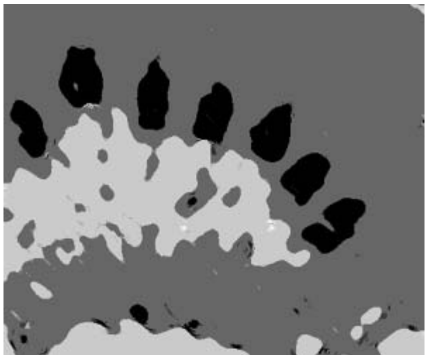

INTERDISCIPLINARY LIVELY APPLICATIONS PROJECT

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CONTENTS

Getting the Salt Out

MATHEMATICS CLASSIFICATIONS:
Calculus, Differential Equations

DISCIPLINARY CLASSIFICATIONS:
Chemistry, Engineering

PREREQUISITE SKILLS:
1. Modeling with an ordinary differential equation with initial condition.
2. Sketching a solution to a differential equation on its direction field.
3. Solving an ordinary differential equation by separation of variables.

PHYSICAL CONCEPTS EXAMINED:
Osmotic pressure, permeability, desalination.

COMPUTING REQUIREMENT:
A program to plot direction fields. (A Mathematica program is available from the authors.)

The UMAP Journal 24 (4) 435-449.

Contents

1. Setting the Scene

When two water (or other solvent) volumes are separated by a semi-permeable membrane, water will flow from the side of low solute concentration to the side of high solute concentration. This is known as osmosis (see **Figure 1**). The flow of solvent across the membrane may be stopped, or even reversed, by applying external pressure on the side of higher solute concentration. This process is called reverse osmosis (see **Figure 2**).

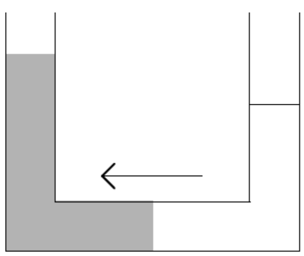

Figure 1. Osmosis.

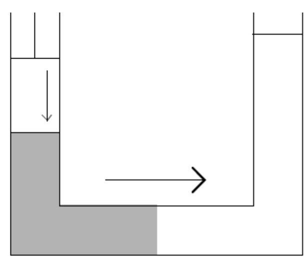

Figure 2. Reverse osmosis.

We will use van't Hoff's equation to model osmosis. Jacobus Henricus van't Hoff (1852–1911) determined that the osmotic pressure Π is given by the equation

$$\Pi = cRT,$$

where

c is the molar solute concentration,

R is the universal gas constant, and

T is the absolute temperature.

Notice that $c = n/V$, where n is the number of moles of solute and V is the volume of solution. Although van't Hoff's equation looks like a restatement of the ideal gas law, $PV = nRT$, it is special because it is being applied to a liquid rather than to a gas. This equation was a significant development; in 1901 van't Hoff received the Nobel Prize in Chemistry "in recognition of the extraordinary services he has rendered by the discovery of the laws of chemical dynamics and osmotic pressure in solutions" [Nobel Foundation 2000].

Consider the case in **Figure 2**, where an external pressure, ΔP, is applied to the side of the membrane with higher solute concentration. The resulting flux through the membrane is proportional to the difference between the osmotic pressure and the applied pressure. That is, if x represents the volume of water that has been extracted from the solution, then

$$\frac{dx}{dt} = \phi A(\Delta P - \Pi), \tag{1}$$

where ϕ is the water permeability constant and$A$ is the membrane area perpendicular to the flow.

It is important to note that Π is not a constant here. If the initial volume of solution is V, and if x units of water have been extracted from the solution at time t, then

$$\Pi(t) = \frac{n}{V-x}\,RT.$$

Substituting this expression into **(1)**, we get the desalination differential equation,

$$\frac{dx}{dt} = \phi A\left(\Delta P - \frac{n}{V-x}\,RT\right) = \phi A\left(\Delta P - \frac{cVRT}{V-x}\right). \tag{2}$$

2. Your Job

Clearwater, Inc., is planning to build a new, portable water purifier to remove salt from seawater. They have designed a machine, shown below in **Figure 3**; but before they go to the expense of building a prototype, they want you to perform a theoretical analysis of their design.

Your task is to analyze how the values of the design parameters for the desalination machine will affect the performance of the machine. Keeping in mind that the machine must be portable:

> *How should the membrane coefficient ϕ, the membrane size A, the volume V of the desalination chamber, and the applied pressure ΔP be chosen to produce a machine that is both efficient and economical?*

Clearwater is counting on you to design a good product, so don't let them down!

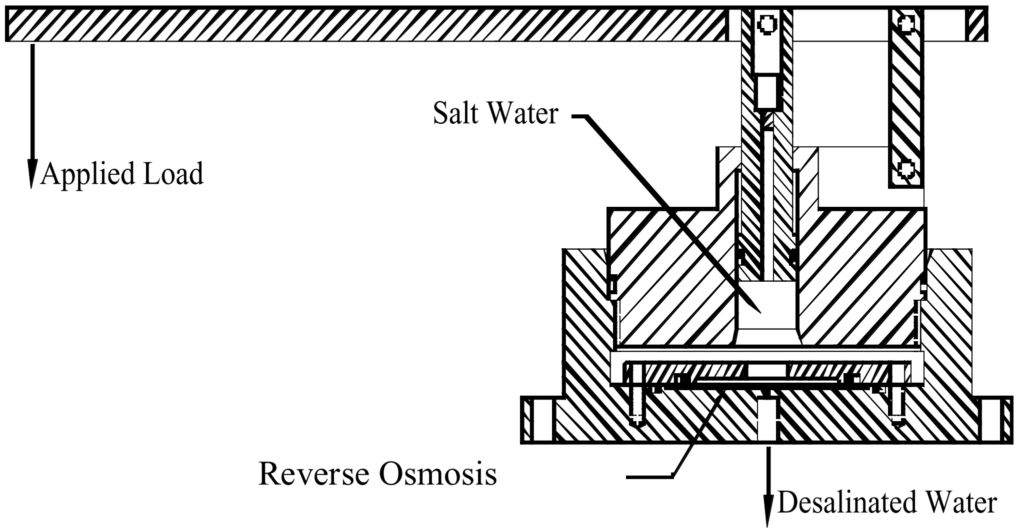

Figure 3. Clearwater's desalination machine.

3. Part 1: Numerical and Graphical Analyses

Requirement 1

Use direction fields and Euler's method (of following along the directions in a direction field) to sketch solutions of **(2)**. Of course, to do that you will need to assign values to the various constants and parameters in the equation. For the physical constants in the problem, use the values

$$c = 0.103\ \frac{\text{moles}}{\text{L}},$$
$$R = 0.082\ \frac{\text{L}\cdot\text{bar}}{\text{mole}\cdot{}^\circ\text{K}},$$
$$T = 293^\circ\ \text{K}.$$

For the design parameters, begin with

$$\phi = 0.1\ \frac{\text{m}^3}{\text{m}^2\cdot\text{day}\cdot\text{bar}},$$
$$A = 1.5\ \text{m}^2,$$
$$\Delta P = 15\ \text{bars},$$
$$V = 4\ \text{L}.$$

Plot a direction field for the desalination differential equation where t (measured in days) goes from 0 to 5 and x (measured in L) goes from 0 to 4. Also, plot the solution curve for x that passes through the point $(0, 0)$.

According to your direction field and solution, how much fresh water can the machine extract from 4 L of sea water?

Approximately how long does it take to extract 2 L of fresh water?

As time goes by, what happens to the rate at which the machine produces fresh water? Does this make sense to you? Can you think of a physical reason why this would happen?

Requirement 2

Suppose that we change the capacity of the machine. For example, suppose that the initial volume of brine is 6 L instead of 4. How much fresh water can we extract? How long does it take to extract 2 L of fresh water? What happens if we begin with 8 L of brine? How sensitive is the time required to extract 2 L of fresh water to the initial volume of sea water in the machine? What relationship seems to exist between the initial volume of sea water and the total amount of fresh water that can be extracted from it? The graphs in **Figure 4** show examples of proportionality relationships that you might look for in your investigations.

Figure 4. Three proportionality relationships: $v \propto u$, $v \propto u^2$, and $v \propto 1/u$.

Requirement 3

Now fix the value of V at 6 L and investigate how the performance of the machine depends on the other design parameters. What effect does increasing or decreasing A have on the amount of fresh water that we can extract from a given volume of brine? On the time required to extract 2 L of fresh water? Answer the same questions for ϕ and ΔP. Of the three variables, which one, when varied, causes the greatest change in the amount of fresh water extracted? On the time required to extract 2 L of fresh water?

Requirement 4

What is the equilibrium solution of **(2)**—that is, the solution when $dx/dt = 0$? Discuss how that solution depends on the design parameters and compare your conclusions to the observations you made in the earlier parts above.

4. Part 2: Let's Get Explicit

Requirement 5

Use separation of variables to obtain the solution of **(2)** that satisfies the initial condition that $x = 0$ when $t = 0$. Hint: Solve for t as a function of x.

Requirement 6

Use the solution of the differential equation to determine how the performance of the Clearwater desalination machine depends on the values of the parameters ϕ, A, and ΔP. Do your results agree with the conclusions that you drew earlier using direction fields?

5. Part 3: What Do You Recommend?

Requirement 7

Prepare a report for the engineers working on the desalination project at Clearwater, Inc. An important issue is how quickly the proposed machine will be able to produce 2 L of fresh water. Your report should include an analysis of how this time depends on each of the design parameters ϕ, A, and ΔP, and on V.

Clearwater's marketing people have reported that, if their machine is to be competitive in the marketplace, it must be able to produce at least 2 L of fresh water per day. If the machine is to be portable, it can handle at most 8 L of seawater at a time. Furthermore, because the walls of the pressure vessel are quite thin, the upper limit on the applied pressure, ΔP, is 30 bars. Filters for this machine are extremely expensive; consequently, the area of the filter is to be no greater than 1.2 m^2. Finally, the best filter available has a permeability coefficient of $\phi = 0.08$. Is it theoretically possible to build a reverse osmosis desalination machine that meets all of these specifications? What is the approximate size of the smallest filter that can be used in this machine to meet the specifications?

To finish your report, give your recommendation for values of design parameters that yield the "best" machine. A "best" machine should be built with some margin for error, so pick your parameter values with some room to maneuver (is 5–10% possible?) if you can.

The engineers who will be reading your report are familiar with van't Hoff's equation. Therefore, you do not need to derive or explain that equation. However, you do need to provide mathematical explanations and justifications for all of the conclusions in your report. You should include all relevant graphs in an orderly fashion.

Title: Getting the Salt Out

Instructor's Solution

Part 1: Numerical and Graphical Analyses

Requirements 1 and 2

With the given values of the physical constants and design parameters, the direction field of **(2)** and the solution through $(0, 0)$ are as shown in **Figure S1**.

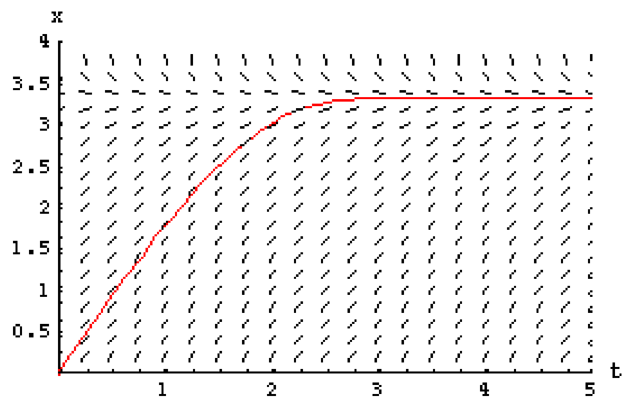

Figure S1. Direction field for $V = 4$ L.

From this graph, it is apparent that $\lim_{t\to\infty} x(t) \approx 3.4$ L. Furthermore, 2 L of fresh water is obtained in approximately 1.1 days. Fresh water is extracted at a decreasing rate because as fresh water is extracted, the concentration of salt in the remaining brine solution increases. To maintain a constant rate of extraction of fresh water, it would be necessary to increase the applied pressure.

With $V = 6$ L and the other design parameters unchanged, it is possible to extract a little more than 5 L of fresh water from the solution, and the first 2 L of fresh water can be extracted in just over 1 day. This is illustrated in **Figure S2**.

For $V = 8$ L, it is possible to extract 6.8 L of fresh water, but the time for 2 L is almost unchanged from when the volume was 4 L or 6 L. With additional experimentation, a student can observe that the total fresh water extractable from a brine solution is proportional to the initial volume of the solution.

Requirement 3

Graphs such as those in **Figure S3** suggest that changing the area of the membrane has no effect on the amount of fresh water extractable from a brine solution. Furthermore, the time for 2 L of fresh water is inversely proportional to the area of the membrane. (In **Figures S3–S5**, the values of the parameters are $\phi = 0.1$, $A = 1.5$ m^2, $\Delta P = 15$ bars, and $V = 4$ L except as indicated.)

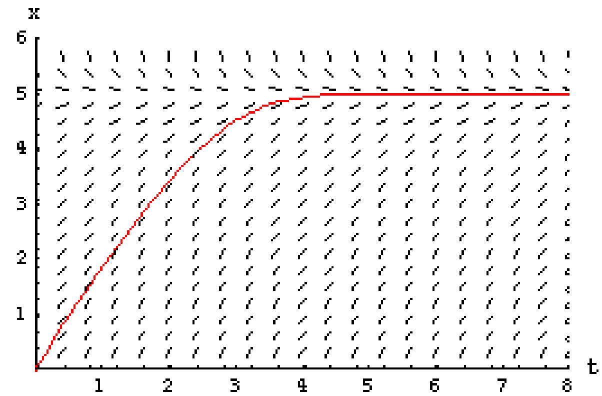

Figure S2. Direction field for $V = 6$ L.

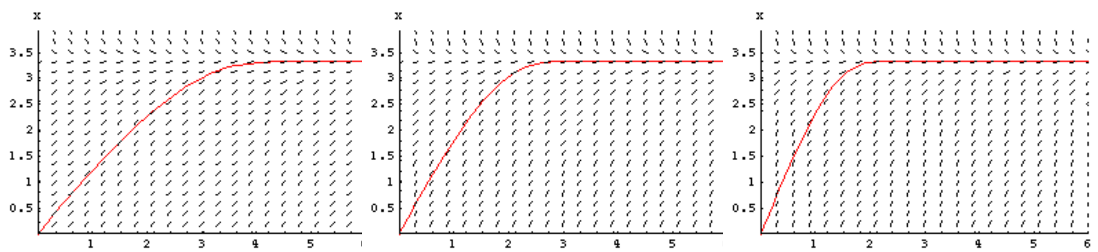

Figure S3. Effect of increasing the membrane size: $A = 1.0, 1.5, 2.0\ \mathrm{m}^2$.

The graphs in **Figure S4** lead to the same conclusions about the relationship between the water permeability constant and the efficiency of the machine.

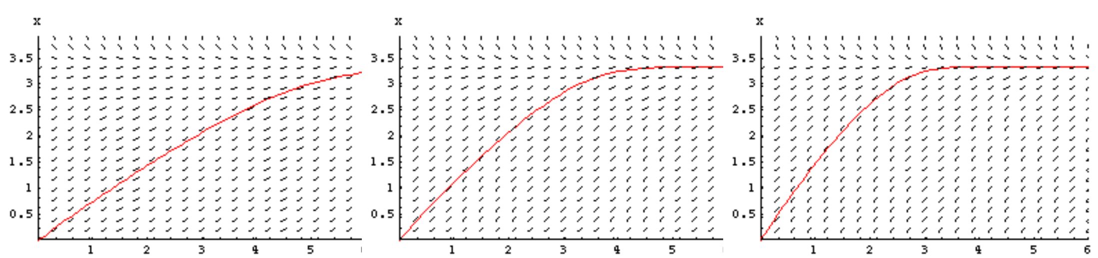

Figure S4. Effect of increasing the water permeability constant: $\phi = 0.04, 0.06, 0.08$ m/day·bar.

The graphs in **Figure S5** show that the total amount of fresh water that can be extracted from a given volume of brine is a (slowly) increasing function of the applied pressure ΔP. The time required to extract 2 L of fresh water from a given solution seems to decrease a little faster than $1/\Delta P$.

These analyses indicate that:

> *We can get more fresh water from the solution only by increasing either the volume V or the applied pressure ΔP, and that we get much more for our efforts by increasing V.*

The time to extract 2 L of fresh water from a given volume of brine can be reduced by increasing any of the parameters ϕ, A, and ΔP; changing ΔP has the greatest effect, but only marginally.

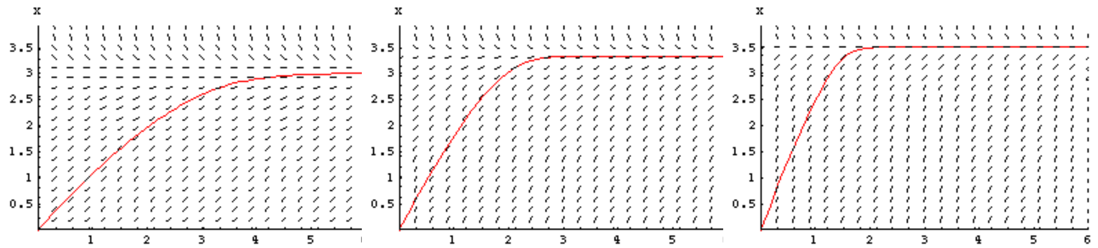

Figure S5. Effect of increasing the applied pressure: $\Delta P = 10, 15, 20$ bars.

Requirement 4

The equilibrium solution of **(2)** is

$$x = V - \frac{cVRT}{\Delta P} = V\left(1 - \frac{cRT}{\Delta P}\right).$$

Therefore, as we predicted, the total amount of fresh water that can be extracted from a given volume of brine is proportional to the initial volume of the solution. Notice that, as expected, the amount of water that can be extracted does not depend on either A or ϕ. The equilibrium solution also shows that the amount of fresh water we can extract increases (gradually) with increasing ΔP.

Part 2: Let's Get Explicit

Requirement 5

We could solve

$$\frac{dx}{dt} = \phi A\left(\Delta P - \frac{cVRT}{V-x}\right)$$

with the initial condition $x = 0$ when $t = 0$ via a computer algebra system, but in fact separation of variables and the integration can be done by hand:

$$\frac{V-x}{\Delta P(V-x) - cVRT}\, dx = \phi A\, dt$$

$$\int_0^x \frac{V-u}{\Delta P(V-u) - cVRT}\, du = \int_0^t \phi A\, dt,$$

$$\frac{x}{\Delta P} - \frac{cRT}{(\Delta P)^2} \ln\left(1 + \frac{\Delta P x}{cVRT - V\Delta P}\right) = \phi A t,$$

$$t(x) = \frac{1}{\phi A \Delta P}\left[x - \frac{cVRT}{\Delta P} \ln\left(1 + \frac{\Delta P x}{cVRT - V\Delta P}\right)\right].$$

Requirement 6

The solution of the initial value problem shows that $t(x)$, the time required to extract a specified volume of fresh water from a brine solution, is inversely proportional to both ϕ and A. Furthermore, the solution shows that $t(x)$ decreases a little faster than $1/\Delta P$, and that there is only a very weak relationship between $t(x)$ and V. The argument of the logarithm approaches 0 as x approaches $V - cVRT/\Delta P$. This is the equilibrium solution that we found before.

The graph of $t(x)$ with $\phi = 0.1$, $A = 1.5$, $\Delta P = 15$, and $V = 6$ is given in **Figure S6**; it is the reflection of the solution curve that we saw in **Figure S1** about the line $x = t$. The explicit form of $t(x)$ makes it possible to determine exact solutions to the **Requirements 1–4** posed in **Part 1** of this project.

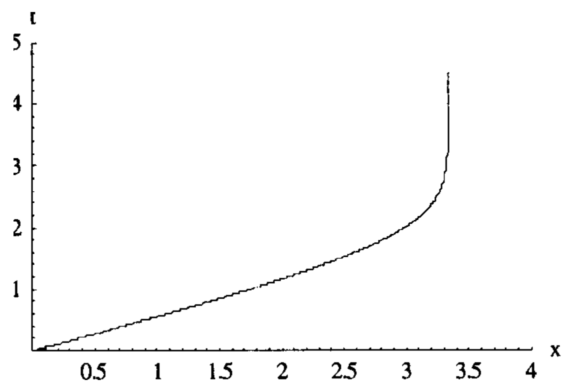

Figure S6. Graph of $t(x)$ for $\phi = 0.1$, $A = 1.5$, $\Delta P = 15$, and $V = 6$.

Part 3: What Do You Recommend?

Requirement 7

It is easy to design a machine that meets the given specifications by using the maximum allowed value of each parameter. Then the machine extracts 2 L of fresh water from 8 L of brine in 18.4 h. The filter size can be reduced to an area of 0.92 m^2 and the machine will still satisfy the fresh water production requirement. **Table 1** gives examples of other results, from trial and error.

Table 1.
Various results.

ϕ	A	ΔP	V	Time (h) for 2 L of fresh water
0.08	1.0	27	6	25.0
0.08	1.1	27	6	22.7
0.07	1.2	28	6	22.9

Students should discuss reasons for their choices of the parameters.

Title: Getting the Salt Out

Notes for the Instructor

Background on Reverse Osmosis

While reverse osmosis is sometimes referred to as a *filtration process*, many researchers and practitioners prefer not to use this term due to the unique aspects of this membrane separation. The mechanism of the separation is the subject of some debate. The most widely accepted theory is that the process proceeds by a solution-diffusion mechanism [Cussler 1997]. The membrane does not have physical holes in it but rather acts as a distinct phase. Both the water and the solute (salt in our case) dissolve in the membrane the same as they might in an adjacent immiscible liquid phase. The components then diffuse through the membrane and finally dissolve into the outlet liquid phase. This is a rate-based separation where the water is purified because it diffuses more easily, and therefore more quickly, through the membrane than the salt does. The flux of water through the membrane is proportional to the pressure above osmotic. The flow of solute is proportional to the concentration difference across the membrane.

The example discussed in this project is a "dead end" batch configuration of the separation process where all the water is being pushed through the membrane. In practice, almost all reverse osmosis systems are designed in a continuous cross-flow arrangement where the flow of the liquid is tangential to the surface of the membrane. In this arrangement, there are two outlet streams, a purified stream of the water that has passed through the membrane and a concentrated stream of the material that has been retained by the membrane. Either of these streams may be the product depending on whether the goal is to produce purified water or a concentrated product.

Water purification is the largest use of reverse osmosis. However, this process is also used for concentrating various products, including orange juice in the production of frozen concentrate and maple sap in the production of maple syrup (where the approximately 3% solids sap must be raised to over 65% solids in the final syrup). In the cross-flow configuration, the temporal problem of increasing salt concentration explored in this paper becomes a spatial problem where the concentration is increasing as we move along the filter. More background on this separation can be found in a short article by Eykamp [1997] or in an article on the engineering project related to this problem [Moor et al. 2004].

Van't Hoff's equation provides only an approximation of the osmotic pressure, and the approximation is best for low concentrations of solute. In fact, the equation overpredicts the osmotic pressure by 3–5% in the range of concentrations used in this project. Furthermore, our model neglects the fact that a small amount of salt migrates through the filter along with the water. This is relatively inconsequential early in the extraction process. However, as water is removed from the brine, the concentration of salt in the remaining solution increases and, consequently, the difference between the applied pressure and the osmotic pressure decreases. Eventually, while the rate at which water is being extracted from the solution is decreasing, the rate of flow of salt through the membrane actually goes up.

Notes on the Problem Solution

One can get a good idea of the nature of solutions of the desalination differential equation,

$$\frac{dx}{dt} = \phi A \left(\Delta P - \frac{cVRT}{V - x} \right),$$

by examining its form. Initially, the rate of desalination is essentially directly proportional to both ϕ and A. Furthermore, if the amount of fresh water that has been removed from the salt water is small compared with the total volume of salt water, then

$$\Delta P - \frac{cVRT}{V - x} \approx \Delta P - cRT = \Delta P - \Pi.$$

Therefore, at the beginning of the desalination process, the rate at which fresh water is being extracted is nearly constant. This is consistent with the solution curves generated in the **Sample Solution**. As the value of x increases, $V - x$ decreases and $\Delta P - cVRT/(V - x)$ gets closer to zero. Therefore, as more and more fresh water is extracted, the rate of extraction decreases.

The equilibrium solution of the differential equation, the constant value of x for which $dx/dt = 0$, is of interest. Physically, equilibrium occurs when enough fresh water has been removed from the solute so that the osmotic pressure equals the applied pressure. Mathematically, equilibrium occurs when

$$x = V \left(1 - \frac{cRT}{\Delta P} \right),$$

and this value represents the maximum amount of fresh water that can be extracted from a solution of given volume using a given applied pressure ΔP. The domain of the solution

$$t(x) = \frac{1}{\phi A \Delta P} \left(x - \frac{cVRT}{\Delta P} \ln \left(1 + \frac{\Delta P x}{cVRT - V\Delta P} \right) \right)$$

is

$$0 \leq x < V \left(1 - \frac{cRT}{\Delta P} \right).$$

There is a more rigorous way to determine appropriate parameter values for this project. Start by making a nonoptimal choice for two of the parameter values, say $A = 1.1$ and $V = 7$. Now substitute these values in the formula for $t(x)$ and evaluate at $x = 2$. The resulting expression is a function of two variables $z(\phi, \Delta P)$. Graph $z(\phi, \Delta P)$ and $z = 1$ together; the portion of $z(\phi, \Delta P)$ that lies below $z = 1$ contains permissible values for ϕ and ΔP. For example, **Figure S7** shows the permissible values of $0.04 \leq \phi \leq 0.08$ and $25 \leq \Delta P \leq 30$ when $A = 1.1$ and $V = 7$. Therefore, the values $(A, V, \phi, \Delta P) = (1.15, 7.5, 0.075, 29) \pm (0.05, 0.5, 0.005, 1)$ all result in an acceptable desalination machine.

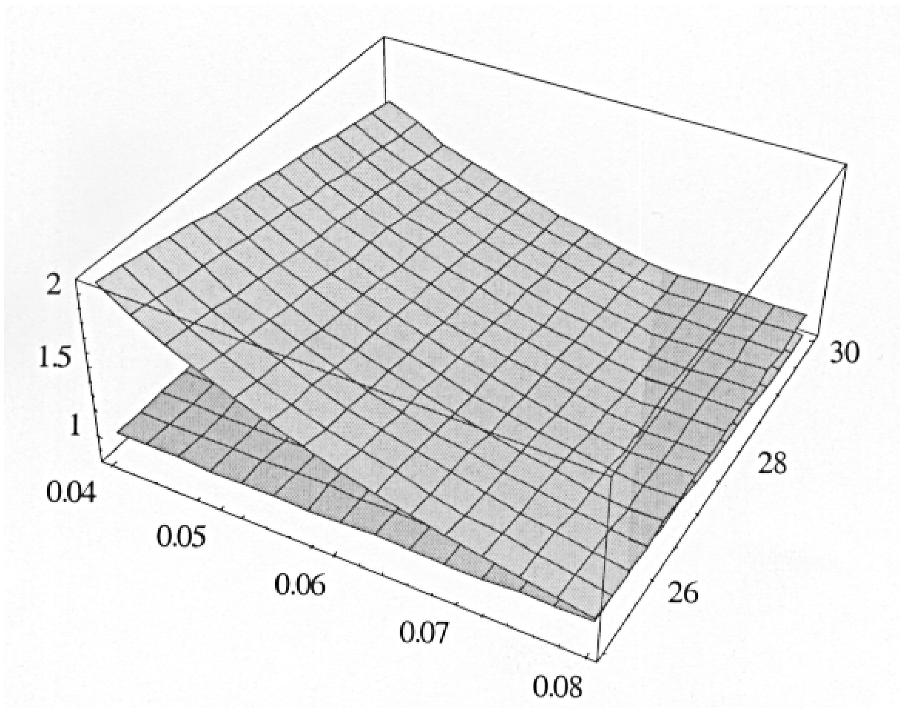

Figure S7. Determining permissible values for ϕ and ΔP.

Pedagogical Advice

The instructor has a number of options concerning the administration of this project. The project can be assigned all at once. As an alternative, when we gave this project to our students, we spread the objectives out over a week's time. We spent part of a class period deriving the desalination differential equation, to ensure that our students were familiar with the meaning of each parameter. We then assigned Part 2 of the project, the explicit solution of the differential equation, to be handed in before the laboratory session in which the students worked on Part 1. We supplied the correct solution to the differential equation within the lab itself. In this way, an incorrect solution to the differential equation did not hamper any student's analysis of the problem.

This project was developed jointly by engineering faculty and mathematics faculty at Lafayette College. During the course of the semester, first-year engineering students built and tested the desalination pump shown in **Figure S8**.

Figure S8. Desalination pump designed by first-year engineering students.

We designed the mathematical analysis to give students an idea of the types of important questions they could answer using basic differential equations. In the semester-end evaluations, a number of the calculus students specifically mentioned that they appreciated seeing this application of the material. We note that the parameter values we chose for this project were reasonably consistent with the machine our students built, although the water permeability constant is about 10 times actual value; the instructor should feel free to experiment with other values as he or she chooses.

The graphs in the solution to this project were produced using Mathematica. The slope field package that generated the graphs is freely available; contact the authors for a copy.

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Ethan Berkove is Assistant Professor of Mathematics at Lafayette College. Ethan studied mathematics and Japanese as an undergraduate at the University of Michigan, then shifted over to mathematics for his Ph.D. at the University of Wisconsin, Madison. His research field is algebraic topology, but his interests include applications of mathematics and mathematical recreations.

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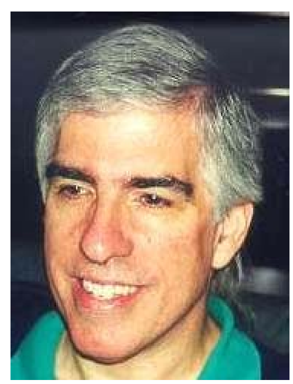

Scott Moor is Assistant Professor of Chemical Engineering at Lafayette College. He received B.S. and M.S. degrees in Chemical Engineering from M.I.T. After over a decade in industry, he returned to academia at the University of California at Berkeley, where he received a Ph.D. in Chemical Engineering and an M.A. in Statistics. He is a registered Professional Chemical Engineer in the State of California. His research interests include the development of materials for science, mathematics and engineering education, applied statistics, and visualization of spray and particle system dynamics.