ A \delta \alpha \ll 1 \]  
\[ \alpha A \delta \left( \frac{1}{V_1} + \frac{1}{V_2} \right) \ll 1 \]  
\[ \alpha A \delta \left( \frac{1}{V_1} + \frac{1}{V_2} \right) \ll 1 \]  
\[ \alpha A \delta \left( \frac{1}{V_1} + \frac{1}{V_2} \right) \ll 1 \]  

We purposely made the \( C_2 = 0 \) assumption to simplify the algebra. We shouldn’t need to. Here’s the more general derivation. First, we want to combine Eqs. (2a) and (3a) to give

\[ \frac{d(C_1 - C_2)}{dt} = -\frac{AD_A\alpha}{\delta} \left( \frac{1}{V_1} + \frac{1}{V_2} \right) (C_1 - C_2) \]  
\[ t_c \frac{d(C_1 - C_2)}{dt} = -(C_1 - C_2) , \quad t_c = \left[ \frac{AD_A\alpha}{\delta} \left( \frac{1}{V_1} + \frac{1}{V_2} \right) \right]^{-1} \]  
with the solution

\[ C_1 - C_2 \approx C_{1o} - C_{2o} \approx e^{-t/t_c} \]  

We manipulate Eqs. (2a) and (3a) to the form in (11) for a good reason. It calculates the difference of the concentrations between the two compartments. Mass transport stops when the concentrations are the same.

The more complete quasi-steady state criterion as analogous to Eq. (10) is

\[ \alpha A \delta \left( \frac{1}{V_1} + \frac{1}{V_2} \right) \ll 1 \]  
which carries the same physical interpretation as before.

The bottom line is that it is not terribly difficult to design an experiment which meets this condition. The use of quasi-steady state is very common in membrane transport, which is the basis of a good many problems in introductory mass transport.