A mathematical model for an exhaust oxygen sensor.

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1 Introduction

By federal and state regulations the U.S. auto industry is forced to develop strategies to control emission whereas rising gas prices demand higher fuel economy. An important mechanism that is used in this process of control is the exhaust oxygen sensor.

An oxygen sensor is a chemical device that is constantly making a comparison between the level of oxygen inside the exhaust manifold and air from outside the engine.
The result of this comparison is detected with voltage that is generated at all times. The oxygen sensor is active any time the engine is hot enough, typically with a working temperature of 700°C.

![Diagram of an oxygen sensor](image)

Figure 1: Schematic diagram of an oxygen Sensor

During combustion the so-called fuel air ratio (A/F) ratio determines the different concentrations of the exhaust gases. The A/F ratio is defined to be the ratio of the mass of air to the mass of fuel going into the engine. To good approximation, this ratio is independent of the engine speed. In the fuel-rich region there is not enough oxygen to burn off all the combustible gases. For instance, if not all the gases are burned, a high concentration of CO (a dangerous pollutant) is generated and and fuel is wasted. On the other hand, in the fuel-lean region there is too much oxygen left over which has been shown to oxidize nitrogen at high temperatures (again a pollutant.) Hence it is important to keep the A/F ratio at the optimal point, where there is exactly enough oxygen to burn off all the fuel, the so-called stoichiometric point.
In this paper we deal with a mathematical model for an oxygen sensor that is widely used in the automotive industry. A technical description follows. The sensor produces a voltage difference that essentially depends on the difference in oxygen concentration on the two different chambers of exhaust gases and air. A schematic diagram of the oxygen sensor is shown in figure 1.

The oxygen sensor uses a voltage drop to detect when the $A/F$ ratio changes from too rich to too lean. This information is used by the engine to adjust the air/fuel ratio. Experiments have shown that the sensor displays a voltage drop at a point slightly in the fuel lean region. See figure 2

![Stoichiometry](image.png)

Figure 2: Voltage response of an oxygen Sensor

**Technical Description of the sensor**

The oxygen sensor consists of four different layers, two of which serve as electrodes. The important layers are: a solid electrolyte layer that helps in the creation of the voltage drop, two porous platinum layers that serve as catalysts of the reactions and as electrodes, and a porous spinel layer on one electrode that protects the device from particles in the
exhaust gases. The other electrode is directly exposed to air. The two platinum layers are in an open circuit configuration and connected to a device capable of measuring voltage. See figure 3.

![Porous Spinel Layer Diagram](image)

Figure 3: Different layers of an oxygen Sensor

Certain level of diffusion takes place in the porous spinel layer. It is possible to assume that the effect of the chemical reaction away of the platinum layer is negligible compared with the effects due to this diffusion and the reaction close to the platinum.

The important chemical reactions take place very close to the platinum layer in contact with the exhaust gases. On the other hand, the layers of the sensor are very thin compared to the height of the device. These two facts, will allow us to assume that locally the chemical reactions and diffusive transport don't feel the effect of curvature and so we can use a one dimensional model.

2 Background for our model

2.1 Basic Chemistry

Although there are many gases in the exhaust the main components that influence voltage response are $\text{N}_2$, $\text{O}_2$, CO, CO$_2$, H$_2$ and H$_2$O. The outside air consists of roughly 21% oxygen
and 79% nitrogen, whereas the nitrogen concentration in the exhaust tends to be around 60-68% with less than 4% oxygen.

The exhaust gases react with each other according to the following schemes:

The platinum electrode is prone to develop so-called vacancies which we denote by the symbol S. Carbon Monoxide, hydrogen and oxygen molecules attach themselves to these vacancies and become adsorbed. We have the following adsorption reactions. (The reverse reaction is called a desorption reaction.)

\[
\begin{align*}
O_2 + 2S & \rightleftharpoons 2O_{ad} \\
H_2 + 2S & \rightleftharpoons 2H_{ad} \\
CO + S & \rightleftharpoons CO_{ad}.
\end{align*}
\]

At the platinum electrode the adsorbed carbon monoxide and hydrogen and the oxygen react to produce carbon dioxide and water in gaseous form.

\[
\begin{align*}
CO_{ad} + O_{ad} & \rightleftharpoons CO_2 + 2S \\
2H_{ad} + O_{ad} & \rightleftharpoons H_2O + 3S
\end{align*}
\]

As a starting point, we will assume that the high air temperature in the exhaust pipes and the platinum coating (a catalyst) have ensured that all the above reactions are in equilibrium. Hence we can combine them into the two reactions:

\[
\begin{align*}
\frac{1}{2}O_2 + CO & \rightleftharpoons CO_2 \\
H_2 + \frac{1}{2}O_2 & \rightleftharpoons H_2O.
\end{align*}
\]

At equilibrium we have that the mole fractions of the gases obey:

\[
\begin{align*}
X_{O_2}^{1/2}X_{CO} = K_I P^{-1/2}X_{CO_2}, \\
X_{O_2}^{1/2}X_{H_2} = K_{II} P^{-1/2}X_{H_2O},
\end{align*}
\]

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where $K_I, K_{II}$ are equilibrium constants and $P$ is the pressure. The electrochemical reaction:

$$O_{ad} = O^{2-} + S$$

is responsible for the voltage response. The adsorbed oxygen adsorbs two electron from the platinum electrode and enters the electrolyte. This reaction results in a positive electrochemical potential at the electrodes. The magnitude of that electrochemical potential depends the mole fraction. The greater the mole fraction of oxygen at the electrode the greater is the positive electrochemical potential. In what follows we denote the electrode in the exhaust air by electrode 1 and the (reference) electrode in fresh air by electrode 2. Hence there is a greater positive electrochemical potential at electrode 2 than at electrode 1. The difference in electrochemical potentials between electrode 2 and electrode 1 is the voltage measured. This difference is positive in our case. There is no current between the two electrodes. Since the oxygen concentration in the outside air is constant the voltage observed measures the mole fraction of oxygen in the exhaust gas. In our reaction 4 electrons per $O_2$ molecule are being exchanged. Hence in our setting a Nernst type equation computes the voltage $V$ by:

$$V := -(RT/4F)[\ln\left(\frac{[X_{O_2}]}{0.21}\right)].$$

Here $F = 96487$ Coulomb/mol is Faraday's constant. This description assumes that the number of vacancies $S$ in the platinum is large and the ratio of vacancies at electrode 1 and vacancies at electrode 2 is near 1. In fact the observed voltage will depend on the mole fraction of the adsorbed oxygen and hence is only equal to the mole fraction of the gaseous oxygen in equilibrium. The exact mechanics of that electrochemical process are still an area of research. It has been observed experimentally that the voltage jumps near the so-called stoichiometric point. This can be explained by the fact that the oxygen concentration is very close to zero (on the order of $10^{-20}$) in the fuel-rich region near the stoichiometric point. The potential difference is greater when the oxygen mole fraction at electrode 1 is smaller i.e. in the fuel-rich region than when there is more oxygen i.e. the fuel-lean region. The stoichiometric condition is for the exhaust gases is:

$$2X_{O_2} = X_{CO} + X_{H_2}.$$
We will assume that this relation is satisfied when $\lambda = 1$.

We use our model to explain why and where this voltage jump occurs. We also determine what influences the size and location of the jump and why the voltage jump does not occur at the stochiometric point. A good model will be of use in future designs of oxygen.

2.2 Description of the model

In our model we made the simplifying (starting) assumption that all chemical reactions are in equilibrium and that the exhaust gases are obeying the ideal gas law:

$$pV = nRT,$$

where $R = 8.314 \frac{\text{Joule}}{\text{mol K}}$ (universal Gas constant.) We assume that the (total) pressure of the systems stays constant and denote that constant by $P$. We also assume that the temperature of the outside air is equal to the temperature of the exhaust and stays constant at temperature $T = 973K$. Instead of partial pressures or partial concentrations we will use mole fractions of the 6 gases. The main advantage of mole fractions is that they are dimensionless and we have:

$$X_{H_2} + X_{O_2} + X_{H_2O} + X_{CO} + X_{CO_2} + X_{N_2} = 1.$$ 

1 mole is equal to the number of carbon atoms in 12g of C$^{12}$ or:

$$1 \text{ mol} = 6.02205 \times 10^{23} \text{ atoms}.$$ 

Let $n_i$ denote the density of molecules of gas $i$, and let $X_i$ denote the mole fraction of the gas $i$. Note that $X_i := \frac{n_i}{C}$ where $C$ is the total concentration, that is the total number of molecules per unit volume. We have $0 \leq X_{O_2}, X_{CO}, X_{CO_2}, X_{H_2}, X_{N_2}, X_{H_2O} \leq 1$. We have that

$$X_{N_2} = 1 - (X_{O_2} + X_{CO} + X_{CO_2} + X_{H_2O} + X_{H_2}).$$

We decide to focus our attention on the mole fraction of oxygen. There two processes that we decided to be the main influences.
A. The diffusion across the porous layer: While the main function of the porous layer is to protect the platinum electrode it does “slow the exhaust gases down”. Since the 6 different gases diffuse at slightly different speeds through the porous layer, the mole fraction of the gases at the electrode will be different from the initial mole fractions in the exhaust.

We will assume that the mole fractions $X_{N_2}$, $X_{O_2}$, $CO$, $CO_2$, $X_{H_2}$, $X_{H_2O}$ at the surface of the electrode are in steady state hence there is no time dependence. The diffusion through the porous layer, also called a transport problem, is (under the assumption of steady state) described via the diffusion equation:

$$\nabla^2 X_{O_2} = \nabla^2 X_{H_2} = \nabla^2 X_{CO} = \nabla^2 X_{CO_2} = \nabla^2 X_{H_2O} = 0.$$ 

We will also use the Fick’s Law which is valid near equilibrium to describe the flux $NX$ of the various exhaust gases $X$ through the porous layer:

$$N_{O_2} = -\frac{CD_{O_2}}{\tau} \nabla X_{O_2},$$

$$N_{CO} = -\frac{CD_{CO}}{\tau} \nabla X_{CO},$$

$$N_{CO_2} = -\frac{CD_{CO_2}}{\tau} \nabla X_{CO_2},$$

$$N_{H_2} = -\frac{CD_{H_2}}{\tau} \nabla X_{H_2},$$

$$N_{H_2O} = -\frac{CD_{H_2O}}{\tau} \nabla X_{H_2O}.$$ 

The diffusion coefficients $D_i$ of the various gas components $i$ depend on the physical layout of the molecules and are computed using statistical mechanics. Since all gases are dilute in the nitrogen, we will use diffusion coefficient of the various gases in nitrogen. To see whether this is a good assumption, we used the Stefan - Maxwell equations as well and found good agreement. The diffusion coefficients also depend on the physical properties of the porous layer, such as tortuosity $\tau$ and width $\ell$. In section 3 we will carefully study the dependence of these constants on the physical lay-out of the sensor. This gives design constraints.
B. The chemical reactions between the non nitrogen gases yield different equilibrium concentrations according to different values of $\lambda$. Moreover the equilibrium constants depend on the pressure and temperature. We assume that the porous layer has sufficiently many holes so that the adsorption reactions of hydrogen and oxygen and carbon monoxide are independent of each other and there is no competition for vacant sites. E. Logothesis [2] claims that the rather quick diffusion of the hydrogen in relation to the oxygen leads to the shift of the voltage jump into the fuel-lean region. In order to identify the main reason for the deviation we propose to look at a simplified system involving only $O_2, CO, CO_2$.

3 A simplified model

As an example of how the exhaust sensor works, we suppose that the exhaust contains only four species of gas molecules: $O_2$, $CO$, $CO_2$ and $N_2$. It is assumed that the nitrogen is inert. Very close to the electrode, platinum catalyzes the reaction

$$CO + \frac{1}{2}O_2 \rightleftharpoons CO_2.$$ 

Far enough away from the electrode, at the exhaust, we assume that the gas mixture remains fixed. Specifically, it's taken that the mole fraction of each species depends on the fuel to air ratio supplied to the engine. This ratio is parameterized by $\lambda$, a quantity selected so that stoichiometry (a situation where, for this model, oxygen concentration is half that of carbon monoxide) occurs at $\lambda = 1$. Data points for the mole fractions of each chemical species far from the plate are taken from [2] with an offset to satisfy our simplified assumption.

For simplicity, a one-dimensional cross section of the sensor is considered, with $x = 0$ at the left edge of the porous layer and $x = \ell$ at the platinum electrode. The width $\ell$ of the porous ceramic layer is assumed to be much greater than the width of the zone in which platinum catalyzes reactions.

The partial differential equations describing the various gas concentrations in the
porous ceramic layer of the device are
\[ \frac{\partial(cX_i)}{\partial t} = -\frac{\partial N_i}{\partial x} \]
where \( X_i \) is the molar fraction of total gas concentration for species \( i \), \( N_i \) [/cm²/s] is molar flux and \( c \) [mol/cm³] is the total concentration of all gas species. Fick’s law of chemical diffusion states that in situations where the diffusing chemical species are essentially unaffected by one another we have the flux \( N_i \) proportional to the gradient for the molar concentration:
\[ N_i = -\frac{D_i}{\tau} \frac{\partial(cX_i)}{\partial x} \]
where \( D_i \) [cm²/s] is chemical diffusivity of gas \( i \) and \( \tau \) is tortuosity of the porous ceramic layer. This gives a system of diffusion equations
\[ \frac{\partial X_i}{\partial t} = \frac{\partial}{\partial x} \left( \frac{D_i}{\tau} \frac{\partial X_i}{\partial x} \right) . \]
We seek a steady state solution for the differential equations, and because we are working with a one dimensional model, it is assumed that \( N_i \) is constant for each species. Since we assume that \( c \) is constant, the differential equations become
\[ \frac{\partial X_i}{\partial x} = \text{constant} . \quad (3.1) \]
The concentrations for the chemical species at \( x = 0 \) are denoted \( X_{CO_2}^{exh} \), \( X_{CO}^{exh} \), and \( X_{O_2}^{exh} \) [mol/cm³] and are obtained as known functions of \( \lambda \) [1].

At the platinum electrode, we make the steady state assumption that the rate at which CO₂, CO and O₂ are being created or destroyed must be balanced by the incoming fluxes of these species. That is,
\[ r (K_i \sqrt{p} X_{CO} X_{O_2}^{\frac{1}{2}} - X_{CO_2}) = \frac{c D_{CO_2}}{\tau} \frac{\partial X_{CO_2}}{\partial x} \]
\[ r (K_i \sqrt{p} X_{CO} X_{O_2}^{\frac{1}{2}} - X_{CO_2}) = -\frac{c D_{CO}}{\tau} \frac{\partial X_{CO}}{\partial x} \quad (3.2) \]
\[ \frac{\tau}{2} (K_i \sqrt{p} X_{CO} X_{O_2}^{\frac{1}{2}} - X_{CO_2}) = -\frac{c D_{O_2}}{\tau} \frac{\partial X_{O_2}}{\partial x}. \]
To obtain tractable boundary conditions for the equation describing the diffusion of species through the porous layer, first note that (3.2) leads to

\[ \mathcal{D}_{CO_2} \frac{\partial X_{CO_2}}{\partial x} = - \mathcal{D}_{CO} \frac{\partial X_{CO}}{\partial x} \]

\[ \mathcal{D}_{CO_2} \frac{\partial X_{CO_2}}{\partial x} = - 2 \mathcal{D}_{O_2} \frac{\partial X_{O_2}}{\partial x} . \]  

(3.3)

Now choosing one of the equations from (3.2) and dividing through by \( r \), obtain

\[ (K_I \sqrt{\rho} X_{CO} X_{O_2}^{1/2} - X_{CO_2}^r) = \frac{c \mathcal{D}_{CO_2}}{r \tau } \frac{\partial X_{CO_2}}{\partial x} . \]  

(3.4)

If we make the substitution \( x = \ell \xi \) we get the non-dimensional group of parameters

\[ \frac{c \mathcal{D}_{CO_2}}{r \tau \ell} . \]

The right hand side of (3.4) will be negligible if either the diffusivity is small relative to the other parameters, or if \( \ell \) or \( \tau \) are large relative to other parameters. Physically, this means that the reaction at the platinum electrode will be in equilibrium if the diffusion of species to the plate is very slow relative to the rate at which the species are being created or destroyed. Similarly, if the tortuosity \( \tau \) is large, molecules have a difficult time making it through the porous layer, and if the thickness \( \ell \) of the porous layer is large, the flux through the porous layer is low and species will be diffusing into the electrode slowly.

For the purposes of our model, we will simply assume that the parameter group

\[ \frac{c \mathcal{D}_{CO_2}}{r \tau \ell} \ll 1. \]

From the discussion above, the equilibrium condition,

\[ K_I \sqrt{\rho} X_{CO} X_{O_2}^{1/2} - X_{CO_2} = 0 , \]

or

\[ \frac{X_{CO_2}}{X_{CO} X_{O_2}^{1/2}} = K_I \sqrt{\rho} \]  

(3.5)

holds. This, in conjunction with (3.3) gives us the three equations to solve for \( X_{O_2} \), \( X_{CO} \) and \( X_{CO_2} \) at the right edge of our domain. All that remains is some non-dimensionalization and algebraic simplifications.
First, given that the derivatives of the molar fractions are constant, we know that all the $X_i$ are linear functions in $x$, and so we can write (3.3) in terms of just the exhaust and electrode values of the $X_i$

\[
\frac{D_{\text{CO}_2}}{l} (X_{\text{CO}_2} - X_{\text{CO}_2}^{\text{exh}}) = -\frac{D_{\text{CO}}}{l} (X_{\text{CO}} - X_{\text{CO}}^{\text{exh}}) \\
\frac{D_{\text{CO}_2}}{l} (X_{\text{CO}_2} - X_{\text{CO}_2}^{\text{exh}}) = -2\frac{D_{\text{O}_2}}{l} (X_{\text{O}_2} - X_{\text{O}_2}^{\text{exh}}).
\]  

(3.6)

We can also introduce a non-dimensionalization for the diffusivities by dividing each diffusion coefficient by a nominal diffusivity, $D_0$:

\[
D_i = \frac{D_i}{D_0},
\]

$D_0$ may be chosen to be one of the diffusion coefficients in the system.

It is known that $K \gg 1$ (in fact $K \sim 10^{10}$) so we introduce

\[
\epsilon = \frac{1}{K \sqrt{p}}.
\]

The molar fractions are non-dimensional and the system of equations can be written in non-dimensional form:

\[
X_{\text{CO}} X_{\frac{3}{2} \text{O}_2} = \epsilon X_{\text{CO}_2}, \\
D_{\text{CO}_2} (X_{\text{CO}_2} - X_{\text{CO}_2}^{\text{exh}}) = -D_{\text{CO}} (X_{\text{CO}} - X_{\text{CO}}^{\text{exh}}) \\
D_{\text{CO}_2} (X_{\text{CO}_2} - X_{\text{CO}_2}^{\text{exh}}) = -2D_{\text{O}_2} (X_{\text{O}_2} - X_{\text{O}_2}^{\text{exh}}).
\]

(3.7)

4 Analysis of the simple model

Given the steady-state equations (3.7) describing diffusion in the porous layer and equilibrium at the platinum plate for the simplified Fick’s law model, we derive an asymptotic expansion in terms of the small parameter $\epsilon$. Two different expansions arise, corresponding to the relative abundances of oxygen and carbon monoxide. If the exhaust contains excess carbon monoxide relative to oxygen, then the chemical reactions at the platinum
excess carbon monoxide relative to oxygen, then the chemical reactions at the platinum will nearly deplete the oxygen. This situation corresponds to a rich fuel to air ratio, i.e., $\lambda < 1$. In this case the leading order terms of the asymptotic expansion are

\[
X_{CO} \sim X_{CO}^{\text{rich}} \equiv X_{CO}^{\text{exh}} - \frac{2D_{O_2}}{D_{CO}} X_{O_2}^{\text{exh}} \\
X_{CO_2} \sim X_{CO_2}^{\text{rich}} \equiv X_{CO_2}^{\text{exh}} + \frac{2D_{O_2}}{D_{CO_2}} X_{O_2}^{\text{exh}} \\
X_{O_2} \sim X_{O_2}^{\text{rich}} \equiv \varepsilon^2 \left( \frac{X_{CO_2}}{X_{CO}} \right)^2.
\]

The other possible solution describes the situation where the exhaust contains abundant oxygen relative to carbon monoxide, so that the carbon monoxide is depleted while some oxygen remains. This corresponds to a lean fuel to air ratio, or $\lambda > 1$. The leading order terms of the asymptotic expansion are

\[
X_{O_2} \sim X_{O_2}^{\text{lean}} \equiv X_{O_2}^{\text{exh}} - \frac{D_{CO}}{2D_{O_2}} X_{CO}^{\text{exh}} \\
X_{CO_2} \sim X_{CO_2}^{\text{lean}} \equiv X_{CO_2}^{\text{exh}} + \frac{D_{CO}}{D_{CO_2}} X_{CO}^{\text{exh}} \\
X_{CO} \sim X_{CO}^{\text{lean}} \equiv \varepsilon \frac{X_{CO_2}}{\sqrt{X_{O_2}}}.
\]

These asymptotic expressions agree very well with numerical solutions (error of order $10^{-6}$) away from the steep intermediate region. Compare Figure 4 (mole fractions of gases in exhaust) with Figures 5 and 6 (mole fractions of gases near the platinum plate).
Figure 4: Comparison of mole fractions of $O_2$ and $CO$ in the exhaust.

We define the switching point as the point separating the regions where the different asymptotic expansions are valid. This switching point occurs when $\lambda$ satisfies the equation

$$D_{O_2} X_{O_2}^{exh} = \frac{1}{2} D_{CO} X_{CO}^{exh}.$$ 

Notice the similarity of this equation to the equation for stochiometry

$$X_{O_2}^{exh} = \frac{1}{2} X_{CO}^{exh}.$$ 

While stochiometry occurs at $\lambda = 1$, the switching point between depleted oxygen and excess oxygen is shifted by diffusion to $\lambda = 0.999433$. The relative magnitudes of the diffusion constants $D_{O_2}$ and $D_{CO}$ affects the position of the switching point. If $D_{O_2}$ were increased, this shift would be pushed farther to the left (recall that $\lambda < 1$ corresponds to a rich fuel to air ratio). If $D_{CO}$ were increased, the shift would be pushed to the right. Note that for this simple model the switching point lies to the left of stochiometry, while in the actual data it lies to the right.
Figure 5: Mole fraction of O₂ for the simplified Fick's law model as λ varies.

The existence of the two different asymptotic expansions explains another behavior of the oxygen sensor: two regions of fairly constant voltage separated by a region of very rapidly changing voltage. The voltage for the region \( \lambda < 0.999433 \) is approximately \( V(X_{O_2}^{\text{rich}}) \approx 0.9 \), while the voltage for the opposite region is roughly \( V(X_{O_2}^{\text{lean}}) \approx 0.05 \). The steepness of the intermediate region is due to the very small order of \( \varepsilon \) (recall \( \varepsilon \approx 10^{-10} \)). Since the reactions at the platinum plate are in equilibrium, either nearly all of the oxygen or of the carbon monoxide will be depleted, depending on their relative concentrations in the exhaust. The mole fraction of oxygen is relatively low for \( \lambda < 1 \) since the fuel to air ratio is rich, while the mole fraction for carbon monoxide is large. Hence at the platinum plate the oxygen will be depleted but the excess carbon monoxide will remain present. For \( \lambda > 1 \) exactly the opposite situation happens. See Figure 7.
Figure 6: Mole fraction of CO for the simplified Fick’s law model as $\lambda$ varies.

Figure 7: Voltage across the oxygen sensor for the simplified Fick’s law model.
Figure 8: Initial concentrations of exhaust gases as a function of $\lambda$.

5 A more general model

We now add hydrogen and water to our system. This forces us to introduce a second reaction to our model, with equilibrium constant $K_{II}$. The initial concentration of all the gas species is shown in figure 8.

The following steady-state equations describe diffusion in the porous layer and equilibrium at the platinum plate for this six-species Fick's law model:

\[
D_{CO_2}(X_{CO_2} - X_{CO_2}^{exh}) = -D_{CO}(X_{CO} - X_{CO}^{exh})
\]
\[
D_{H_2O}(X_{H_2O} - X_{H_2O}^{exh}) = -2D_{H_2}(X_{H_2} - X_{H_2}^{exh})
\]

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\[
D_{O_2}(X_{O_2} - X_{O_2}^{\text{exh}}) = \frac{1}{2} D_{CO}(X_{CO} - X_{CO}^{\text{exh}}) + \frac{1}{2} D_{H_2}(X_{H_2} - X_{H_2}^{\text{exh}})
\]

\[
X_{CO} \sqrt{X_{O_2}} = \varepsilon X_{CO_2}
\]

\[
X_{H_2} \sqrt{X_{O_2}} = a \varepsilon X_{H_2O}
\]

(where \(a = \frac{K_L}{K_{II}} = 1.4668\)).

Using an asymptotic expansion in terms of the small parameter \(\varepsilon = \frac{1}{K_{I} \sqrt{\beta}}\), we find that two solutions exist, corresponding to the relative abundance of oxygen and carbon monoxide. If carbon monoxide and hydrogen are in excess, then the chemical reactions at the platinum electrode will nearly deplete the oxygen. This situation corresponds to a rich fuel to air ratio, i.e., \(\lambda < 1\). In this case the leading order term of the asymptotic expansion of oxygen is:

\[
X_{O_2} \sim X_{O_2}^{\text{rich}} \equiv \zeta^2 \varepsilon^2
\]

where \(\zeta\) is obtained by solving:

\[
D_{CO} \left( \frac{D_{H_2} X_{H_2}^{\text{exh}} + D_{CO} X_{CO}^{\text{exh}}}{D_{CO} + D_{H_2} \zeta} \right) + D_{H_2} \left( \frac{D_{H_2} X_{H_2}^{\text{exh}} + D_{H_2O} X_{H_2O}^{\text{exh}}}{D_{H_2} + \frac{D_{H_2O}}{a} \zeta} \right)
\]

\[
= 2 \left( \frac{1}{2} D_{CO} X_{CO}^{\text{exh}} + \frac{1}{2} D_{H_2} X_{H_2}^{\text{exh}} - D_{O_2} X_{O_2}^{\text{exh}} \right)
\]

The other possible solution describes the situation where the exhaust contains relatively abundant oxygen relative to carbon monoxide and hydrogen, so that these gases are depleted while some oxygen remains. This corresponds to a lean fuel to air ratio, or \(\lambda > 1\). In this case, the leading order term of the asymptotic expansion of oxygen is:

\[
X_{O_2} \sim X_{O_2}^{\text{lean}} \equiv X_{O_2}^{\text{exh}} - \frac{1}{2} \frac{D_{CO}}{D_{O_2}} X_{CO}^{\text{exh}} - \frac{1}{2} \frac{D_{H_2}}{D_{O_2}} X_{H_2}^{\text{exh}}
\]

These asymptotic expressions give voltages (shown in figure 10) that agree very well with numerical solutions.
Figure 9: Asymptotic $O_2$ concentration as a function of $\lambda$, for the more general model.

The switching point between these two solutions occurs when $\lambda$ satisfies the equation

$$D_{O_2} X_{O_2}^{\text{exh}} = \frac{1}{2} D_{CO} X_{CO}^{\text{exh}} + \frac{1}{2} D_{H_2} X_{H_2}^{\text{exh}}$$

Notice the similarity of this equation to the equation for stochiometry

$$X_{O_2}^{\text{exh}} = \frac{1}{2} X_{CO}^{\text{exh}} + \frac{1}{2} X_{H_2}^{\text{exh}}.$$  

While stochiometry occurs at $\lambda = 1$, the switching point between depleted oxygen and excess oxygen is shifted by the diffusion constants to $\lambda = 1.01797$. In figure 9 we see the asymptotic $O_2$ concentration. Note the switch at $\lambda \approx 1.02$

The relative magnitudes of the diffusion constants $D_{O_2}$, $D_{H_2}$, and $D_{CO}$ affect the
Figure 10: Asymptotic voltage as a function of $\lambda$, for the more general model.

position of the switching point. If $D_{O_2}$ were increased, the above shift would be pushed to the left, i.e., a "rich" shift (recall that $\lambda < 1$ corresponds to a rich fuel to air ratio). If $D_{CO}$ or $D_{H_2}$ were increased, the shift would be pushed to the right, i.e., a "lean" shift. Note that for this model, as opposed to the simple model, there is a lean shift, as is seen in the experimental data (shown as dots in figure 10) [1].

The existence of the two different asymptotic expansions explains another behavior of the oxygen sensor: two regions of fairly constant voltage separated by a region of very rapidly changing voltage. (See figure 10)

The voltage for the region $\lambda < 1.01797$ is approximately $V(X_{O_2}^{\text{rich}}) \approx 0.9$, while the voltage for the opposite region is roughly $V(X_{O_2}^{\text{lean}}) \approx 0.05$ (the values of lean and
rich oxygen formulas depend on \( \lambda \), so the voltage varies somewhat as \( \lambda \) does. Since the reactions at the platinum plate are in equilibrium, almost all of the oxygen will be depleted, or both the carbon monoxide and the hydrogen will be depleted, depending on their relative concentrations in the exhaust. The mole fraction of oxygen is relatively low for \( \lambda < 1 \) since the air to fuel ratio is rich, while the mole fraction for carbon monoxide and hydrogen is large. Hence at the platinum plate the oxygen will be depleted but the excess carbon monoxide and hydrogen will remain. For \( \lambda > 1 \), the opposite occurs.

6 A new transport law

6.1 The Stefan-Maxwell equations

In the previous models, we used Fick’s law to relate the flux to the gradient of the concentration of the species. This law unfortunately introduces physical inconsistencies into the model. One manifestation of this arises when integrating the differential equations from Fick’s law and finding that the sum of the mole fractions does not always equal one. The Stefan-Maxwell equations provide a better physical model for transport (i.e., diffusion) of gas species which remedies this problem [3, p. 570]. These equations account for the fact that gases diffuse at different rates depending on the presence of other gases and are given by:

\[
\nabla X_i = \sum_{j=1}^{n} \frac{1}{cD_{ij}} (X_iN_j - X_jN_i),
\]

(6.8)

where the \( X_i \) are the mole fractions of the species, \( N_i \) are the fluxes, \( c \) is the total mole concentration, \( D_{ij} \) is the diffusivity of the pair \( i - j \) in a binary mixture, and \( \nabla \) is the spatial gradient. (In our current case, \( \nabla = \frac{\partial}{\partial \xi} = \cdot \).

We list a few properties of the Stefan-Maxwell equations:

1. In the appropriate limit, the Stefan-Maxwell equations become Fick’s law. Assume a binary gas mixture where \( X_1 = O(\epsilon) \) and \( X_2 = 1 - X_1 \). Also assume that the averaged mass flow is zero, i.e., \( \sum_i m_iX_i = 0 \). We write \( X_1 = \epsilon \tilde{X}_1 \) where \( \tilde{X}_1 = O(1) \),
and the Stefan-Maxwell equations give
\[ \epsilon \frac{\partial X_i}{\partial \xi} = \frac{1}{cD_{12}} \left( \epsilon \bar{X}_1 N_2 - (1 - \epsilon \bar{X}_1) N_1 \right). \]

Taking the limit of the above equation as \( \epsilon \to 0 \) we find that \( N_1 = O(\epsilon) \). Using this, the averaged mass flow equations tells us that \( N_2 = O(\epsilon) \). So writing \( N_1 = \epsilon \bar{N}_1 \) and \( N_2 = \epsilon \bar{N}_2 \) we get
\[ \frac{\partial \bar{X}_1}{\partial \xi} = \frac{1}{cD_{12}} \left( \epsilon \bar{X}_1 \bar{N}_2 - (1 - \epsilon \bar{X}_1) \bar{N}_1 \right). \]

Taking the limit as \( \epsilon \to 0 \) we find
\[ \frac{\partial \bar{X}_1}{\partial \xi} = -\bar{N}_1/(cD_{12}) \]

which (after multiplying by \( \epsilon \)) is Fick's law for the diffusion of \( X_1 \).

2. Since \( D_{ij} = D_{ji} \) for all \( i \) and \( j \), adding all the equations in (6.8) yields
\[ \nabla \sum_{i=1}^{n} X_i = \sum_{i,j=1}^{n} \frac{1}{cD_{ij}} (X_i N_j - N_j X_i) = 0. \]

(6.9)

It follows that \( \sum_{i=1}^{n} X_i \) is a constant (= 1); that is, solutions to the Stefan-Maxwell equations have the property that the total mole concentration is space invariant, in agreement with our assumption that the temperature and pressure are space invariant.

3. If we write the Stefan-Maxwell equation as \( \nabla \bar{X} = A(\bar{X}) \bar{N} \) where \( \bar{X} = (X_1, \ldots, X_n)^T \) and \( \bar{N} = (N_1, \ldots, N_n)^T \) are two vectors, and \( A(\bar{X}) \) is an \( n \times n \) matrix with entries depending on \( \bar{X} \). From (6.9), one sees that \( A \) is degenerate. Also, since all \( D_{ij} \) are positive and all \( X_i \) are non-negative with \( \sum_{i=1}^{n} X_i = 1 > 0 \), one can show that \( A \) has rank \( n - 1 \). Hence, we can solve for \( \bar{N} \) from the equation \( \nabla \bar{X} = A \bar{N} \) (assuming \( \sum_{i=1}^{n} X_i = 1 \)). There are infinitely many solutions for \( \bar{N} \). The general solution can be written as
\[ \bar{N} = C \bar{X} + \bar{N}^s(\bar{X}, \nabla \bar{X}), \]

(6.10)

where \( \bar{N}^s \) is any special solution and \( C \) is an arbitrary constant. To relate the flux uniquely with the fractional molar concentration of species, one needs an additional condition, besides the Stefan-Maxwell equation. Hence, we can enforce the
conservation of mass condition:

\[ \sum_{i=1}^{n} m_i N_i = 0, \]  

(6.11)

where \( m_i \) is the molar weight of a molecule of gas species \( i \).

6.2 Applications: Simple case

We now develop a model for the oxygen sensor which is based on the Stefan-Maxwell equations instead of Fick's law. For simplicity, we present the model where the only reactive agents are CO, O\(_2\), and CO\(_2\). The model equations are as follows

- Stefan-Maxwell:

\[
\begin{align*}
\partial X_{\text{co}} / \partial x &= \frac{\tau}{cD_{\text{co},\text{o}_2}} (X_{\text{co}} N_{\text{o}_2} - X_{\text{o}_2} N_{\text{co}}) + \frac{\tau}{cD_{\text{co},\text{co}_2}} (X_{\text{co}} N_{\text{co}_2} - X_{\text{co}_2} N_{\text{co}}) \\
&\quad - \frac{\tau}{cD_{\text{co},N_2}} X_{\text{co}} N_{\text{co}}, \\
\partial X_{\text{o}_2} / \partial x &= \frac{\tau}{cD_{\text{o}_2,\text{co}}} (X_{\text{o}_2} N_{\text{co}} - X_{\text{co}} N_{\text{o}_2}) + \frac{\tau}{cD_{\text{o}_2,\text{co}_2}} (X_{\text{o}_2} N_{\text{co}_2} - X_{\text{co}_2} N_{\text{o}_2}) \\
&\quad - \frac{\tau}{cD_{\text{o}_2,N_2}} X_{\text{o}_2} N_{\text{o}_2}, \\
\partial X_{\text{co}_2} / \partial x &= \frac{\tau}{cD_{\text{co}_2,\text{co}}} (X_{\text{co}_2} N_{\text{co}} - X_{\text{co}} N_{\text{co}_2}) + \frac{\tau}{cD_{\text{co}_2,\text{o}_2}} (X_{\text{co}_2} N_{\text{o}_2} - X_{\text{o}_2} N_{\text{co}_2}) \\
&\quad - \frac{\tau}{cD_{\text{co}_2,N_2}} X_{\text{co}_2} N_{\text{co}}, \\
\partial X_{\text{N}_2} / \partial x &= \frac{\tau}{cD_{\text{N}_2,\text{co}}} X_{\text{N}_2} N_{\text{co}} + \frac{\tau}{cD_{\text{N}_2,\text{o}_2}} X_{\text{N}_2} N_{\text{o}_2} + \frac{\tau}{cD_{\text{N}_2,\text{co}_2}} X_{\text{N}_2} N_{\text{co}_2}.
\end{align*}
\]

- The equilibrium equation at the electrode:

\[
\frac{X_{\text{co}_2}}{X_{\text{co}} X_{\text{o}_2}^{1/2}} = K_I \sqrt{P} \text{ at } x = \ell.
\]

- Mass conservation at the electrode:

\[
\begin{align*}
N_{\text{co}} &= -N_{\text{co}_2} \\
N_{\text{co}} &= 2N_{\text{o}_2} \\
N_{\text{N}_2} &= 0
\end{align*}
\text{ at } x = \ell.
\]
There are eight unknown quantities in these equations: four mole fractions \( X_i \) and four fluxes \( N_i \). One way to think about this model is as a two point boundary value problem for a set of eight ordinary differential equations. Since we are considering steady state in a one-dimensional diffusion problem, the differential equations which describe the evolution of the \( N_i \) are trivially given by \( \partial N_i / \partial x = 0 \). Now we need eight boundary conditions. Four are given by specifying the composition of the gas in the exhaust corresponding to values of \( X_i \) at \( x = 0 \). The other four are given at the electrode (\( x = \ell \)) and are the equilibrium equation and mass conservation equations. In the differential equations given above we have already incorporated the knowledge that \( N_{N_2} \equiv 0 \) to eliminate some terms.

We can make the above equations dimensionless by using the transformations

\[
K_I \sqrt{P} = \frac{1}{\varepsilon} \\
x = \ell \xi \\
N_i = \frac{cD}{\ell \tau} \tilde{N}_i \\
D_{ij} = D_{ij}.
\]

The quantity \( 1/\varepsilon \) was introduced in order to indicate the expected large value of \( K_I \sqrt{P} \) and \( D \) is a reference diffusivity which we will choose to be \( D_{O_2,N_2} \). Thus, in dimensionless form and dropping the tildes on the fluxes, the model equations are

- Stefan-Maxwell:

\[
\begin{align*}
\frac{\partial X_{CO}}{\partial \xi} &= \frac{1}{D_{CO,O_2}}(X_{CO}N_{O_2} - X_{O_2}N_{CO}) + \frac{1}{D_{CO,CO_2}}(X_{CO}N_{CO_2} - X_{CO_2}N_{CO}) \\
&\quad - \frac{1}{D_{CO,N_2}}X_{N_2}N_{CO}, \\
\frac{\partial X_{O_2}}{\partial \xi} &= \frac{1}{D_{O_2,CO}}(X_{O_2}N_{CO} - X_{CO}N_{O_2}) + \frac{1}{D_{O_2,CO_2}}(X_{O_2}N_{CO_2} - X_{CO_2}N_{O_2}) \\
&\quad - \frac{1}{D_{O_2,N_2}}X_{N_2}N_{O_2}, \\
\frac{\partial X_{CO_2}}{\partial \xi} &= \frac{1}{D_{CO_2,CO}}(X_{CO_2}N_{CO} - X_{CO}N_{CO_2}) + \frac{1}{D_{CO_2,O_2}}(X_{CO_2}N_{O_2} - X_{O_2}N_{CO_2}) \\
&\quad - \frac{1}{D_{CO_2,N_2}}X_{N_2}N_{CO_2},
\end{align*}
\]

\[24\]
\[
\frac{\partial X_{N_2}}{\partial \xi} = \frac{1}{D_{N_2,CO}} X_{N_2} N_{CO} + \frac{1}{D_{N_2,O_2}} X_{N_2} N_{O_2} + \frac{1}{D_{N_2,CO_2}} X_{N_2} N_{CO_2}.
\]

- The equilibrium equation at the electrode:

\[
\frac{X_{CO_2}}{X_{CO} X_{O_2}^{1/2}} = 1/\varepsilon \text{ at } \xi = 1.
\]

- Mass conservation at the electrode:

\[
\begin{cases}
N_{CO} = -N_{CO_2} \\
N_{CO} = 2N_{O_2} \\
N_{N_2} = 0
\end{cases}
\text{ at } \xi = 1.
\]

Note that the only parameters that remain in the problem are \( \varepsilon \) and the diffusivity ratios \( D_{ij} \). Once again, the thickness of the porous layer and its tortuosity do not directly impact the solution, but we have implicitly assumed when writing these equations that the diffusion is slow enough so that equilibrium of the gases is attained at the platinum electrode.

### 6.3 Application: The general case.

#### A. Problem Setting.

Now we go back to our sensor problem. We use 1, 2, 3, 4, 5, 6 to denote, in the order given, the species \( O_2, CO, CO_2, H_2O, H_2, N_2 \). We use \( p \) and \( q \) to denote the flux of \( CO \) and \( H_2 \), respectively. Then we have, by the discussion in the previous sections,

\[
\begin{align*}
N_1 \ (= N_{O_2}) &= \frac{1}{2} (p + q), \\
N_2 \ (= N_{CO}) &= p, \\
N_3 \ (= N_{CO_2}) &= -p, \\
N_4 \ (= N_{H_2O}) &= -q, \\
N_5 \ (= N_{H_2}) &= q, \\
N_6 \ (= N_{N_2}) &= 0.
\end{align*}
\]
Here we remark that the last equation $N_6 = 0$ is consistent with the equation (6.11). In fact, we can calculate

$$
\sum_{i=1}^{6} m_i N_i = p \left( m_{\text{CO}} + \frac{1}{2} m_{\text{O}_2} - m_{\text{CO}_2} \right) + q \left( m_{\text{H}_2} + \frac{1}{2} m_{\text{O}_2} - m_{\text{H}_2\text{O}} \right) + m_{N_2} N_6
$$

$$
= m_{N_2} N_6,
$$

by using the fact that the molar weights satisfy $m_{\text{CO}} + \frac{1}{2} m_{\text{O}_2} = m_{\text{CO}_2}$ and $m_{\text{H}_2} + \frac{1}{2} m_{\text{O}_2} = m_{\text{H}_2\text{O}}$. Thus, the condition $N_6 = 0$ is equivalent to (6.11).

Now using $X_6 = 1 - \sum_{i=1}^{5} X_i$ to eliminate $X_6$, we can write the Stefan-Maxwell equations in the following (non-dimensional) form:

$$
x'(\xi) = b(p, q) + G(p, q)x, \quad \xi \in (0, 1), \tag{6.13}
$$

where $x = (X_1, X_2, X_3, X_4, X_5)^T$, $b = (b^1(p, q), b^2(p), b^3(q), b^4(q), b^5(q))^T$ is a known linear vector function of $p$ and $q$, and $G$ is a known $5 \times 5$ matrix with entries which are linear functions of $p$ and $q$.

Remark. In the Fick's law formulation, we took the diffusion coefficients $D_i$ as $D_{i,6}$, the diffusion coefficients of species $i$ in $N_2$. It is then an easy exercise to check that with the notation of (6.13), Fick’s law gives the equation

$$
x'(\xi) = b(p, q). \tag{6.14}
$$

Consequently, if the magnitude of $x$ is small, Fick’s law (6.14) and the Stefan-Maxwell law (6.13) are not very different.

With the initial condition

$$
x(0) = x_0
$$

the solution of (6.13) can be expressed as

$$
\tilde{x}(\xi) = \exp[G(p, q)\xi]x_0 + G^{-1}[p, q]\left( \exp[G(p, q)\xi] - I \right)b(p, q)
$$

where $I$ is the identity $5 \times 5$ matrix.
Finally, using the equilibrium conditions $X_{\text{CO}} \sqrt{X_{\text{O}_2}} = \varepsilon X_{\text{CO}_2}$ and $X_{\text{H}_2} \sqrt{X_{\text{O}_2}} = a \varepsilon X_{\text{H}_2 \text{O}}$, we obtain the algebraic equations for $p, q$:

$$
\begin{align*}
\left\{ \begin{array}{l}
x_2(p, q) \sqrt{x_1(p, q)} - \varepsilon x_3(p, q) = 0, \\
a x_2(p, q) x_4(p, q) - x_5(p, q) x_3(p, q) = 0.
\end{array} \right.
\end{align*}
$$

(6.15)

where $x_i(p, q)$ are given by

$$(x_1, x_2, x_3, x_4, x_5)^T = \exp[G(p, q)\xi] x_0 + G^{-1} \left( \exp[G(p, q)\xi] - I \right) b(p, q).$$

B. Numerical Technique.

There are two ways to solve (6.15), a system of two unknowns with two algebraic equations.

The first way is to use Mathematica by calling the command

\text{NSolve[ \{equation1,equation2\}, \{p,q\}]}

In such an application, one does not even need to know how the Mathematica program deals with such a complicated system.

The second way to solve (6.15) is an iteration method briefly described as follows:

Step 1. Pick the solution from Fick's law as our initial guess; we call it $(p^{old}, q^{old})$.

Step 2. Calculate $x(p, q, \xi)$ with $(p, q) = (p^{old}, q^{old})$.

Step 3. Observe that in leading order, for any small $\delta p, \delta q$,

$$x(p^{old} + \delta, q^{old} + \delta, \xi) \sim x(p^{old}, q^{old}, \xi) + [b_p \delta p + b_q \delta q] \xi$$

where $b_p := \frac{\partial}{\partial p}$ and $b_q := \frac{\partial}{\partial q}$ are constant vectors. Hence, assuming that $p = p^{old} + \delta p$ and $q = q^{old} + \delta q$ we can solve for $\delta p$ and $\delta q$ from the system

$$
\begin{align*}
\left(x_2(p^{old}, q^{old}) + b^2_p \delta p\right) \sqrt{x_1(p^{old}, q^{old}) + b^1_p \delta p + b^1_q \delta q} = \varepsilon \left(x_3(p^{old}, q^{old}) + b^3_p \delta p\right), \\
\left(a x_2(p^{old}, q^{old}) + b^2_p \delta p\right) \left(x_4(p^{old}, q^{old}) + b^4_q \delta q\right) = \left(x_5(p^{old}, q^{old}) + b^5_q \delta q\right) \left(x_3(p^{old}, q^{old}) + b^3_p \delta p\right).
\end{align*}
$$

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Step 4. Update \((p^{old}, q^{old})\) by \((p^{old} + \delta p, q^{old} + \delta q)\) and goto step 1 or exit the process if \(\delta p\) and \(\delta q\) are small enough.

C. Numerical Result.

We implemented the second scheme mentioned. The rate of convergence is extremely fast. In three to four iterations, \(\delta p\) and \(\delta q\) will be smaller than \(10^{-7}\). The solution is depicted in the following figures.

![Comparison of Fick's law (solid curve) and Stefan-Maxwell's law (dots).](image)

Figure 11: Comparison of Fick's law (solid curve) and Stefan-Maxwell's law (dots).
7 Conclusions

In sections 3, 4 and 5, models using Fick's law are given and the results are presented; in section 6, a model implementing the Stephan-Maxwell law is discussed. In section 5, where the solution of the simple model is presented, an important part of the results is figure 10. From this graph, we note that the outcome of our asymptotic analysis differs slightly from Logothetis' [2] experimental results. In fact, our tutor advised us that Logothetis' results are not accurate on the lean side, but they are reasonable elsewhere. On the other hand, our results seem reasonable on the lean side when comparing them to experimental data from other sensors. So we are left to explain the inaccuracy in our results on the rich side and at the stoichiometric point $\lambda = 1$.

As a whole, our investigations provide a good understanding how the oxygen sensor works. We do observe the jump in the graph of voltage versus $\lambda$ as expected. We've also learned what tools can be used to improve the model for future work.

Fick's law is used to establish the relation between the flux and the concentration gradients for the various chemical species. The accuracy of this law increases as the concentration of nitrogen becomes greater relative to the concentrations of other gases. Unfortunately the application of Fick's law does not preserve the total mole fractions. The Stephan-Maxwell law does preserve the mole fractions of the reactant species as well as maintaining other basic assumptions of electrochemical reactions. However, our computational results show little difference between the two types of model. Thus it seems that the changes in mole fractions of the reactants as computed when using Fick's law are indeed negligible. What's more, our asymptotic analysis shows that computational precision of both models is sufficient for comparison with the real experimental data. Hence the inaccuracy in the models arises from other factors.

The equilibrium assumption states that a certain ratio of the concentrations of reactants to the concentration of product is a known constant (3.5). In fact this constant can be found in the literature. To say this in less technical words, recall that in the sensor the gases first diffuse through the porous layer before reaching the platinum where the reaction happens. In the equilibrium assumption we take it that the reaction happens
very rapidly relative to the gas diffusion. Thus the concentrations of gas species at the platinum electrode depend on the porosity of the ceramic layer and not on the flux of gas species spawned by the reactions occurring at the electrode.

References

