

DIFFUSION PRELAB

Ch En 385 – Knotts

Lab Learning Objectives

1. Be able to quantify the process of evaporation of a liquid out of an open container and explain how it occurs in terms of mass transfer.
2. Be able to determine the concentrations of the evaporating species at different locations in the film.
3. Be able to describe advection and how it differs from pure diffusion. Be able to quantify the effects of advection on the system.

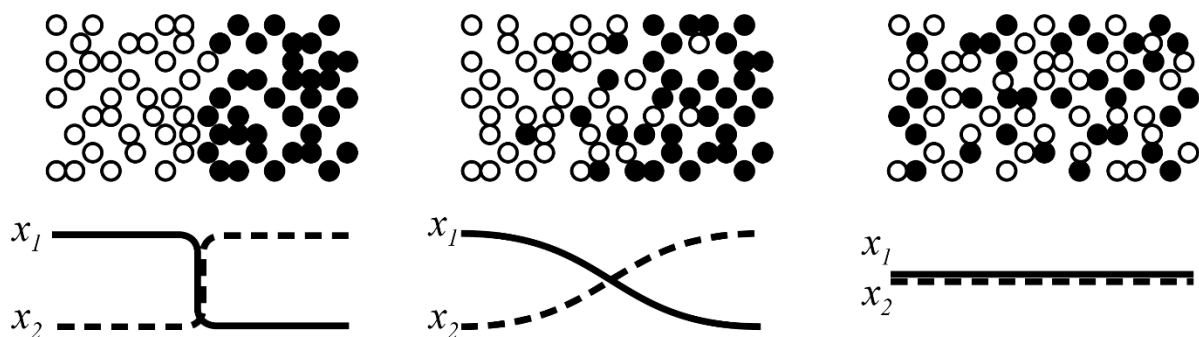
Introduction

Mass transfer is one of the most important concepts that define the field of chemical engineering because one of the main applications of the phenomena is separations. The products of most reactions and processes, and most raw resources available in nature, are *mixtures*, so individual compounds of interest must be purified (*separated* from other materials) to be of use. Performing this separation process in an economical way is often the defining challenge of taking technology from the lab to large-scale production.

Mass transfer can occur through *diffusion* or *convection*. Convective mass transfer is movement of mass through space *due to external flow of the fluid* and is analogous to convective heat transfer. For example, wind blowing across a lake will move water molecules from the lake surface into the air. With diffusion, mass moves from areas of high concentration to low concentration *in the absence of external flow* due to the concentration gradient and is analogous to conductive heat transfer. This lab focuses on the latter.

Theoretical Background (Linking to and Expanding upon Previous Knowledge)

On a molecular level, diffusion occurs because molecules at temperatures above zero Kelvin are always randomly moving from thermal energy. The individual movements of each molecule are random, but when a concentration gradient of a species exists the collective motion of the molecules for that species has a preferred direction. This is illustrated below.



Consider the left panel where a concentration gradient exists for both species. The left half of the domain is pure white particles (high mole fraction x_1) and the right half of the domain is pure black particles (high mole fraction x_2). Due to random thermal motion, more black particles than white particles will cross the center plane moving *to the left* because there are more black particles than white particles on the right of the line. Conversely, more white particles than black particles will cross the center plane moving *to the right* because there are more white particles than black particles on the left.

As the middle panel shows, this situation of more black than white particles moving to the left and more white particles than black particles moving to the right will continue at any arbitrary vertical plane in the domain *as long*

as there are more black than white particles on the right of the plane and vice versa (as long as a concentration difference exists). It is only when the concentration gradient disappears (the system becomes well mixed) that an equal number of white and black particles move to the right or left of the plane. (See right panel.) In summary, the random motion of each individual particle produces a net movement of the species from regions of high concentration to regions of low concentration. (Keep reading the previous two paragraphs, and examining the figure, until you understand the concepts being presented.)

A common mass transfer situation (which also involves thermodynamics) is evaporation of a liquid. For convenience, consider water as the species of interest. Evaporation situations can occur either by diffusion (evaporation out of a cup sitting in a room) or convection (wind blowing across a lake). In either case, as long as the ambient conditions are such that the relative humidity is less than 100%, water molecules at the liquid/vapor interface will vaporize (become “steam” molecules) and move away from the surface of the liquid. Vaporization is a thermodynamic process that happens because there is a difference in the chemical potential of liquid water (high) and ambient vapor water (low), and the system is seeking to establish equilibrium. Once in the vapor phase, the water (steam) molecules near the surface are at a higher concentration than farther away from the surface, so diffusion occurs. At the surface, the concentration of water in the vapor phase mixture is at 100% relative humidity because thermodynamics demands that the two-phase region occur at saturation. If the relative humidity is less than 100% away from the surface, the vapor-phase water molecules will diffuse away from the surface towards the ambient conditions.

Diffusive mass transfer was mathematically quantified in ChEn 376. Recall that the absolute molar flux of species A (\mathbf{N}_A'') in a mixture of A and B is

$$\mathbf{N}_A'' = -CD_{AB}\nabla x_A + x_A(\mathbf{N}_A'' + \mathbf{N}_B'') \quad (1)$$

where C is the total concentration of molecules, D_{AB} is the diffusivity (binary diffusion coefficient), x_A is the mole fraction of species A, and \mathbf{N}_B'' is the absolute molar flux of species B. The term on the left is Fick’s law for diffusion. The term on the right is the *advection* and is needed because the diffusion itself causes movement of molecules, and to absolute molar flux depends on the reference frame from which you view the mass transfer. The reference frame most useful to engineering is one where the observer is *fixed in space* and observes the movement of the molecules. The advection accounts for this fixed reference frame. If the reference frame moved along with the bulk motion of the molecules (the observer was shrunk down to the size of a molecule and was riding on a raft the moved with the “current” produced by the net movement of species A, then the advection would not be needed. Heat transfer by conduction does not have an analogous term because molecules don’t move in such situations.

From a practical mathematical standpoint, the absolute mole flux equation cannot be solved analytically because it is coupled with an analogous equation for \mathbf{N}_B'' producing a system of inhomogeneous differential equations. The math becomes much easier if *advection* can be assumed negligible. This is the subject of the *Stationary Media Approximation* learned in Ch En 376. Fortunately, this occurs for many systems of interest such as gases diffusing through liquids or solids. The advection can also be simplified for the evaporation case. In this case, the total term isn’t negligible, but one half is zero so the resulting differential equation is separable and integratable in one dimension. This is the case for evaporation of a liquid out of a container, or, in mass transport language, *diffusion through a stagnant film*.

Consider evaporation of liquid A in a container (See Figure 1). The surface area of liquid A container can any shape as long as the vertical sides (of length L) are the same size. At steady state, within the film from $x = 0$ to $x = L$, only species A experiences a net flux. The net flux of Species B (air in most cases) is zero because the container bottom is impermeable to B. If such were not the case, and B was either entering or

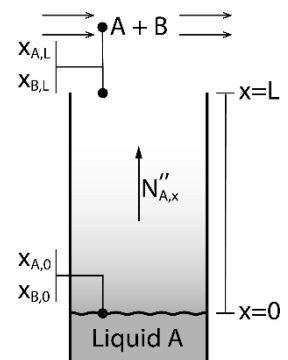


Figure 1 Schematic of diffusion through a stagnant film (evaporation of a liquid in a container).

leaving the liquid phase or the film, accumulation of B would occur—a fact impossible at steady state. Since $N_B'' = 0$, and net movement of A only occurs in one direction (x), Equation 1 simplifies to

$$N_{A,x}'' = -CD_{AB} \frac{dx_A}{dx} + x_A(N_{A,x}'') \quad (2)$$

From here, one could be tempted to invoke the stationary phase approximation, but this would be problematic. This assumption is only valid if 1) $N_B'' = 0$, and 2) $x_A \ll 1$. The first is valid in this case, but the second is questionable. Equation 2 is a separable ordinary differential equation, and its solution is

$$N_{A,L}'' = \frac{CD_{AB}}{L} \ln \left[\frac{1 - x_{A,L}}{1 - x_{A,0}} \right] \quad (3)$$

Here, $x_{A,0}$ is the mole fraction of Species A in the vapor phase at the liquid/vapor interface ($x = 0$) and $x_{A,L}$ is the mole fraction of Species A at $x = L$.

In this lab, you will take measurements on an apparatus set up like Figure 1 for three different compounds (three different Species A): water, acetone, and ethanol. The measurements will allow you to calculate an experimental $N_{A,L}''$ from which you can determine D_{AB} . To do so, you will also need the experimental values for $x_{A,L}$ and $x_{A,0}$. The apparatus will be set up in the lab, so you can safely assume that $x_{A,L} = 0$ for acetone and ethanol. For water, you will need to calculate the ambient mole fraction using the ambient relative humidity and pressure.

You learned about relative humidity in Ch En 273. Recall that relative humidity (ϕ) is the ratio of the partial pressure of water in the air (P_{H_2O}) to the vapor pressure of water ($P_{H_2O}^{sat}$) at the temperature of the system. Mathematically,

$$\phi = \frac{P_{H_2O}}{P_{H_2O}^{sat}}$$

Since water and air behave ideally at typical atmospheric conditions, the partial pressure of water in the air/water mixture is related to the mole fraction of the water in the mixture (x_{H_2O}) through

$$P_{H_2O} = x_{H_2O}P$$

where P is the total pressure of the system (ambient pressure in this case). This means that $\phi = \frac{x_{H_2O}P}{P_{H_2O}^{sat}}$ or

$$x_{H_2O,L} = \phi \frac{P_{H_2O}^{sat}}{P} \quad (4)$$

The mole fraction of Species A in the vapor phase at $x = 0$, $x_{A,0}$ is obtained by realizing that vaporization is occurring at this location in the system. That means that Species A is at *saturated* conditions. In relation to Equation 4, saturated means $\phi = 1$ and

$$x_{A,0} = \frac{P_A^{sat}}{P} \quad (5)$$

The final term variable in Equation 3 that requires discussion is C . Recall that C is the total concentration of species in the film over which the diffusion occurs. In this case, the film is a vapor at relatively low pressures, so the ideal gas equation of state may be used to calculate C .

Prepare for a Safe Experiment

Task 1: Read and Commit to Follow the General Lab Safety Rules

1. No food or drink is allowed in the laboratory.

2. All personnel in the laboratory area are required to wear safety glasses, long pants, and covered shoes (no sandals or flip-flops).
3. Experimental work should be completed during the regular class periods. If additional time is needed in the laboratory, you must clear it with your instructor and make an appointment to use the laboratory with a TA. At least two students must be present during those additional hours. (No one is permitted to work in the lab alone).
4. At least two students from each team must be physically in the lab when running experiments. These students should be monitoring the experiment so that emergency procedures can be enacted if problems occur.
5. Students who operate *any* equipment in *any* unsafe manner or in a manner that damages the equipment or results in a user-preventable accident will incur a *significant* grade penalty. This includes not knowing how to run the equipment or shut it down as per instructions provided. *All team members are required to know how to safely run the equipment as instructed.*

Task 2: Become Informed about the Chemicals (10 Minutes)

Under normal operation, students will not need to handle the chemicals used in this lab, but you should be aware of the potential hazards involved. Three chemicals are used in this lab.

1. Reverse Osmosis Water: RO water is water from which dissolved minerals have been removed by a reverse osmosis process. According to its SDS is not considered hazardous.
2. Ethanol: According to its SDS, ethanol is highly flammable. It is also acutely toxic if swallowed, can cause damage to internal organs through repeat exposure, and can harm unborn children. In case of skin contact, rinse the affected area with soap and water.
3. Acetone: According to its SDS, acetone is highly flammable and can cause eye irritation. It is also acutely toxic if swallowed and can cause damage to internal organs through repeat exposure. In case of skin contact, rinse the affected area with water for several minutes.

Do the following.

- A. Download the SDS for ethanol and acetone.
- B. Review the SDS of the compound and identify potential hazards. Pay attention to the following:
 - o Hazard Statement found in Section 2.
 - o Precautionary Statements found in Section 2.
 - o NFPA "Safety Square" found in Section 2.
 - o First Aid Measures found in Section 4.
- C. Commit to handle the compound safely.

Task 3: Review the Following Lab-specific Safety Statements and Procedures

- A. Wear gloves when handling ethanol and acetone. A lab coat is recommended. (Under normal operation, students will never handle the chemicals, but follow this guideline should a situation arise.)
- B. Work with acetone and ethanol in the fume hoods. Do not remove the apparatus with these compounds out of the hood.
- C. Do not ingest any of the liquids.
- D. Do not inhale the fumes from acetone or ethanol.

Task 4: Learn about the Lab Equipment

Apparatus

Figure 2 is a picture of the experimental apparatus for water. It consists of three graduated cylinders of different sizes, 500 ml, 1000 ml and 2000 ml cylinder. Two similar sets of three cylinders are found in the fume hood for acetone and ethanol.

Each graduated cylinder is partially filled with liquid (water, acetone, or ethanol) and held fixed with a lab stand. An inverted burette is clamped above each cylinder so that the open end of the burette is at the level of the liquid in the cylinder. The burette serves two purposes. First, it keeps the liquid level in the cylinder constant. Second, it provides a measurement of the amount of liquid that has evaporated.



Figure 2 Diffusion apparatus

Reading the Fluid Level in the Burette

- Make sure to position the meniscus at eye level when taking a reading.
- Read the position at the bottom of the meniscus.
- Two different types of burettes are used in the lab. The first is completely transparent. The second has a white background. See Figure 5 for a picture of the former and Figure 6 for a picture of the latter.



Figure 3 Meniscus of a transparent burette and where to read the fluid level.



Figure 4 Meniscus of a burette with a white background and where to read the fluid level.

Obtaining the Ambient Conditions

The ambient conditions are displayed on the device attached to the side of the south fume hood (See Figure 5). The relative humidity gauge is very sensitive, so do not breath on the device when taking readings. Three values are reported: relative humidity, temperature, and absolute ambient pressure. Make sure to note the units when recording data.



Figure 5 Ambient conditions meter located on the south fume hood.