Computational Mass Transfer Modeling of Flow through a Photocatalytic Oxygen Generator

by

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ABSTRACT

A self-contained, portable oxygen generator would be extraordinarily useful across a broad spectrum of industries. Both safety and energy-efficiency could be enhanced tremendously in fields such as coal mining, commercial airlines, and aerospace.

A novel device is proposed which employs a photocatalytic process to produce oxygen from water. Oxygen is generated through a reaction that utilizes the interaction between an ultraviolet light and a titanium dioxide thin film to catalyze the decomposition of water into dissolved oxygen and hydrogen ions. The dissolved oxygen is then transported into a volume of gaseous nitrogen through a diffusion process. A pair of parallel microfluidic channels is employed to expedite the oxygen transport by reducing diffusion lengths, and thereby diffusion times.

In the following, a computational simulation of the convection-diffusion relation was developed in order to characterize the performance of the proposed microfluidic chip. Specifically, the time to reach airflow steady state is determined for several geometries. Information from fluid dynamic modeling was then used to estimate the system performance characteristics such as power requirements, output oxygen concentration, output flow rate, and rise time of the proposed oxygen generator in a variety of applications.

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Chapter I

Introduction

Coal-based power generation provides over half the energy produced in the United States, and 5.5 billion metric tons of coal were produced globally in 2006. Although accident rates have decreased steadily in the United States, coal mining remains a dangerous industry. Structural inadequacies place miners at risk of roof collapse, while release of methane gas, spontaneous combustion of coal, mining-induced seismic activity, and flooding pose additional threats. Last year alone 33 miners were killed in the United States and fatalities in China were estimated at a staggering 3,800.

Since 2006, more than 50,000 self-contained self-rescue units have been distributed annually and all underground coal miners in the United States have received training regarding their use. These products are filter-type respirators that protect against carbon monoxide, and function for 20 to 60 minutes. Consequently, they are of no practical use for miners trapped in collapsed shafts for periods longer than one hour or in closed spaces with insufficient oxygen supplies.

Oxygen storage systems exist, but are uncommon and largely impractical due to capacity, size, cost, and safety constraints. An open circuit self-contained self-rescuer is commercially available that provides its own supply of compressed oxygen, but it is capable of only one hour of life support, in most cases an insufficient period to rescue a trapped miner. By contrast, the most commonly used closed-circuit breathing apparatus, the BioPak 240S, can sustain a user for up to four hours. The trade-off is that the BioPak weights roughly 35 pounds and costs approximately $5,500. Additionally, both open and closed-circuit systems store compressed oxygen, which creates an explosion risk.

A novel design for a self-contained life support system is proposed in (6) whereby oxygen is generated from water stored in a portable pack through a photocatalytic process. With an appropriate power supply, the proposed device has the potential to provide 12 hours or more of breathable oxygen.
without the risks of explosion inherent in compressed oxygen supplies. Preliminary analyses made in (2) estimate the total system mass at 7kg, plus the mass of the power supply.

The same technology could be easily applied to benefit a variety of industries. A safe, lightweight, portable oxygen generation device would be of tremendous interest to the commercial airline industry. The decrease in oxygen density at high elevations limits the altitude at which passengers can safely fly. Jet engines generally operate more efficiently at high altitudes because the outside temperature is lower, and a lower temperature “cold reservoir” improves the efficiency of the Brayton heat-engine cycle that these engines perform. Drag forces are also reduced at high altitudes as the air density decreases, further improving efficiency. Employing the proposed device to pump oxygen into an airplane cabin could allow planes to fly at higher elevations. The rising price of fuel only accelerates the drive of the airline industry to reduce costs by improving efficiencies.

Additionally, it is easy to imagine the utility of such a device in the field of aerospace engineering. The space shuttle already employs electrolysis reactions to produce oxygen for the shuttle crew. Plentiful solar energy, particularly in the UV spectrum normally blocked by the earth’s ozone layer, could readily drive a photon-catalyzed reaction. This oxygen generation technology could then be utilized on the space shuttle, as well as upcoming bases on the moon or Mars.

In the following, a computational design tool is developed which models the diffusive oxygen transfer through the fluid elements of the proposed device. This model is then used to predict the time required for the device to deliver target quantities and concentrations of oxygen. Finally, fluid dynamic modeling was used to estimate system performance characteristics such as power requirements, output oxygen concentration and output flow rate of the proposed oxygen generator.
Core Technologies

The proposed design of a self-contained, portable oxygen generator hinges on two fundamental technologies. The first is photocatalytic oxygen production, the use of a thin-film transition metal to generate dissolved oxygen from water in the presence of an ultraviolet light. This method of obtaining oxygen is attractive because the production rate is highly controllable, and because it obviates the need for bulky and potentially dangerous pressurized oxygen storage chambers. The second is multi-layer soft-lithography microfluidics. Following the production of dissolved oxygen, a pair of parallel microfluidic channels is employed in order to transport the oxygen into a stream of air. The use of microfluidics is intended to overcome slow diffusion rates by conducting diffusive mass transfer on an extremely small length scale. The relevant physics and manufacturing techniques involved in these two technologies are outlined in the following sections.

Photolytic Chemistry

Photocatalytic reactions are simply a class of chemical reactions that are driven by energy derived from light. Photolysis represents a subset of photocatalytic reactions in which a chemical compound is broken down by light energy. The thin film considered here emulates a portion of a common biological photolytic process, photosynthesis. Specifically, it is modeled on Photo System II, wherein plants extract oxygen molecules directly from water.  

Photo System II involves two distinct mechanisms: the photoactive pigment chlorophyll absorbs light, and a transition metal oxide cluster of manganese uses this energy to induce a charge-separation that drives the photolysis of water. A robust semi-conducting metal oxide film described in (8) is capable of acting both as the photo-absorption element and the site of the charge separation required for the photolysis of water. The film is composed of titanium dioxide in anatase form. The TiO$_2$ film generates oxygen through the following steps:
1) UV light is absorbed by the TiO$_2$ film, and the light energy, $hv$, is transferred to electrons within the TiO$_2$. This energy allows the electrons to move freely within the solid, leaving behind positively charged electron “holes”, or electron vacancies within the crystal.

2) Holes drive the conversion of water into a hydrogen peroxide intermediate.

3) Hydrogen peroxide spontaneously disproportionates into dissolved oxygen and water.

4) An external applied voltage conducts free electrons away from the film in order to prevent a back reaction of these electrons with the hydrogen peroxide intermediate.

The balanced chemical reactions are thus given by Eqns. 1.1 and 1.2.

Photolysis:

$$2H_2O + hv \xrightarrow{\text{TiO}_2(\text{anatase})} H_2O_2 + 2H^+ + 2e^- \quad (1.1)$$

Disproportionation:

$$H_2O_2 \rightarrow O_2(aq) + H_2O \quad (1.2)$$

Figure 1.1 provides an illustration of the TiO$_2$ - catalyzed oxygen production process.
The accumulation of \( H^+ \) ions can be avoided by adding a buffer such as bicarbonate to the water, so that carbonic acid is produced\(^9\). This reaction is shown in Eqn. 1.3.

\[
H^+ + HCO_3^- \rightarrow H_2CO_3
\]  

Titanium dioxide ceramic is significantly more durable than Photo System II pigments, and it can be manufactured to have nano-scale pores in order to provide a high reaction surface area. It is selectively excited by a narrow UV bandwidth, which limits the waste of radiation energy through transmission or heat generation.\(^8\) Additionally, the oxygen yield of the reaction can be precisely controlled by adjusting the amount of UV energy input, \( hv \), making feedback control possible.

### Photolytic Film Manufacture, Validation, and Performance

A \( \text{TiO}_2 \) photocatalytic layer and an ITO conductive layer can be coated onto a glass substrate as thin films through direct current reactive magnetron sputtering as in (10)\(^10\). Sputtering processes rely on an energetic plasma of inert gas such as argon to collide with a target and to eject target material onto a substrate\(^11\), as shown in Fig. 1.2.

![Argon ions colliding with a target and ejecting material onto a substrate](image)

**Fig. 1.2:** Argon atoms ejecting metal onto a substrate in a magnetron sputtering process

For example, an ITO target would be used to produce the conductive layer in the proposed photocatalytic chip. Metal oxide layers are typically formed through the use of metal target and a
sputtering chamber filled with oxygen and an inert gas. A TiO$_2$ layer can thus be produced by using a pure titanium target, and allowing the metal to oxidize as it is deposited onto a substrate. Fig. 1.3 shows a two-layer chip which could be easily manufactured through DC reactive magnetron sputtering.

![TiO$_2$ Film](image)

**Fig. 1.3:** Photolytic chip manufactured in layers through a deposition process

In a proof-of-concept experiment described in (7), UV light filtered to a wavelength of 365nm with an intensity of 88.1 mW/cm$^2$ was delivered to a photolytic surface submerged in buffered water. A bias potential of 1 Volt was also applied to mitigate the back reaction. In order to test the efficacy of oxygen generation, the bias potential was cycled on and off while the water’s gas concentration was monitored by an electrode gas sensor. The results are shown in Fig. 1.4

![Graph](image)

**Fig. 1.4:** The efficacy of a photocatalytic film to produce oxygen in the presence of both an ultraviolet light and a bias voltage is demonstrated.
The data confirms that oxygen production is dependent upon both a UV light source to activate the TiO$_2$ photocatalyst, and a bias voltage to limit a back-reaction.

More recent experiments by Gilbert et al. have achieved oxygen production rates of $1.0 \times 10^{-8}$ mol/sec with a photolytic area of 9.6 cm$^2$. The photolytic film was illuminated by a 365nm wavelength UV source with an intensity of 36mW/cm$^2$ ($360$ W/m$^2$). The oxygen production rate per unit area, $J_{O_2}$, is calculated in Eqn. 1.4. This value of the oxygen flux across the film surface will be utilized in all subsequent analysis.

$$
J_{O_2} = \frac{1.0 \times 10^{-8} \text{ mol/sec}}{9.6 \text{ cm}^2} = 1.085 \times 10^{-6} \text{ mol/m}^2 \text{ sec} \tag{1.4}
$$

Improving photocatalytic efficiency is a key challenge that must be overcome in order for the propose device to be realized. The present generation of films requires power on the order of kilowatts to support physiological oxygen consumption rates of around 250mL/min. Fortunately, a number of strategies have been proposed to increase the oxygen production rate. These include acid pretreatment of photocatalysts to activate the surface wettability of the oxide, variations in film thickness, vacuum application of film coatings, changes in substrate material, as well as changing chemical composition, crystal composition, and defect states of the metal oxide.

*Photolytic Chemistry*

From a fluid dynamics perspective, the previous section can be condensed into the statement that a constant flux of oxygen, $J_{O_2}$, is released from a film of a fixed area into a volume of water. This situation is shown in Fig. 1.5.
In order to demonstrate the need for a microfluidic network to expedite oxygen transport, we consider a volume of water with a height $H_{\text{water}} = 10\text{cm}$. The “nominal diffusion time”, $t_D$, an estimate of the time it takes to diffuse over a given distance, is given by Eqn. 1.5:

$$t_D = \frac{L^2}{D}$$

where $L$ represents the characteristic diffusion distance considered and $D$ is the diffusion coefficient, a measure of the speed of diffusion within a material. The diffusion coefficient of oxygen in water is equal to $2.1 \times 10^{-9} \text{ m}^2/\text{s}$ at room temperature. Using Eqn. 1.5, the nominal diffusion time for oxygen to migrate 10cm is roughly 4,762,000 seconds, about 55 days. Such a large time scale is unacceptable for most practical applications. By contrast, the nominal diffusion time is merely 0.05 seconds across a diffusion length of 10 microns. Clearly this is a much more acceptable length of time to expect a person to forgo breathing while their oxygen generator starts up.

Multi-layer microfluidic channels are employed to limit diffusion distances to micron scales. Figure 1.6 illustrates a pair of microfluidic channels which can be used to transport dissolved oxygen into nitrogen or oxygen-deficient air.
Fig. 1.6: Dissolved oxygen diffuses through a PDMS membrane, and into a channel of flowing air. Oxygen-rich air is carried out of the upper channel through convection.

Dissolved oxygen produced at the surface of the TiO$_2$ film diffuses through the water, down a concentration gradient, and away from the film. Diffusion then drives the oxygen across a silicon rubber (PDMS) membrane and into an oxygen-poor air solution. Air flows through the top channel so that oxygen is continuously driven from the water into a stream of oxygen-deficient air. Because a quantity of water is broken down in the photolysis reaction, a low fluid velocity is required in the bottom channel to replenish the depleted water. However, for the oxygen production rates cited above from (10), the required water velocity is sufficiently low that it can be considered stationary in modeling mass transfer.

Figure 1.7a shows a cross-section of one such fabricated microchannel array with a height to width ratio of 1:1, while Fig. 1.7b includes a top view of the same device. Much wider channels are visible at the inlet of the microchannel array, and channels with height to width ratios of 1:100 can be easily manufactured. This is significant, because wider channels utilize a larger fraction of available photolytic surface area, resulting in increased oxygen production.
Photolytic Film Manufacture, Validation, and Performance

The channels pictured above are made of polydimethylsiloxane (PDMS), a type of silicon rubber which was selected for its ease of rapid fabrication, high permeability to oxygen, non-toxicity, and low cost. Arrays of microchannels are produced through multi-layer soft-lithography, a process in which micro-scale features are formed from elastomers using stamps created by a conventional photolithography procedure. Multi-layer refers to the production and bonding together of several elastomeric layers to form integrated, stacked devices. A schematic of the soft-lithography process used to manufacture the proposed parallel channel chip is shown in Fig. 1.8
Fig. 1.8: Schematic of multi-layer soft lithography fabrication steps

Fig. 1.8A shows a mold created through conventional photolithography, and B illustrates the same mold after a layer of PDMS has been spin-coated onto it. The PDMS is then baked at a temperature of 80°C, until it solidifies sufficiently through cross-linking to be removed from the mold (step C). Steps A through C are repeated to make a second PDMS molding. In Fig. 1.8 D, the second molding is aligned above the first, and the multi-layered device is baked a second time to cross-link the PDMS, bonding the two layers together. Finally, Fig. 1.8E shows a PDMS molding bonded to a substrate through a plasma oxidation process. Here, the substrate is the photolytic TiO₂ film discussed earlier.
Chapter 2: Mass Transport Physics

The following sections develop analytical and numerical schemes for predicting the oxygen transport through the proposed device, and the results are used to predict the performance characteristics of such an oxygen generation system.

Mass Transport Mechanisms

Two physical processes are involved in the transport of oxygen throughout the proposed device: diffusion and convection. Diffusion is the movement of particles from an area of high concentration to an area of low concentration, which arises from the random motion of particles within a system. By contrast, convective mass transfer is the result of bulk motion of a fluid.

Although diffusive mass transport occurs in solids, liquids and gases, the mechanisms involved vary. In a gas, particles can travel distances that are very large compared to the particle size before being scattered by collisions with other particles, and diffusion can be understood as the random motion predicted by kinetic molecular theory of gases. In condensed states (solids and liquids) diffusion occurs in a process through which atoms or molecules are able to exchange positions with neighboring particles due to thermal fluctuations. 13

At the macroscopic scale, however, the mathematical description of diffusion is similar for all states of matter. Random molecular motion results in an average motion of diffusing molecules from regions of higher concentration to regions of lower concentration. This behavior is characterized in 1-dimension by Fick’s First Law, Eqn. 2.1

\[ J_A = -D_{AB} \frac{\partial c_A}{\partial x} \] (2.1)
where \( J_A \) is the flux of solute A in a binary solution of A and B, \( C_A \) is the concentration of this solute, and \( D_{AB} \) is the constant of proportionality known as the diffusion coefficient. The diffusion coefficient is a measure of how quickly diffusion occurs, and is a function of temperature, pressure, material and state of the solute and solvent. The negative sign indicates that mass flows in the direction of decreasing concentration gradient. Fick’s First law is analogous to Fourier’s law of heat conduction, which states that heat flux is proportional to temperature gradient, Eqn. 2.2

\[
q = -k \frac{\partial T}{\partial x}
\]  

(2.2)

Thus the diffusion coefficient, \( D_{AB} \), plays the same role as the thermal conductivity, \( k \), plays in Fourier’s law.

By combining Fick’s First law with an equation of mass conservation, a time-dependent diffusion equation can be developed. In 1-dimension, mass conservation provides that,

\[
\frac{\partial C_A}{\partial t} = \frac{\text{solute entering per unit time}}{\text{volume}} - \frac{\text{solute leaving per unit time}}{\text{volume}} = \frac{A_j_1 - A_j_2}{A \Delta x} = \frac{j_1 - j_2}{\Delta x}
\]  

(2.3)

In the limit as \( \Delta x \to 0 \),

\[
\frac{\partial C_A}{\partial t} = - \frac{\partial j_A}{\partial x}
\]  

(2.4)

Substituting this result into Fick’s First Law,

\[
\frac{\partial C_A}{\partial t} = - \frac{\partial j_A}{\partial x} = - \frac{\partial}{\partial x} (-D_{AB} \frac{\partial C_A}{\partial x}) = D \frac{\partial^2 C_A}{\partial x^2}
\]  

(2.5)

This relationship is known as Fick’s Second law, and can be applied to unsteady diffusion problems. In one dimension, an analytical solution to this partial differential equation requires knowledge of the initial concentration everywhere within the region of interest, and two boundary conditions. The boundary conditions describe the concentration (or some function of it) at the edges of the region of interest as a function of time. Figure 2.1 illustrates the proposed oxygen generation chip labeled with appropriate boundary conditions.
Fig. 2.1: A pair of gas exchanging channels are shown with all boundary conditions labeled. The oxygen concentration was then solved for explicitly in space and time.

The simplest possible initial condition is one in which the region of interest is initially at equilibrium, and so the concentration is everywhere uniform. The two most commonly encountered boundary conditions involve either a constant concentration at each boundary, or a constant flux of solute across each boundary. Physically, a constant concentration boundary condition occurs when two solutions are placed in contact with each other, and one solution contains enough material that its concentration does not change appreciably over the time scale of interest. This situation is analogous to a constant temperature reservoir in heat transfer problems. Constant flux boundary conditions most often arise when a reaction takes place at one boundary, yielding a constant quantity of solute per unit area per unit time. The oxygen solute produced by splitting water molecules at the surface of a photocatalytic TiO₂ film provides an example of a constant flux boundary condition. Table 2.2 lists examples of constant flux and constant concentration boundary conditions.
Each of these problems can be solved analytically, and used to check the accuracy of the presented numerical model, if the model boundary conditions are modified appropriately. The solution for a constant concentration problem where the initial concentration in the region of interest is everywhere equal to zero, the concentration at $x=0$ is $C_s$, and the concentration at $x=\infty$ is zero, is given below by Eqn. 2.6.

$$C(x, t) = C_s [1 - \text{erf} \left( \frac{x}{\sqrt{D t}} \right)]$$

(2.6)

Where $t$ represents the time in seconds, $D$ represents the diffusion coefficient, and erf() signifies the error function, which is the integral of the normal distribution, and is defined in Eqn. 2.7

$$
\text{erf}(a) = \frac{2}{\sqrt{\pi}} \int_0^a e^{-t^2} \, dt.
$$

(2.7)

If the initial concentration were some constant $C=C_0$ instead of zero, by superposition, the new concentration distribution is:

$$C(x, t) = C_0 + (C_s - C_0)[1 - \text{erf} \left( \frac{x}{\sqrt{D t}} \right)]$$

(2.8)

The solution is plotted in Figure 2.3 for various times.
Fig. 2.3: The solution to a constant flux diffusion problem is plotted for $t_3 > t_2 > t_1$.

The solution for a constant flux problem where the initial concentration in the region of interest is everywhere equal to $C_o$, the flux at $x=L$ is equal to $J_o$ and the flux at $x=0$ is equal zero, is given by:

$$C = C_o + \frac{J_o L}{D} \left( \frac{Dt}{L^2} + \frac{3x^2 - L^2}{6L^2} - \frac{2}{\pi^2} \sum_{n=1}^{\infty} \frac{(-1)^n}{n^2} e^{-Dn^2(\frac{x}{L})^2} \cos \left( \frac{n\pi x}{L} \right) \right)$$  \hspace{1cm} (2.8)

The behavior of this function is illustrated in Fig. 2.4

Fig. 2.4: The behavior of a one-dimensional constant flux diffusion problem is shown. Note the direction of increasing time.
Naturally, the equations and solutions presented can be applied to higher-dimensional problems.

Generalized in three dimensions, Fick’s First law is given simply by Eqn. 2.9

\[ J_A = -D_{AB} \nabla C_A \]  

(2.9)

And Fick’s second law is given by:

\[ \frac{\partial C_A}{\partial t} = D \nabla^2 C_A \]  

(2.10)

**Convection**

While diffusive mass transport describes the motion of a solute relative to a solvent, solute particles can also be transported through net motion of the solute. This bulk motion of solute and solvent particles in response to an applied force is referred to as convection. In the device presented, nitrogen flows into a micro-channel, increases its oxygen concentration through contact with an oxygen-rich membrane, and then the nitrogen-air solution flows out. In order to model this process, the convective motion of these gases must be characterized.

The Navier-Stokes equation, Eqn. 2.11, describes the linear momentum of an incompressible, Newtonian fluid undergoing fully-developed laminar flow.

\[ \rho \frac{D\vec{V}}{Dt} = -\nabla P + \rho \vec{g} + \mu \nabla^2 \vec{V} \]  

(2.11)

In the above equation, \( \rho \) represents the fluid density, \( \vec{V} \) represents the fluid velocity, \( P \) represents the pressure field, and \( \vec{g} \) is the gravitational field. The character \( \mu \) represents the viscosity, a material property that provides a measure of a fluid’s frictional resistance to flow. The term *Newtonian fluid* denotes that the strain rate of a fluid is linearly proportional to the applied viscous stress, and \( \mu \) is the constant of proportionality. Air, water, nitrogen, oxygen, and most commonly-encountered gases and liquids act as Newtonian fluids.

The terms on the right hand side of the Navier-Stokes equation represent the net force per unit volume acting on a fluid particle, as shown below:
The left-hand term of Eqn. 2.12 is the change in momentum per unit time of a fluid volume, and thus the Navier-Stokes equation is simply a statement of Newton’s second law for fluids. The equation is a non-linear, second-order, partial differential equation, and because of its non-linear nature, general solutions do not exist. Nonetheless, solutions can be obtained for special cases where non-linear terms vanish.

The micro-fluidic device proposed here has the following characteristics:

- Air is driven through the micro-channel array by a pressure differential created by a pump.

- The pressure gradient must be the same at every position along the direction of flow in order to keep the fluid moving at the same average velocity through the channel.

- The height of the channels is sufficiently small (on the order of 10-100 microns) that the effect of gravity on fluid flow can be neglected.

- The height of the air channel << the width of the channel, such that edge effects at the sides of the channel can be ignored and the channel can be examined as 2-dimensional.

- "No-slip" boundary conditions in which the velocity is zero at the top and bottom surfaces of the device are assumed.

This type of pressure-driven flow is called plane Poiseuille flow, and is a special case in which an analytical solution can be obtained from the Navier-Stokes equation. Applying these parameters, the velocity distribution as a function of channel height above a centerline, $y$, is given by Eqn. 2.13

$$V_x(y) = \frac{a^2}{2\mu} \frac{\partial p}{\partial x} \left[ \frac{y^2}{a^2} - 1 \right]$$
The distribution is parabolic with a maximum velocity occurring at the centerline of the channel, $y=0$. This maximum velocity is given by:

$$V_{\text{maximum}} = -\frac{\partial P}{\partial x} \frac{a^2}{2\mu} \quad (2.14)$$

By integrating the velocity distribution over the cross-sectional area of the channel, the volumetric flow rate can be found, as shown in Eqn. 2.13. The negative sign enters the equation because the flow is in the direction of decreasing pressure.

$$Q = \int_{-a}^{a} V_x dA = \int_{-a}^{a} V_x b dy = \frac{\partial P}{\partial x} \frac{a^3b}{2\mu} \int_{-a}^{a} \left( \frac{y^2}{a^2} - 1 \right) dy = -\frac{\partial P}{\partial x} \frac{a^3b}{3\mu} = -\frac{\partial P}{\partial x} \frac{H^2b}{24\mu} \quad (2.15)$$

The average fluid velocity $V$ is the flow rate $Q$ per unit cross-sectional area $b*H$. Therefore, by dividing 2.15 and 2.14 it is clear that the $V=\frac{3}{4}V_{\text{maximum}}$. Finally, this tells us that the pressure required to drive the flow is equal to:

$$\frac{\partial P}{\partial x} = \frac{12 V \mu}{H^2} \quad (2.16)$$

It was mentioned earlier that the Navier-Stokes equation applies to incompressible fluids. Although it was derived from a description of incompressible fluids, the equation describes the motion of compressible fluids with reasonable accuracy for flows with Mach numbers below 0.3. Thus, the model is suitable for a low-speed microfluidic model. This means we are able to combine diffusion physics and the Navier-Stokes description of convective mass transfer to obtain Eqn. 2.17. It is assumed here that a bulk velocity $V_x$ points in a direction along the channel length.

$$\frac{\partial c}{\partial t} = D \left( \frac{\partial^2 c}{\partial x^2} + \frac{\partial^2 c}{\partial y^2} \right) - V_x \frac{\partial c}{\partial x} \quad (2.17)$$
Chapter 3: Developing a Numerical Model

In order to design an effective oxygen delivery system, it is crucial to characterize the device output concentration and volume as a function of time. Before steady-state is reached, obtaining values for these two parameters requires knowledge of the oxygen concentration and fluid velocity everywhere within the micro-channel. Thus, a solution to the transient convection-diffusion equation is required. A computational method for solving for the oxygen distribution within the proposed micro-fluidic device is developed in the following section.

Finite Difference Model

A finite-difference model was employed to calculate an approximate solution to the convection-diffusion equation. The two main features characterize finite difference methods:

1) A fluid continuum is divided into an array of nodes.

2) Derivatives are approximated between nodes using the Taylor series.

Fig. 3.1: Nodes mapped over a gas-exchanging channel
Fig. 3.1 illustrates an array of nodes mapped over a microfluidic channel. A value is stored at each point representing the oxygen concentration as a function of time. As the spacing between nodes becomes sufficiently small, there is little variation in concentration between neighboring points, and the node concentration becomes a good estimate for the average concentration within the dashed volume surrounding it. These average concentrations are used to determine the fluid outflow characteristics.

**Derivatives and Truncation Error**

Taylor’s theorem states that any smooth function can be approximated as a polynomial, and it provides a procedure to predict the value of a function at one point based on the value of the function and its derivatives at another nearby point. The value of a function, \( f \), at a step size \( h \) away from a known point \( x_i \) is given by Eqn. 3.1

\[
\begin{align*}
  f(x_{i+1}) &= f(x_i) + f'(x_i)h + \frac{f''(x_i)}{2!} h^2 + \frac{f'''(x_i)}{3!} h^3 + \frac{f^{(4)}(x_i)}{4!} h^4 + \cdots + \sum_{n=1}^{\infty} \frac{f^{(n)}(x_i)}{n!} h^n \\
  &= R_n
\end{align*}
\] (3.1)

Any numerical approximation of an exact mathematical procedure results in an introduction of inaccuracy known as truncation error. The remainder term, \( R_n \), is included to account for all terms larger than \( n+1 \) in an infinite series, and is equal to the truncation error of an \( n \)th order Taylor series approximation. In computer science, the remainder term is frequently expressed as in Eqn. 3.2.

\[
R_n = O(h^{n+1})
\] (3.2)

where the term \( O(h^{n+1}) \) signifies that the truncation error is on the order of \( h^{n+1} \). While this formulation provides no information about the magnitude of the error, it is useful in comparing the relative error of different numerical representations. For example, if the error is \( O(h^1) \), doubling the step size will double the error, while if the truncation error is \( O(h^2) \), doubling the step size will quadruple the error.¹⁶
Alternately, by rearranging the Taylor series, it is possible to obtain the derivative of a function at one point as a function of its values and derivatives at nearby points. Equation 3.1 can be rewritten as:

\[
f'(x_i) = \frac{f(x_{i+1}) - f(x_i)}{h} - \frac{f''(x_i)}{2} h + O(h^2)
\]  

(3.3)

When this expression is truncated by discarding the second and higher-order derivative terms, the result is called the forward-difference approximation. It is given this nomenclature because the expression for the derivative at the point \(x_i\) involves only values of the function at the point \(x_i\) itself and at \(x_{i+1}\), a point forward of \(x_i\).

Further manipulation of this equation yields formulas for obtaining higher derivatives. For example, the second derivative at point \(x_i\) can be found by:

\[
f''(x_i) = \frac{f(x_{i+1}) - 2f(x_i) + f(x_{i-1})}{h^2}
\]  

(3.4)

Eqn. 3.4, by contrast, is denoted as a centered-difference formula because the function values at \(x_{i+1}\) and \(x_{i-1}\) both factor into the value of the derivative at point \(x_i\). Centered-difference schemes have the advantage of being more accurate than forward (or backward) difference schemes, with \(O(h^2)\) errors or better. Accordingly, the schemes are slightly more computationally intensive, and so can slow a program down when executed from within a loop that undergoes many millions of cycles.

**The Discretization of Diffusion Physics**

A two-dimensional finite difference representation of the convection-diffusion equation is given by Eqn. 3.5. This formulation is centered in space and forward in time, and \(C\) describes the amount of solute at a particular set of temporal and spatial coordinates. Time (t) coordinates are represented by the index \(i\), coordinates along the height of the channel (y) are represented by the index \(j\), and coordinates along the length of the channel (x) are given by the index \(k\). \(i, j,\) and \(k\) are then positive.
integers such that \( t = i \Delta t, x = j \Delta y, \) and \( y = jk \Delta x, \) where the step size is represented by \( \Delta \) followed by the respective coordinate. It is assumed that the bulk fluid velocity \( V_x \) is everywhere parallel to the channel, and so there is never a \( y \)-component of the convective fluid velocity.

\[
\frac{C_{i+1,j,k} - C_{i,j,k}}{\Delta t} = D \left( \frac{C_{i+1,j,k} - 2C_{i,j,k} + C_{i-1,j,k}}{\Delta y^2} + \frac{C_{i,j+1,k} - 2C_{i,j,k} + C_{i,j-1,k}}{\Delta x^2} \right) - V_x \left( \frac{C_{i,j,k+1} - C_{i,j,k-1}}{2\Delta x} \right)
\]  
(3.5)

Solving Eqn. 3.5 for \( C_{i+1,j,k} \), the value of the concentration at point \( (j,k) \) at the next time step, \( t+1 \), yields Eqn. 3.6

\[
C_{i+1,j,k} = C_{i,j,k} + D\Delta t \left( \frac{C_{i+1,j,k} - 2C_{i,j,k} + C_{i-1,j,k}}{\Delta y^2} + \frac{C_{i,j+1,k} - 2C_{i,j,k} + C_{i,j-1,k}}{\Delta x^2} \right) - V_x \Delta t \frac{C_{i,j,k+1} - C_{i,j,k-1}}{2\Delta x}
\]  
(3.6)

Once the correct boundary conditions are applied, the solute concentration throughout the microchannels at a desired time can be found by repeatedly solving this equation for all spatial values at each time step, and then looping through a series of time steps. To produce a constant flux boundary condition, an extra row (or column) of nodes is added along the border of interest. These nodes do not represent physical points and are merely a vehicle for enforcing the boundary conditions. For example, to set a constant flux normal to the \( y=0 \) boundary, the value of each unphysical node is given by:

\[
C_{i,0,k} = C_{i,1,k} + \frac{\Delta y}{\Delta x} j_{02}
\]  
(3.7)

The above can also be applied to impermeable walls because these are simply a degenerate case of a constant flux where \( J_{02} = 0 \).

**Stability Conditions**

As discussed earlier, the error in a finite difference scheme is prescribed by the step size chosen in calculating temporal and spatial derivatives. This step size also determines the stability of the numerical scheme. Understanding the stability criteria of a model is critical because stability is required for the model to correctly predict the physical behavior of a system. For comparison, Fig. 3.2 provides an example of an unstable output of the diffusion-convection model.
Fig. 3.2: Plot of an unstable solution to the discretized diffusion-convection equations. Note the steep changes in slope and negative concentration values.

A number of general methods may be used to determine stability criteria, most notably the Fourier stability analysis described in (17). For the model considered here, however, the most straightforward approach is insuring that the concentration is everywhere always non-negative. This approach utilizes the fact that a negative solute concentration at a point is unphysical and attains the same stability criteria as can be obtained through a more rigorous Fourier analysis. First, Eqn. 2.17 is rearranged so that the concentration at each point in space is isolated and has a constant coefficient.

\[
C_{i+1,j,k} = C_{i,j,k} \left[ 1 - \frac{2 D \Delta t}{\Delta x^2} - \frac{2 D \Delta t}{\Delta y^2} \right] + C_{i,j,k+1} \left[ \frac{D \Delta t}{\Delta x^2} - \frac{V_x \Delta t}{2 \Delta x} \right] + C_{i,j,k-1} \left[ \frac{D \Delta t}{\Delta x^2} + \frac{V_x \Delta t}{2 \Delta x} \right] + C_{i,j+1,k} \left[ \frac{D \Delta t}{\Delta y^2} \right] + C_{i,j-1,k} \left[ \frac{D \Delta t}{\Delta y^2} \right]
\]

Equation (3.8)

The requirement that \(C_{i+1,j,k}\) must always be positive dictates that coefficients 1 through 5 must also be positive. This requirement is always met for coefficients 4 and 5, as well as coefficient 3 because
it represents the sum of two positive values. Enforcing this condition on coefficient 1 yields the stability requirement shown in Eqn. 3.9

\[ \Delta t \leq \frac{1}{2D \left( \frac{1}{\Delta x^2} + \frac{1}{\Delta y^2} \right)} \]  

(3.9)

Additionally, a positive value for coefficient 2 is attained when the following criterion is met:

\[ \Delta x \leq \frac{2D}{V_x} \]  

(3.10)

These two criteria set the maximum spacing between nodes in a finite difference representation of the diffusion process considered here. Both equations 3.9 and 3.10 depend on the diffusion coefficient, a material property, and so the maximum allowed spacing changes within different materials. Table 3.3 presents the diffusion coefficients of water, PDMS, pure nitrogen gas and air.

<table>
<thead>
<tr>
<th>Material</th>
<th>Diffusion Coefficient [m²/s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>(2.1 \times 10^{-9})</td>
</tr>
<tr>
<td>PDMS</td>
<td>(6.0 \times 10^{-9})</td>
</tr>
<tr>
<td>N₂</td>
<td>(2.0 \times 10^{-5})</td>
</tr>
<tr>
<td>Air</td>
<td>(2.1 \times 10^{-5})</td>
</tr>
</tbody>
</table>

Table 3.3: Diffusion coefficients of oxygen in relevant materials

For simplicity, the computational model developed employs equal grid spacing across all material regions. Therefore, to guarantee that Eqn. 3.8 is satisfied, the largest diffusion coefficient, that of air, should be used. Because the air channel is the only material region with a nonzero velocity, only the diffusion coefficient of air (or nitrogen as is appropriate) needs to be considered to satisfy Eqn. 3.9.

While this grid spacing ensures stability, it is important to note that truncation errors are still present, as in any numerical model, and must be evaluated through alternate processes. Decreasing the grid
spacing beyond the stability criteria decreases the truncation error at the cost of increasing computation time.

Chapter 4: Model Validation and Results

Validation

Because calculating error in numerical models is generally a very difficult task, it is crucial to develop tests to gauge the accuracy of a numerical model of a physical problem. One strategy is to test the model by modifying the boundary conditions such that the problem is reduced to one that can be solved analytically. A second is to vary the size of the grid spacing, to verify that the system converges to a stable solution as the grid size is reduced. Finally, all solute mass can be totaled within the model to confirm that the model is conservative - that no mass is created or destroyed.

The first strategy employed was to decouple the different material regions by adding an impermeable “wall” between the water chamber and PDMS membrane. The result was then compared to the constant flux problem introduced in Section 2. Fig. 4.1 plots for a channel cross-section the analytical and numerical oxygen concentrations as a function of height. The strong agreement of the numerical and analytical curves suggests that diffusion within the water chamber is modeled accurately, however it gives no information about the boundaries.
Fig 4.1: Comparison of numerical and analytical solutions along a cross-section of a water channel. The dashed lines represent the analytical solution, while the solid lines represent the numerical solution. Concentrations are shown at three different times labeled as t=0.0005 sec, t=0.005 sec, and t=0.05 sec.

Figure 4.2 illustrates that the numerical solution converges to the analytical solution as the number of nodes, N, increases. This behavior further supports the accuracy of the numerical model.
Fig 4.2: The three solid lines indicate numerical solutions found using 5 nodes, 10 nodes, and 50 nodes in the y-direction, while the dashed line is the analytical solution to the constant flux problem posed in Eqn. 2.8.

Finally, Figures 4.3 a-c provide a graphical representation of the oxygen concentration distribution throughout the device the water chamber, PDMS membrane, and air channel. Similar plots can be easily generated for any dimensions and time scales. The following plots use an average velocity of 1 micron/sec, after diffusion has taken place for 5 microseconds. The heights of the water channel, PDMS membrane, and air channel are all equal to 10 microns in the graphs.
Fig. 4.3a: Concentrations in water chamber after 5 microseconds of diffusion

Fig. 4.3b: Concentrations in PDMS membrane after 5 microseconds of diffusion
Although graphics can be helpful for visualizing fluid behavior, the real benefit of this design tool is the ability to track the behavior of key system performance parameters over a range of variable inputs. Figures 4.4 and 4.5 illustrate how the time to reach a desired steady state concentration varies as a function of device height. The air channel height, water channel height, and PDMS membrane are all scaled by a constant factor and are equal to the height listed in the graphs, though the model also allows a user to manipulate these variables independently. Here \( V_{x\, \text{avg}} = 1 \text{micron/sec}, J_0 = 10^5 \text{mol/sec} \), and \( L = 1 \text{ cm} \).
Fig. 4.4: The time to reach a desired oxygen concentration is plotted vs. log(device height).

Fig. 4.5: The time to reach a desired oxygen concentration is plotted against the device height for three different desired volume fraction concentrations: C=21%, 40%, and 60%.

Similar analysis can be made for any combination of geometries, flow rates, and output oxygen concentrations.
Chapter 5: System Performance

Additional performance characteristics of the microfluidic oxygen-exchanger can be obtained through simple analytical fluid modeling based on conservation of mass considerations. At steady state, by definition, no oxygen can accumulate within the device. Thus, the mass of oxygen leaving the channel is equal to the mass of oxygen entering it. The mass of oxygen entering the microfluidic chip per second is equal to the film flux, $J_{\text{O}_2}$, multiplied by the film area. Furthermore, the volume of oxygen that escapes from the channel is given by the escaping oxygen mass divided by the oxygen density, $\rho_{\text{O}_2}$. If we define $C_o$ to be the bulk oxygen concentration of the oxygen-nitrogen solution exiting the device (total oxygen volume escaping per second / total gas volume escaping per second) then mass conservation dictates that:

$$O_2 \text{ In} = C_o V_x H b = O_2 \text{ out} = J_{\text{O}_2} \rho_{\text{O}_2} L b$$

provided the flow is modeled as incompressible as discussed in Section 2. Here, $H$ represents channel height, $b$ represents channel width and $L$ represents channel length. Rearranging Eqn. 5.1 yields:

$$C_o = \frac{J_{\text{O}_2}}{V_x} \ast \frac{L}{H} \ast \frac{1}{\rho_{\text{O}_2}}$$

which shows that for a given geometry, $\frac{L}{H}$, a desired concentration can be achieved simply by lowering the fluid velocity $V_x$. Commercially available pumps are able to deliver fluid on less than micro-liter scales, making it feasible to create high oxygen-concentration steady-state flows. It is also important to note that the quantity of oxygen produced per second depends only on the photolytic film area, and the film efficiency at producing oxygen. The device oxygen production rate of a photolytic surface area, $A$, is:

$$O_2 \text{ Production} = J_o A = J_o L b$$

The flux, $J_{\text{O}_2}$, essentially provides a measure a film’s efficiency in using area.
Next, the power needed to pump gases through the device will be considered. The power required to drive a fluid through a conduit is equal to the product of the flow rate and the pressure drop. The bulk fluid flow rate, \( Q \), through a channel is given by:

\[
Q = V_x \times \text{Area} = V_x \times b \times h
\]  

(5.4)

The pressure profile within a microchannel was given above in Eqn. 2.16. Because the pressure drop across the channel is constant, simply multiplying the differential pressure drop by the channel length yields:

\[
\Delta P = \frac{12 V_x \mu L}{H^2} \times L
\]  

(5.5)

Therefore the pumping power is given by Eqn. 5.6.

\[
\text{Power} = \Delta P \times Q = \frac{12 V_x^2 L \mu b}{H}
\]  

(5.6)

Assuming that output concentration and oxygen production rate are constant functional requirements set by customer need, Eqns. 5.2 and 5.3 can be substituted into Eqn. 5.6 to yield the following expression for fluid power:

\[
\text{Power} = \frac{12 \beta_0 \mu L^2 A}{C_2 H^3 \rho_{O_2}}
\]  

(5.7)

Because this expression depends only channel length, channel height, and constants, it is clear that the power required to drive fluid flow varies inversely with the cube of channel height and scales with the square of length. However, minimizing device volume is also a critical functional requirement for a portable device. The smallest possible volume of the device is the product of the photolytic area, \( A \), and the channel height. If a constant value, \( h \), is added to the channel height to account for the thickness of the conducting layers, photocatalyst layer, and substrate, then the resulting space-utilization efficiency can be defined:

\[
\frac{O_2 \text{ Production Rate}}{\text{Device Volume}} = \frac{J_o L b}{L b (H + h)} = \frac{J_o}{H + h}
\]  

(5.8)
Table 5.1 provides a design roadmap for the selecting geometric and functional parameters for the proposed integrated oxygen-generation device with a fixed O$_2$ production rate and concentration.

<table>
<thead>
<tr>
<th>Performance Parameter</th>
<th>Physical Relationship</th>
<th>Design Recommendation</th>
<th>Limitation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Limit Device Volume</td>
<td>$\frac{1}{H}$</td>
<td>Minimize and decrease L to limit pumping power</td>
<td>Microchannels can be easily manufactured to micron sizes, though capillary forces not modeled here add resistance and cannot be neglected in nano-scale devices.</td>
</tr>
<tr>
<td>Limit Fluid Pumping Power</td>
<td>$\frac{L^2}{H^3}$</td>
<td>Minimize L and decrease V$_x$ to achieve correct output O$_2$ concentration</td>
<td>Limiting channel lengths to even millimeter scales complicates assembly and adds complexity by requiring integration of many layers</td>
</tr>
<tr>
<td>Achieve Desired O$_2$ Concentration</td>
<td>$\frac{L}{H V_x}$</td>
<td>Match V$_x$ to L/H ratio</td>
<td>Micro-liter pumps are commercially available, but maintaining a precise fluid speed in a safety-critical application is a challenge.</td>
</tr>
<tr>
<td>Achieve Desired O$_2$ Production Rate</td>
<td>$\sim L b$</td>
<td>Select an acceptable level of device complexity and use this criterion to set a maximum b</td>
<td>When $b \gg L$, channels have to be divided and stacked to create a reasonable footprint for a portable device. Additional processing steps increase cost and complicate the assembly process.</td>
</tr>
</tbody>
</table>

Table 5.1: Key design trade-offs in production of a portable artificial oxygen generator

Using values of H, L, and V$_x$, easily attainable with current technology, the power required to drive fluid flow was found to be 0.053 W, and the total device volume of 0.0049m$^3$ for an oxygen output of 250ml/min and oxygen output concentration of 21% by volume (Appendix 1). Thus the microfluidic elements sufficient to sustain a human being could easily be made portable and battery powered.

In conclusion, a computational simulation of the convection-diffusion relation was developed in order to characterize the performance of a proposed oxygen-producing microfluidic chip. Specifically, the time to reach steady state was determined to be less than 1sec over a wide range of geometries. Information from fluid dynamic modeling was then used to determine that the fluid power, and device volume are small enough to be practically employed for use in applications such as mining rescue, high-altitude airplane cabin oxygenation, and aerospace.
Appendix 1: Ch. 5 Calculations

Oxygen Density
Ideal Gas Law:
P: pressure, N: # of moles, M: molar mass, R: Universal gas constant, ρ: density

\[ \rho = \frac{P \times M}{R \times T} \]

For oxygen gas at P=1atm, T=20°C, M=32g/mol, \( ρ = 1.330 \text{ kg/m}^3 \)

Oxygen Flux
The flux of oxygen, \( J_{O_2} \), across a photolytic area, A:

\[ J_{O_2} = \frac{1.085 \times 10^{-6} \text{ moles } O_2}{m^2 \times \text{sec}} \times \frac{0.032 \text{ kg}}{\text{mol } O_2} \times \frac{m^3 O_2}{1.33 \text{ kg}} = 2.61 \times 10^{-8} \text{ m}^3 O_2 \times \text{m}^2 \times \text{sec} = 2.61 \times 10^{-5} \frac{L O_2}{m^2 \times \text{sec}} \]

Photolytic Area
At rest, a human requires \( 2.5 \times 10^{-4} \text{ m}^3 \) of oxygen/min \(^6\), thus:

\[ A = \frac{2.5 \times 10^{-4} \text{ m}^3 O_2}{\text{min}} \times \frac{1 \text{ min}}{60 \text{ sec}} \times \frac{m^2 \times \text{sec}}{2.61 \times 10^{-8} \text{ m}^3 O_2} = 159.6 \text{ m}^2 \text{ Photolytic Area} \]

159.6 m\(^2\) Photolytic Area are needed to sustain a person.

Light Power
A 365nm ultraviolet light with an intensity of 36mW/m\(^2\) is required for this oxygen output. Thus:

\[ \text{Light Power} = 159.6 \text{ m}^2 \times \frac{36 \text{ mW}}{\text{cm}^2} \times \frac{10^4 \text{ cm}^2}{\text{m}^2} = 57.456 \text{ MW} \]

Clearly the light power efficiency needs to improve immensely (5-6 orders of magnitude) before the film becomes commercially viable.

Device Volume
Height = Water Channel Height + PDMS Membrane Height + Air Channel Height + Light Source Height + TiO\(_2\) film height + Cathode Height + Anode Height

Assume:
Water Channel Height = 10μm, PDMS Membrane Height = 10μm, Air Channel Height=10μm, TiO\(_2\)+Cathode+Anode Height = 1 μm
All dimensions can be manufactured or purchased easily with currently available technology. Total height = 3.10x10^{-5} m. Thus the minimum device volume (without a power supply) is:

\[
\text{Device Volume} = 3.1 \times 10^{-5} \text{ m} \times 159.6 \text{m}^2 = 0.0049 \text{m}^3
\]

Thus, the device could fit into a 17x17x17cm box.

**Mass Water**

To produce 250ml of oxygen per minute, the photolytic reaction consumes water at a rate of:

\[
\frac{2.5 \times 10^{-4} \text{ m}^3 \text{ O}_2}{\text{min}} \cdot \frac{1440 \text{ min}}{1 \text{ day}} \cdot \frac{1.33 \text{kg} \text{ O}_2}{\text{m}^3} \cdot \frac{1 \text{ mol} \text{ O}_2}{2 \text{ mols H}_2\text{O}} \cdot \frac{0.018015 \text{ kg}}{1 \text{ mol} \text{O}_2} \cdot \frac{0.032 \text{kg}}{1 \text{ mol H}_2\text{O}} = \frac{0.54 \text{ kg}}{\text{day}}
\]

This fluid occupies a volume of 0.539 L. The water channels have a volume of:

\[
V_{\text{water channel}} = (10 \text{ microns}) \cdot 159.6 \text{ m}^2 = 0.0015 \text{m}^3 = 1.60 \text{ L}
\]

Thus enough water to produce 2.97 days worth of air is housed within the proposed device, and no external water containers are necessary.

**Fluid Power**

Each fluidic chip requires inlet and outlet holes to be punched into it. Assume: \( L \geq 1 \text{mm} \) to make this process manageable with current techniques.

Assume: The desired \( C_0 = 0.2095 \), the concentration of oxygen in air at sea level. \( \mu_{\text{air}} = 1.82 \times 10^{-5} \text{ kg/s*m} \) at \( T=20^\circ \text{C} \) Then:

\[
\text{Fluid Power} = \frac{12 \frac{J}{s} \cdot \mu \cdot L^2 A}{C_0 H^3 \rho_{O_2}} = 0.53 \text{ Watts}
\]
Appendix 2: Matlab Script

% Developer: Erin Koksal
% Last Modified: 9 May, 2008

%Calculates the oxygen concentration throughout a 2-D pressure-driven flow
%through a semi-infinite rectangular channel (plane Poiseuille flow).

%Generates a time stamp
TempTime = clock;
ts = ['(' num2str(TempTime(4),'%02.0f') ' ':' num2str(TempTime(5),'%02.0f') ' ':' num2str(TempTime(6),'%02.0f') ')']

%Density of oxygen at T=20C, P=1atm in kg/m^3
rho = 1.330;

%Desired final oxygen concentration of exit flow in (volume O2)/(volume N2)
C = 0.21*rho;

%Diffusion coefficients of oxygen in m^2/sec
%Note: diffusion constants do not change as a function of concentration
%in this model
Dwater = 2.1*10^-9; %@T=20C, 1atm. From White, Heat and Mass Transfer p. 626
Dpdms = 6*10^-9; %From Gilbert-Thorsen NIH Grant
Dair = 2.1*10^-5; %In nitrogen @ T=20C, 1atm. From White, Heat and Mass Transfer p. 705 [2.0*10^-9 for air]

%flux of oxygen in (kg solute)/(sec * m^2 film)
flux = 3.4722*10^-8;

%time step
dt = 1*10^-9;
%For testing: end time
time = dt*10^10;

%Number of distance steps in y (height)
% **User: increase N to improve accuracy in y direction
% **User: decrease N to decrease computing time
N = 10;

%**User: Vary heights as desired
%Height of water channel in meters (10 microns)
Hwater = 10*10^-6;
%height of PDMS membrane in m (10 microns)
Hpdmss = 10*10^-6;
%height of air channel in m (10 microns)
Hair = 10*10^-6;

%Stepsize in y (height)
%Height is divided by N-1 because an artificial point is needed to model
%constant flux boundary condition at y=0
dyWater = Hwater / (N-i);
%Height is divided by N because no artificial points are needed
dyPdms = Hpdms / (N);
%Height is divided by N-i because an artificial point is needed to model
%zero flux boundary condition at y=Hair
dyAir = Hair / (N-1);

%Number of distance steps in x (length)
% **User: increase M to improve accuracy in y direction
% **User: decrease M to decrease computing time
M = 20;

%Length of channel in meters (1 cm)
% **User: vary lengths as desired
Length = 1*10^-2;
%stepsize along length of channel
%Length is divided by M-1 because an artificial point is needed to model
%zero flux boundary condition at x=Length
dx = Length / (M-1);

%Velocity along y direction in m/s; Velocity is parallel to channel
V = 0;

%Average velocity along x direction in m/s (set to achieve correct exit O2
%concentration at steady state)
Uavg = flux * Length / (C * Hair * rho);
%For plane Poiseuille flow through infinite parallel plates Umax=(3/2)*Uavg
Umax = 1.5 * Uavg;

%Setting parabolic velocity distribution
U(N) = 0;
%Nf is the/a the location with the highest velocity, U = Umax
Nf = floor(N/2);
for i = 1:Nf
    U(i) = Umax * (1 - (Nf-i)^2 / (Nf-1)^2);
    U(N-i) = U(i);
    if (N/2) == floor(N/2);
        U(N/2) = Umax;
    end
end
U = Uavg * U / ((sum(U)) / (N-1));

%Initialize concentrations to zero
WaterC0 = zeros(N, M);
WaterC = WaterC0;
PdmsC0 = zeros(N, M);
PdmsC = PdmsC0;
AirC0 = zeros(N, M);
AirC = AirC0;

%Total oxygen mass to flow out of channel
O2exit = 0;
%Oxygen concentration at exit of channel
outletC=0;

i=0;
while outletC <= 0.93*C
  %For testing: for i=0:dt:time
  
  %Total oxygen mass to flow out of channel
  O2exit =0;
  outletC=0;

  %Zero flux boundary conditions at k=1 corners
  WaterC(1,1) = WaterCO(2,2);
  WaterC(N,1) = WaterCO(N,2);
  %Zero flux boundary conditions at k=M corners
  WaterC(1,M) = WaterCO(2,M-1);
  WaterC(N,M) = WaterCO(N,M-1);

  for k=2:M-1
    for j=2:N-1
      %Finite difference model of diffusion-convection equation
      WaterC(j,k) = WaterCO(j,k)-(dt*V/dx)*(WaterCO(j,k+1)-WaterC(j,k-1))+(dt*Dwater)*((WaterCO(j-1,k)-
      2*WaterCO(j,k)+WaterCO(j+1,k))/dyWater^2+(WaterCO(j,k)-
      2*WaterCO(j,k)+WaterCO(j,k+1))/dx^2);

      %Zero flux boundary conditions at k=1 and k=M edges
      WaterC(j,1) = WaterCO(j,2);
      WaterC(j,M) = WaterCO(j,M-1);
    end;

  %For testing : zero flux boundary conditions at j=1 and k=N edges
  %PdmsC(1,k) = PdmsC(2,k);
  %PdmsC(N,k) = PdmsC(N-1,k);

  %Constant flux boundary condition
  WaterC(1,k) = WaterCO(2,k)+dyWater*flux/Dwater;

  %Boundary conditions along Water-PDMS interface (diffusion along
  %y-direction neglected)
  WaterC(N,k) = WaterCO(N,k)+(dt*Dwater/dyWater^2)*(WaterCO(N-1,k)-
  2*WaterCO(N,k)+PdmsC(1,k));
  PdmsC(1,k) = PdmsC(2,k)+(dt*Dwater/dyWater^2)*(WaterCO(N,k)-
  2*PdmsC(1,k)+PdmsCO(2,k));
  end

  %Zero flux boundary conditions at k=1 corners
  PdmsC(1,1) = PdmsCO(1,2);
  PdmsC(N,1) = PdmsCO(N,2);
  %Zero flux boundary conditions at k=M corners
  PdmsC(1,M) = PdmsCO(1,M-1);
  PdmsC(N,M) = PdmsCO(N,M-1);

  for k=2:M-1
    for j=2:N-1
\[ PdmsC(j,k) = PdmsCO(j,k) + (dt*Dpdms)*((PdmsCO(j-1,k) - 2*PdmsCO(j,k) + PdmsCO(j+1,k))/dyPdms^2) \]

%Zero flux boundary conditions at k=1 and k=M edges
\[ PdmsC(j,1) = PdmsCO(j,2); \]
\[ PdmsC(j,M) = PdmsCO(j,M-1); \]

end;

%For testing: zero flux boundary conditions at j=1 and k=N edges
\[ PdmsC(1,k) = PdmsC(2,k); \]
\[ PdmsC(N,k) = PdmsC(N-1,k); \]

end

\[ PdmsC(N,k) = PdmsCO(N,k) + (dt*Dpdms/dyPdms^2)*((PdmsCO(N-1,k) - 2*PdmsCO(N,k) + PdmsCO(N+1,k))/dyPdms^2) \]

%Zero concentration boundary condition at k=1 corners
\[ AirC(1,1) = 0; \]
\[ AirC(N,1) = 0; \]

%Zero flux boundary conditions at k=M corners
\[ AirC(1,M) = AirC0(1,M-1); \]
\[ AirC(N,M) = AirC0(N,M-1); \]

for k=2:M-1
    for j=2:N-1
        \[ AirC(j,k) = AirC0(j,k) - (dt*U(j)/(2*dx))*(AirC0(j,k+l)-AirC0(j,k-l))+(dt*Dair)*((AirC0(j-1,k)-2*AirC0(j,k)+AirC0(j+1,k))/dyAir^2+(AirC0(j,k-1)-2*AirC0(j,k)+AirC0(j,k+1))/dx^2); \]
    end
end

%For testing: zero flux boundary condition at k=1 edge
\[ AirC(j,1) = AirC(j,2); \]

%Zero flux boundary conditions at k=1 and k=M edges
\[ AirC(j,1) = 0; \]
\[ AirC(j,M) = AirC0(j,M-1); \]
\[ AirC(j,M) = AirC0(j,M) - (dt*U(j)/(dx))*(AirCO(j-1,M) - AirCO(j,M-1))+(dt*Dair)*((AirC0(j-1,M)-2*AirC0(j,M)+AirC0(j,M+1))/dyAir^2+(AirC0(j,M-1)-2*AirC0(j,M)+AirC0(j,M+1))/dx^2); \]

if k==M-1
    %Total oxygen to leave device through channel outlet in kg
    O2exit = O2exit + AirC(j,M)*U(j)*Hwater/N;
    %Assume outlet C is equal to C just before outlet
    %Concentration at outlet in kg/m^3
    outletC= outletC+AirC(j,M)/N;
end
end;

%For testing: zero flux boundary condition at j=1 edge
%AirC(1,k) = AirC(2,k);

%Zero flux boundary conditions j=M edge
AirC(N,k) = AirC(N-1,k);

end

WaterCO = WaterC;
PdmsCO = PdmsC;
AirCO = AirC;

i=i+dt;
end;
end;

time=i;

%Eliminates boundary points that do not represent real concentration values
%Constant flux boundaries at j=1 and k=M are eliminated
realWaterC=WaterC(2:N,1:M-1);
%Constant flux boundary at k=M is eliminated
realPdmsC=PdmsC(1:N,1:M-1);
%Constant flux boundaries at j=N and k=M are eliminated
realAirC=AirC(1:N-1,1:M-1);

%Matrix of x values (length) within channels
lengthX = linspace(0,Length,M-1);

%Matrix of y values (height) within water channel
WaterY = linspace(0,Hwater,N-1);
%Matrix of y values (height) within pdms membrane
PdmsY = linspace(0,Hpdms,N);
%Matrix of y values (height) within air channel
AirY = linspace(0,Hair,N-1);

%Plots water concentration as f(x,y)
figure(1)
title('Water Concentration')
[X,Y]=meshgrid(lengthX,WaterY);
surf(X,Y,realWaterC);

%Plots PDMS concentration as f(x,y)
figure(2)
title('PDMS Concentration')
[X,Y]=meshgrid(lengthX,PdmsY);
surf(X,Y,realPdmsC);

%Plots air concentration as f(x,y)
figure(3)
title('Air Concentration')
[X,Y]=meshgrid(lengthX,AirY);
surf(X,Y,realAirC);
% Totals oxygen mass remaining in each material over 2 matrix dimensions
waterRem=dyWater*dx*sum(sum(realWaterC),2);
pdmsRem=dyPdms*dx*sum(sum(realPdmsC),2);
airRem=dyAir*dx*(Length/M)*sum(sum(realAirC),2);
O2rem=waterRem+pdmsRem+airRem;

% Mass of oxygen that flows into channel in given time; Length functions
% as an area because it is a 2-D problem
O2in=flux*time*Length;

% Checks if mass is conserved in model; =1 is perfect mass conservation
MassCons=(02rem+02exit)/O2in

% Stability conditions
% dt must be smaller than dtmax
   dtmax=1/(2*Dair*(1/dx^2+1/dyAir^2));
% dx must be smaller than dxmax
   dxmax=2*Dair/Uavg;

% Combining to a single plot
TotalPlot=zeros(N*3-2,M-1);
for k=1:(M-1)
   for j=1:(N-1)
      TotalPlot(j,k)=realWaterC(j,k);
   end
   for j=1:N
      TotalPlot((j+N-1),k) = realPdmsC(j,k);
   end
   for j=1:(N-1)
      TotalPlot((j+2*N-1),k) = realAirC(j,k);
   end
end
theXplot=linspace(dx,dx,M-I);
theYplot=linspace(dyPdms,dyPdms,3*N-2);
[X,Y]=meshgrid(theXplot,theYplot);
surf(Y,X,TotalPlot);

% Generates a time stamp
TempTime=clock;
ts = ['(' num2str(TempTime(4),'%02.0f') ' ':' num2str(TempTime(5),'%02.0f') ' ':' num2str(TempTime(6),'%02.0f') ')']
References Cited


9 Thorsen, Todd. Personal communication. 2 May 2008.


