Molecular Diffusion Through a Porous Medium

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Introduction
The demonstration and instruction of mass transfer on a molecular scale is a difficult task due to
the level of abstraction and complexity of its variables and effectors. Presentation of a valid
method for the explanation of mass transfer necessitates a system that allows not only simplifying
assumptions but also rapid, visible, and qualitative results. Below is a simplified model that
explains several facets of molecular diffusion, specifically through a porous solid medium. The
system incorporates a solid membrane separating a solution of potassium iodide from a solution of
cornstarch. The novelty of this design is that it allows qualitative analysis of the magnitude of
diffusion through a finite area over a given time at controlled conditions. This is made possible by
the indicator reaction of iodide with cornstarch, which results in the cornstarch solution changing
from clear to a purple color. The focus of this specific experiment, although not limited to, is the
temperature dependence of diffusivity and thus the rate of diffusion through a porous medium.

Background
Differential Mass Transfer
Mass Transfer is a physical process, which involves the transport of molecules within a system.
The driving force behind this transfer is a difference in the concentration of a given molecule
between two regions. There are many different situations that are classified as mass transfer and
all of these cases can be modeled using the General Equation of Mass Transfer (Equation 1). The
first term denotes the accumulation of mass with respect to time, the second term describes mass
transfer due to diffusion, and the third term represents molecular generation due to a reaction.\(^1\)

\[
\frac{\partial C_A}{\partial t} + \nabla \cdot N_A = R_A
\]

(Equation 1)

In our experiment we look at mass transfer of iodide molecules across a porous semi-permeable
membrane. We have a conical containing a water and cornstarch mixture that is placed in a
solution of iodide with a porous membrane separating the two solutions (Figure 1). Since this is a
specific mass transfer scenario, we make assumptions simplifying Equation 1 to reflect the
controlled environment of our setup.

\[ \text{The first assumption that we make is that the concentration of iodide (} C_A \text{) in the beaker and on the} \]
\[ \text{outside of the membrane remains constant throughout the duration of our trial. We can make this} \]
\[ \text{assumption because the amount of iodide that actually diffuses through the membrane, for the} \]
\[ \text{amount of time that we run the experiment, is very small relative to the amount of iodide initially in} \]
\[ \text{the beaker. In addition, we assume that the reaction between the iodide and the cornstarch is an} \]
\[ \text{instantaneous reaction, implying that there is never an accumulation of free iodide inside the} \]
\[ \text{conical (} C_A = 0 \text{). Furthermore, the pores of the membrane are small enough that we assume no} \]
cornstarch diffuses into the membrane and therefore no reaction takes place inside the theoretical control boundary of the membrane (Figure 1). We also assume that there is negligible surface resistance at the cornstarch-membrane interface signifying that the concentration of iodide in the cornstarch solution after it diffuses through the membrane is zero; the same as the concentration of iodide throughout the conical. These assumptions imply that the concentration gradient of iodide never changes, allowing our experiment to be classified as steady state.\(^1\)

\[ \nabla \cdot N_A = 0 \] \hspace{1cm} (Equation 2)

Once we simplify the equation to reflect our steady state experiment, we assume that the iodide only diffuses through the membrane in the z-direction. The z-direction in our system refers to the horizontal distance when viewing the membrane from the side, i.e. the membrane’s thickness. This assumption allows us to simplify the general equation of mass transfer down to just the equation for flux (\(N_A\)).\(^1\)

\[ N_A = -D_{AB} \frac{dc_A}{dz} + x_A(N_A + N_B) \] \hspace{1cm} (Equation 3)

Flux is defined as the amount of a given molecule that diffuses through a set area during a specific duration of time. There are two expressions in the equation for flux that contribute to its total value: the first term is the effects of the concentration gradient (driving force) and the second term denotes contributions from bulk flow. Bulk flow is the influence of molecules flowing in the same direction as a given molecule on the individual molecule’s rate of diffusion. Through the porous membrane of our system the rate of diffusion is slow enough that contributions from bulk flow can be assumed to be negligible. After the stated simplifications and integration the flux (Equation 4) is only dependent on the change in concentration (\(c_A\)) per change in position (\(z\)) and the diffusivity (\(D_{AB}\)). Diffusivity is a constant that accounts for the species diffusing and the diffusion environment, which implies a direct correlation between rate of flux and diffusivity.\(^1\)

\[ N_A = -D_{AB} \frac{(c_A - c_{A1})}{(z_2 - z_1)} \] \hspace{1cm} (Equation 4)

A simplified non-abstract way to understand flux is to consider people walking through a wide doorway from a crowded to empty room. The number of people that can walk through a wide doorway during a certain amount of time can be considered the “flux” of the people. The rate at which they walk through the doorway depends on the characteristics of the people and the circumstances in which they are walking. If the people are very large, fewer people are able to fit through the doorway at the same time. If some exogenous factor causes the people to run rather then walk, more people would pass through the doorway. These are some of the determining factors in calculating the “flux” of the people. Molecular flux is governed by factors analogous to the size and circumstance of the people going through the doorway. Certain aspects of the molecules and the conditions under which the diffusion takes place affect the flux. These variables are taken into consideration when calculating the coefficient of diffusion for a given molecule (A) in a given system (B), diffusivity (\(D_{AB}\)). The diffusivity of iodide into water can be predicted using the Wilke-Chang equation.\(^1\)

\[ D_{AB} = 1.173 \times 10^{-16}(\Phi B)\frac{\mu B}{\mu A} \frac{1}{V^A} \] \hspace{1cm} (Equation 5)

The Wilke-Chang equation predicts the value of \(D_{AB}\) by taking into consideration \(N_T\), the molecular weight of solvent B; \(\mu_B\), the viscosity of B; \(V_A\), the solute molar volume at the boiling point; \(\Phi\), an “association parameter” of the solvent; and T, the temperature. The size of the pores and the construction of the membrane also affect the diffusivity and needs to be accounted for. The pore size will accounted for in the void fraction (\(\varepsilon\)), the ratio of open space to total space, and the membrane construction will give the tortuosity (\(\tau\)), how far the molecule has to travel opposed to
just the straight line distance. The equation for the effective $D_{AB}$ based on void fraction and tortuosity is:  
\[
D_{AB/eff} = \frac{\varepsilon}{\tau} D_{AB}
\]  
(Equation 6)

In our experiment we hold all variables constant except for temperature, to show the effect temperature has on diffusivity and subsequently the flux. Changing any of the variables in the Wilke-Chang equation will alter the predicted value of the diffusivity.

\[
N_A = \text{(Constant)} \cdot (T)
\]  
(Equation 7)

Flux is a given amount per time per area, therefore rearranging Equation 7 and incorporating a constant area will result in a relationship between the time (t) necessary for a given magnitude of diffusion and the temperature (T).

\[
t \alpha \frac{1}{T}
\]  
(Equation 8)

Discussion

Materials (Cost*)
- Thermometer ($6.00)
- 3 0.4 μm pore size Polyester Membranes or plastic lunch bags ($1.50)
- 3 Conicals (15 mL) or similar clear container ($3.00)
- Corn Starch ($3.50 per class)
- Tap Water
- Ice
- Hot plate or other source of hot water e.g. coffee maker ($150.00 each)
- About 100ml 0.01 M Potassium Iodide antiseptic iodide works too ($1.00)
- 3 glass containers to hold iodide solutions ($9.00)
- Measuring cup for corn starch solution ($3.00)
- Container for hot/cold mixtures ($1.50 each)

Experimental Setup and Procedure
To prepare the cornstarch solution, mix ¼ teaspoon of cornstarch in 1 cup of water. In another container, dilute potassium iodide or antiseptic iodide with water to make a 0.01M solution of iodide. To prepare conical vials, carefully cut a circular hole (1.5 cm diameter) in each conical cap using a scalpel. Make sure to maintain enough of the cap to be able to seal the edges of the conical. Next, fill three conicals with the well-mixed cornstarch solution. Place a membrane over the end of the conical and gently twist the caps on. Invert each conical to ensure that the cornstarch solution does not leak, and to demonstrate that there is no bulk flow though membrane. Prepare an ice bath and heat water to about 60°C. Pour the iodide solution into three cups, placing one in the ice bath, one in the hot water, and leaving one at room temperature. Allow each iodide solution enough time to reach the temperature.

Figure 2. a) Carefully remove the center portion of the caps. b) After filling the conical seal the membrane into place by carefully twisting the top. c) The membrane and cap in place. d) The entire experimental setup.
condition. Use a thermometer to determine when the temperature of each iodide solution has reached a constant equilibrium with its surroundings. Shake each conical and place one into each of the three cups of iodide solution. After two minutes, remove and analyze the hue of the purple in each vial. Shake conicals and repeat every two minutes for about 6 minutes.

**Results**

Our hypothesis that the higher temperature solutions would experience higher flux and thus a darker purple color relative to the colder solutions in the same time period was confirmed. Higher temperatures resulted in higher diffusivities according to the Wilke-Chang equation (*Equation 5*). Increased diffusivity caused an increase in the flux through the membrane. Therefore, at each time period, the warmer solutions experienced more diffusion of iodide through their membranes. The darkness of the purple corresponds directly to the magnitude of iodide diffused. The results of the experiment illustrated in *Figure 3* justify the mathematical explanation that time to turn purple is inversely proportional to temperature (*Equation 8*).

![Figure 3. The time course evaluation of temperature effects on diffusivity from t=0 through 4 minutes.](image)

**Cost**

The approximate costs per item are listed along with the materials above. The total cost comes out to about 25 dollars (assuming that hot water can be obtained without a hotplate). All of the items can be reused as long as they are washed thoroughly. Only the potassium iodide, corn starch and tap water cannot be reused. The cost of the experiment will then be around a dollar per experiment. Many of the more expensive items like thermometers, glass beakers, and hotplates tend to be generic lab items.

**Alternative Setups**

There are several variations to the experimental setup stated above that could be used to demonstrate similar relationships between the rate of molecular mass transfer and its effectors. Each has its pros and cons depending on the instructional goals and time constraints. The setup most similar to the above setup is to use various concentrations of the potassium iodide solution in order to demonstrate concentration gradients function as the driving force of diffusion. Various concentration iodide solutions could be run in parallel with the hypothesis that higher iodide concentrations will result in higher rates of diffusion; implied by *Equation 4*. The qualitative result of this experiment will be that the higher concentration iodide setups will result in greater diffusion fluxes, and darker shades of purple.

Another variation of the initial setup is to use different types of porous membranes. During preparation of this experiment we tested various inexpensive "membranes" including polyethylene sandwich bags, plastic wraps, and polyester membranes with 0.4 μm pores. The 0.4 μm pores allowed the fastest results and the sandwich bags the slowest results out of all our
setups. For instructional purposes, varying the pore size demonstrates the effects of molecule size and pore size on diffusivity, implied by the effective diffusivity (Equation 6). Thus the result of increasing effective pore size on the magnitude of diffusion can be qualitatively explained and analyzed using the iodide-cornstarch indicator and conical setup explained above, with the hypothesis that the larger the pore size relative to the molecule size the higher the diffusivity.

The most important aspect of the presentation is that it is scalable to the pre-collegiate level. We believe this experiment can be easily replicated in a high school science classroom. Although conicals and micro-porous membranes are useful for the time period of a science fair-type presentation, those materials may not be as readily available to average high school science classes. Various everyday materials may be substituted for our materials. Instead of loading a conical with the cornstarch solution, a bag or pouch of plastic wrap can be placed directly in an iodide solution. This change of setup can be applied to the temperature and concentration variation experiments. Since plastic wrap and plastic sandwich bags produce qualitative results in about 1 or 12 hours respectively, continuous heating is not feasible in a science classroom. Instead, running parallel experiments in both the refrigerator and at room temperature produces results similar to the cooled and heated conditions respectively. Use of a higher concentration of iodide could be useful when using the sandwich bags and the plastic wrap membranes as a way of speeding up the experiment. This setup demonstrates molecular diffusion in a way that is inexpensive, controllable, and visibly qualitative.

Conclusion
The experimental setup stated above provides valid means for explaining several details of mass transfer on a molecular level. This instructional method is valid because it allows simplification to algebraic correlations and allows rapid and qualitative visually interesting results. It is presented in a way that allows for a variety of variables, with multiple experimental setups. Between the simplicity of correlations and diversity of both the setup and experimental setup we believe this is a feasible way to teach molecular mass transfer to a pre-collegiate audience.

References

Molecular Mass Transfer Through a Porous Medium
By: Steve Cavnar, Marc Sehgal, Abdullah Awamleh, and Tony Martus

Overview

Objective:
To demonstrate that concentration gradients are the driving force in molecular diffusion.

To evaluate the effects of molecular size and temperature on the rate of molecular mass transfer through a solid porous membrane.

Materials:
- 3 Thermometers
- 3 Polyester Membranes (Plastic Bags)
- 3 Conical
- 3 Stir Bars
- Tap Water
- Ice
- Water in other source of hot water
- 0.1 M Potassium iodide (pure or anisotropic)
- 2 cups to hold iodide
- Container for hot ice solutions
- Timer

Mass Transfer Definitions:
- Flux: The amount of something that moves per unit time per unit area.

Concentration: The amount of a given thing in an amount of space.

Concentration Gradient: The difference in concentrations that exists between two given points in space.

Diffusivity: \( D_m \), the ease by which a solute (A) moves through a medium (B) with the units length squared per unit time.

The higher, \( A \), the faster solute A will move through the medium B.
The lower, \( B \), the slower solute A will move through the medium B.

General Mass Transfer Equations (Figure 1):

\[ N_x = -D_m \frac{dx}{dz} + x_b (N_b + N_a) \]

Where \( x_b \) is \( \frac{N_b}{N_a + N_b} \), assuming constant overall concentration.

Mass Transfer Through a Solid Porous Medium (Figure 2):

\[ N_x = -D_m \frac{dx}{dz} + x_b (N_b + N_a) \]

Where \( D_m \) is the diffusivity \( \frac{dx}{dz} \) and \( x_b \) is the difference in concentration \( (N_b - N_a) \) over a given distance \( (x_a - x_b) \) and the diffusivity \( D_m \).

Example of Diffusion Through a Porous Solid Medium

Assumptions:
- Tortuosity = 1 through the membrane (straight path).
- Negligible surface resistance at the corn starch membrane interface.
- Instantaneous reaction of corn starch with iodine (implies that darkness of purple is directly proportional to amount of diffusion at a point in time).
- No corn starch in pores only water. (Diffusivity through pores can be calculated for iodide diffusion through water).
- Diffusivity can be approximated using the Wilke-Chang method for determination of diffusivities.
- Concentration of iodide outside of membrane is constant.
- No bulk flow (diffusion through solid).
- Rate of reaction doesn’t decrease over time of experiment (all corn starch is not reacted when experiment ends).
- Steady State (Difference in concentration is consistent across membrane with respect to time).

Step by Step Procedure

Step 1: Mix about 1/4 tsp of cornstarch in 1 cup of water.

Step 2: Measure out the correct amount of potassium iodide or anisotropic iodide.

Step 3: Dilute the iodide to 0.01M.

Step 4: Carefully remove the center of the conical cap.

Step 5: Fill the conical with the well mixed cornstarch solution.

Step 6: Place the membrane over the end of the conical and carefully twist the cap on to the conical.

Step 7: Take note of the seal that the membrane makes and the fact that there should be no flow through.

Step 8: After noting the temperature and an ice bath place the conical in about 20 ml of the ice cooled 0.01M iodide solution. Note the time.

Step 9: After noting the temperature of an ice water bath place the conical in about 20 ml of the heated 0.01M iodide solution (keep the temperature under 60 degrees C). Note the time.

Step 10: Allow the two conicals to sit in the heated and cooled iodide solutions for about 2 minutes, removing both at the same time. Invert the two conicals multiple times to ensure the reaction has occurred and note the relative colors of the solutions both inside and out of the conicals.

Results

Expected Results:

Time = 0
The simplified general flux equation gives

\[ N_x = -D_m \frac{dx}{dz} + x_b (N_b + N_a) \]

Where \( N_x \) = amount (mass)/area, which implies that \( D_m \) is Amount/Area.

Substituting our \( N_x \) equation in for \( N_x \) we get:

\[ Time = \frac{Amount}{D_m \times Area} \]

In this experiment amount (Moles), area of membrane face, concentration and membrane thickness are the same in both temperature conditions so our equation becomes:

\[ Time = \frac{Amount}{D_m \times Area} \]

The Wilke-Chang equation for DAB that we used to approximate the diffusivity value can be simplified to:

\[ D_m = \frac{Amount}{D_m \times Area} \]

Therefore we can see that time is inversely proportional to the temperature, so the hotter the iodine solution is the more purple we should expect to see over a given time period. This contrast is depicted above in the time course images of conicals at the two temperature conditions.