ThINKing about Boundary Conditions:

*Exploring the differences in diffusion with varying boundary conditions*
**Introduction**

**Mass Transfer Basics:**

Mass transfer involves the movement of mass from one location to another. Mass transfer happens everywhere around us. One specific type of mass transfer is diffusion, which happens on a microscopic level. The particles of one material move from one location to another, diffusing through a different substance, the medium. In order for diffusion to take place there needs to be a driving force, or a reason for the mass to move. In the case of our experiment, the driving force is concentration gradient, which is the difference in concentration between two boundaries. Concentration describes the amount of a material present in a region of space. In chemical engineering concentration is often defined as:

\[
    c_A = \frac{\text{Moles of A}}{\text{Total Volume}}
\]

A concentration gradient exists when there is a difference in concentration between two positions within a system. This uneven distribution of material leads to the natural flow, or diffusion, of material from areas of high concentration to low concentration until equilibrium is reached.

There are two different scenarios for mass transfer: steady state and unsteady state. In a steady state situation, the concentration gradient, and therefore driving force, is constant over time. In an unsteady state scenario the concentration is continuously changing and therefore the concentration gradient and driving force is also change with time. We will use the following equations to model our process.

<table>
<thead>
<tr>
<th>Name</th>
<th>Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>General Mass Transfer Equation</td>
<td>[ \nabla N_A + \frac{\partial C_A}{\partial t} - R_A = 0 ]</td>
</tr>
<tr>
<td>Fick’s First Law</td>
<td>[ N_A = -D_{AB} \nabla C_A + y_A \sum_{i=1}^{n} N_i ]</td>
</tr>
<tr>
<td>Simplified Experimental Equation</td>
<td>[ \frac{\partial C_A}{\partial t} = D_{AB} \frac{\partial^2 C_A}{\partial x^2} ]</td>
</tr>
</tbody>
</table>
By combining the general mass transfer equation with Fick’s First Law, and making some assumptions, we can derive a final equation that describes the system. For our process, we are assuming one dimensional diffusion in the paper, which dominates bulk motion. Assuming no chemical reaction takes place, and the system uses Cartesian coordinates we can utilize the simplified equation above. This equation is difficult to solve by hand with analytical solutions. In many situations these types of problems are solved using computer simulators, which is how we modeled our solution.

**Boundary Condition Basics:**

Diffusion takes place because of a concentration gradient. If the goal is to determine how quickly the diffusion happens or to calculate the diffusion properties, the concentration gradient must first be determined. The concentration gradient is set by something called a boundary condition. There are many different kinds of boundary conditions, but they all describe the state of a system at a specific time and location.

Diffusion problems involve boundary conditions that are based on concentrations. One type of boundary condition is known as a constant boundary condition. Constant boundary conditions are often the easiest to work with, because they do not change with time. Some boundary conditions can also change over time; these are called changing boundary conditions.

In the following experiment, the effects of various boundary conditions on the outcome of diffusion will be explored.

**Experiment Background/Rationale**

In this experiment, the goal is to investigate the impact of different types of boundary conditions by comparing how fast diffusion happens in two different situations. The first situation involves a constant boundary condition. In the second situation a changing boundary condition is simulated. Because the concentration gradient changes in both cases, each must be modeled by unsteady state mass transfer.
For this experiment, students will color pieces of paper with washable marker. One piece of paper will be placed in a cup filled with water and the other will have a constant flow of water over the surface. Because there is more ink on the paper than in the water, the ink will diffuse into the water in both scenarios. Students will then compare the relative rate of diffusion by evaluating the changing color on the paper. Due to the difficulty of the experiment, this comparison will be done objectively. This experiment could be done more precisely through computer simulation.

**Experiment Supplies**

- Washable markers (Crayola Classic 8 Pack: $1.97)
- Paper
- 250 ml beaker (demonstrated using cup)
- Water source (preferably a sink. We will use pitchers of water because of limitations)
- Tray of some type (Hefty EZ foil cake pans with covers, 3 count: $3.98)
- Timer

**Experiment Set up**

1. Cut three 1.5”x1.5” sized pieces of paper. Color a decently sized and consistently dark mark on them using a washable marker. Use an equal amount of ink on each piece of paper.
2. At the same time place one of the pieces of paper inside the cup that is filled with water (color side down). Place another piece of paper on the tray (color side up) and run water over top of the piece of paper. Rather than having the water directly land on the ink, have it land above the paper and flow down over the top of it. The third piece of paper will be used for color reference.
3. Start the timer. Run the experiment for 1 minute.
4. After one minute remove the paper from the cup and from the tray and compare the results.

*Other things to consider: Use same temperature of water for both cases and a red marker (or other marker color that contains only one dye). This will allow for experimental consistency.*
ThINKing About Boundry Conditions: Lab Worksheet

Data Collection:

- Time Elapsed: _____.

Below is a Color Scale that will help to compare the color change for the experiment:

<table>
<thead>
<tr>
<th>Flowing Water:</th>
<th>Stagnant Water:</th>
</tr>
</thead>
<tbody>
<tr>
<td>Starting Color According to Gradient Scale: _____</td>
<td>Starting Color According to Gradient Scale: _____</td>
</tr>
<tr>
<td>Final Color According to Gradient Scale: _____</td>
<td>Final Color According to Gradient Scale: _____</td>
</tr>
</tbody>
</table>

Discussion:

- In the stagnant water portion of the experiment, what did you notice about the water in the container as time increased?
- How does the state of the stagnant water compare to the state of the flowing water?
- In the flowing water portion of the experiment, does the boundary condition change over time?
- In the stagnant water portion of the experiment, does the boundary condition change over time?
- In both portions of the experiment, why is the final color different from the starting color?
- Based on our discussion about boundary conditions, why is the final color in the stagnant water portion of the experiment different from the flowing water portion of the experiment?
Expected Results

In order to successfully demonstrate the unsteady state experiment, both of the scenarios were modeled in COMSOL (See Appendix A for description and results). This provided quantified solution in addition to our visual experimental result. Both scenarios show the concentration of ink in paper decreasing with time and depth within the paper; however, the rates of the change in concentration vary between the two cases. We were able to compare the value of concentration of ink halfway into the paper after the 60 seconds in COMSOL to numerically compare our experimental results. The running-water simulation had a concentration that was about half the value of the still-water simulation, $1.5 \times 10^{-8}$ mols/m$^3$ and $3.5 \times 10^{-8}$ mols/m$^3$ respectively. These results are consistent with the qualitative results from the experiment, where the running-water experiment is lighter than the still-water experiment.

Conclusion

These two systems demonstrate the important concept of boundary conditions, and how these parameters affect concentration gradient and driving force. In the flowing water scenario, there was always a concentration of zero as a boundary condition. This allowed for a larger concentration gradient and a larger driving force. Due to the larger concentration gradient, the diffusion happens more rapidly and more ink leaves the piece of paper. In the cup example, the water slowly soaks up more ink. Over time, more ink becomes concentrated in the water and the concentration gradient between the paper and water decreases. This makes the diffusion happen more slowly and therefore results in more ink left on the paper at the end of the time frame.

This demonstration should help you to understand how changing boundary conditions can affect the concentration gradient, therefore changing how quickly the mass transfer/diffusion happens. For further experimentation, other boundary conditions may be tested by incorporating differences in pressure (if testing diffusivity in a gas system), or reactions at a boundary (between the diffusing substance and the boundary itself.)
Appendix A:

In Comsol, a 1-D model was used to represent both systems. This model is of a differential cross section of the paper, which is permissible due to the symmetry of the system.

Due to the lack of literature on the diffusivity of markers, many of the parameters had to be estimated. As long as the simulations are used in tandem and only viewed relative to each other, the importance of the accuracy of these values is minimal.

An estimate for the diffusivity of marker in water was obtained by comparing diffusivities of other materials through water (Welty, p. 693). The approximate value for the effective diffusivity of marker through paper was obtained by analogy of the diffusion of nile red through a carbon nanotube network (Singhal).

Parameters and boundary conditions are included in the summary diagram for each scenario. In addition, a graph of concentration as a function of position and time is provided.
Comsol Summary: Running Water Scenario

BC: $C_0 = 0 \text{ mol/m}^2\text{s}$

Zero Flux BC

Paper:
Length: $L = 0.1 \text{ mm}$
$D_x = 1.2 \times 10^{-10} \text{ m}^2/\text{s}$
$C_0 = 1.0 \times 10^{-6} \text{ mol/m}^2\text{s}$
Comsol Summary: Still Water Scenario

Water:
- \( L = 1 \text{mm} \)
- \( D_{ab} = 1 \times 10^{-9} \text{ m}^2/\text{s} \)
- \( C_{i,0} = 0 \text{ mol/m}^3 \)

Paper:
- \( L = 0.1 \text{mm} \)
- \( D_p = 1.2 \times 10^{-10} \text{ m}^2/\text{s} \)
- \( C_{i,0} = 1 \times 10^{-6} \text{ mol/m}^3 \)
Appendix B: 
ThInKKing About Boundry Conditions: Pre-Lab Worksheet

I. Diffusion
After it rains, puddles on the ground slowly disappear in a process called evaporation. Evaporation involves liquid water evaporating into the air as a vapor. More specifically, evaporation is a form of **diffusion**, which is one of the two types of mass transfer. Diffusion describes a microscopic process, in which particles of one material move from one location to another through a medium.

1. In the example above, water is diffusing through air. What are some other everyday examples of diffusion?

II. Concentration
Concentration describes the amount of a material in a certain space, and is one way to measure the mass transfer. In chemical engineering concentration is often defined as:

\[ c_A = \frac{\text{Moles of } A}{\text{Total Volume}} \]

Some students collected data from the puddle example in part 1 and created this table:

<table>
<thead>
<tr>
<th>Time</th>
<th>0m</th>
<th>15m</th>
<th>30m</th>
<th>45m</th>
<th>60m</th>
</tr>
</thead>
<tbody>
<tr>
<td>Puddle volume (liters)</td>
<td>1.00</td>
<td>0.83</td>
<td>0.51</td>
<td>0.22</td>
<td>0.05</td>
</tr>
<tr>
<td>Volume of air above the puddle (liters)</td>
<td>60</td>
<td>60</td>
<td>60</td>
<td>60</td>
<td>60</td>
</tr>
</tbody>
</table>

2. What is the concentration after 15 minutes? 30 minutes? 60 minutes? (HINT: Remember, one mole of water = .018 liters!)
3. Is the concentration of water in the air increasing or decreasing?

III. Intro to Boundary Conditions Lab
In this experiment, we are going to measure the rate of diffusion by looking at concentrations. In one scenario, we will run a thin layer of water over a piece of paper covered in marker. In another scenario, we will set a similar piece of paper in a cup of water. After some time, we will check how much ink has diffused into the water from the paper.
4. Which conditions are changing between these two scenarios?

5. Which conditions are staying the same?

6. In which scenario will more diffusion take place? (Which paper will have more ink taken off?)
Appendix C: Works Cited
