

# Mathematical Model of Diffusivity in Gases Experiment

Ver 05.10

The Diffusivity in Gases experiment uses a Loschmidt diffusion apparatus in order to estimate the binary diffusivity of two inert gases, nitrogen and carbon dioxide. Experimental procedure consists of filling an insulated cell with carbon dioxide gas then allowing the gas to diffuse into an adjoining cell across a planar interface. The carbon dioxide gas is then flushed from each cell using excess nitrogen into a solid absorbent. The increase in absorbent mass is assumed to be due to absorption of carbon dioxide. The relative amounts absorbed after each cell is flushed are used to estimate the molar fractions in the two cells.

## DERIVATION OF AN ANALYTICAL SOLUTION TO EQUIMOLAR COUNTERDIFFUSION IN AN INSULATED CYLINDER

A Loschmidt diffusion cell is a classic example of the mass diffusion equation applied to an insulated cylinder. The counter diffusion of the two gases is assumed to occur only in one dimension and is governed by the differential equation

$$D_{ab} \frac{\partial^2 X_A}{\partial z^2} = \frac{\partial X_A}{\partial t} \quad (1)$$

where  $D_{ab}$  is the binary diffusion coefficient,  $X_A$  is the molar fraction of species A, and  $z$  is the direction of diffusion. In order to derive a complete, analytical solution to this equation, two boundary conditions and an initial condition are required. The diffusion apparatus setup is shown in Figure 1. The lower diffusion cell is represented by the lower half of the cylinder,  $-L < z < 0$ . The upper cell is shown as the upper half,  $0 < z < L$ . The mathematical representation of the physical system remains accurate if the boundaries are restated as  $0 < z < 2L$  (Figure 1). Insulated conditions at the endpoints of the cylinder provide the required boundary conditions. These boundary conditions can be stated as:

$$\left. \frac{\partial X_A}{\partial z} \right|_{z=0} = 0 \quad (2)$$

$$\left. \frac{\partial X_A}{\partial z} \right|_{z=+2L} = 0 \quad (3)$$

The initial value condition can be deduced from our experimental approach. Each cell is flushed of all gases except one. In the case of the lower cell, carbon dioxide, which is denser than air and nitrogen, remains. In the upper cell, nitrogen persists. The initial function describing molar fraction can be stated as:

$$X_A(z,0) = \begin{cases} 1 & 0 < z < L \\ 0 & L < z < 2L \end{cases} \quad (4)$$

In this system carbon dioxide has been chosen to be species A.

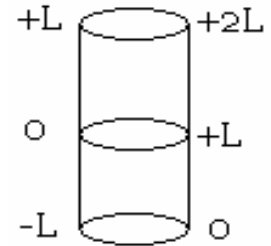


Figure 1: Loschmidt Diffusion Cell

The differential equation (1) with conditions (2-4) has an analytical solution. The boundary conditions (2-3) are homogenous so the method of Separation of Variables can be directly applied. It is assumed that the solution is a product of solutions, namely

$$X_A(z, t) = \phi(z)T(t) \quad (5)$$

This assumed form is substituted into equation (1) to yield:

$$\begin{aligned} D_{ab} \frac{\partial^2 X_A(z, t)}{\partial z^2} &= D_{ab} \frac{\partial^2 (\phi(z)T(t))}{\partial z^2} = D_{ab} \phi''(z)T(t) \\ \frac{\partial X_A(z, t)}{\partial t} &= \frac{\partial (\phi(z)T(t))}{\partial t} = \phi(z)T'(t) \\ D_{ab} \phi''(z)T(t) &= \phi(z)T'(t) \end{aligned} \quad (6)$$

The functions  $\phi(z)$  and  $T(t)$  can be separated by dividing both sides of equation (6) by  $D_{ab}\phi(z)T(t)$ . The result is

$$\frac{D_{ab} \phi''(z)T(t)}{D_{ab} \phi(z)T(t)} = \frac{\phi(z)T'(t)}{D_{ab} \phi(z)T(t)} \rightarrow \frac{\phi''(z)}{\phi(z)} = \frac{1}{D_{ab}} \frac{T'(t)}{T(t)} \quad (7)$$

Values of  $z$  and  $t$  are allowed to range over all possible real numbers simultaneously. Thus, it can be concluded that each side of equation (7) equals a constant. In other words,

$$\frac{\phi''(z)}{\phi(z)} = \frac{1}{D_{ab}} \frac{T'(t)}{T(t)} = -\lambda^2 \quad (8)$$

The choice of the constant  $-\lambda^2$  was arbitrary, chosen for its convenience later. Equation (8) can be seen as two equations,

$$\frac{\phi''(z)}{\phi(z)} = -\lambda^2 \quad (9)$$

$$\frac{1}{D_{ab}} \frac{T'(t)}{T(t)} = -\lambda^2 \quad (10)$$

Grouping all non-zero terms on the left side of equations (9) and (10), two ODE's are obtained,

$$\phi''(z) + \lambda^2 \phi(z) = 0 \quad (11)$$

$$T'(t) + D_{ab} \lambda^2 T(t) = 0 \quad (12)$$

The functions  $\phi(z)$  and  $T(t)$  have now been successfully separated from one PDE into two ODE's.

An accepted form of the solution to equation (12) is

$$T(t) = C e^{-\lambda^2 D_{ab} t} \quad (13)$$

The pre-exponential constant  $C$  is simply assumed to equal 1 and is discarded. (This is acceptable because if the solution where  $C=1$  exists, then any solution where  $C$  is some multiple of 1 also exists).

The solution form assumed for equation (11) is

$$\phi(z) = \alpha \cos(\lambda z) + \beta \sin(\lambda z) \quad (14)$$

The choice of  $-\lambda^2$  is now seen as handy in keeping equation (14) tidy.

The values for  $\alpha$  and  $\beta$  are determined by using the boundary conditions. Substitution of equation (5) into conditions (2) and (3) yields

$$\left. \frac{\partial X_A}{\partial z} \right|_{z=0} = \left. \frac{\partial(\phi(z)T(t))}{\partial z} \right|_{z=0} = T(t) \left. \frac{\partial\phi(z)}{\partial z} \right|_{z=0} = 0 \rightarrow \phi'(0) = 0 \quad (15)$$

$$\left. \frac{\partial X_A}{\partial z} \right|_{z=2L} = \left. \frac{\partial(\phi(z)T(t))}{\partial z} \right|_{z=2L} = T(t) \left. \frac{\partial\phi(z)}{\partial z} \right|_{z=2L} = 0 \rightarrow \phi'(2L) = 0 \quad (16)$$

The derivative operation is performed on equation (14) to give

$$\phi'(z) = -\alpha\lambda\text{Sin}(\lambda z) + \beta\lambda\text{Cos}(\lambda z) \quad (17)$$

The first boundary condition, equation (15), is substituted into equation (17)

$$\phi'(0) = -\alpha\lambda\text{Sin}(0) + \beta\lambda\text{Cos}(0) = 0 \rightarrow \beta\lambda = 0 \quad (18)$$

There are two possibilities that satisfy equation (18). Either  $\beta$  or  $\lambda$  is equal to zero. If  $\lambda = 0$  then the time-dependant solution in equation (13) becomes trivial,  $T(t)=1$ . Consequently, it is concluded that  $\beta = 0$ . The other condition, equation (16), is substituted into equation (17)

$$\phi'(2L) = -\alpha\lambda\text{Sin}(2\lambda L) + \beta\lambda\text{Cos}(2\lambda L) = 0 \rightarrow -\alpha\lambda\text{Sin}(2\lambda L) = 0 \quad (19)$$

The cosine term is discarded because  $\beta = 0$ , shown previously. Equation (19) is satisfied if  $\alpha$ ,  $\lambda$ , or the sine term equals zero. The option  $\alpha = 0$  is unacceptable because it would cause the position-dependant solution to be trivial. The second option,  $\lambda = 0$ , was rejected with the first boundary condition. What remains is the equality

$$\text{Sin}(2\lambda L) = 0 \quad (20)$$

Equation (20) is valid when the argument  $2\lambda L$  is some multiple of  $\pi$ . This occurs when

$$2\lambda L = n\pi \rightarrow \lambda_n = \frac{n\pi}{2L} \quad (21)$$

This equation establishes the eigenvalues  $\lambda_n$  which give rise to the eigenfunctions that satisfy equation (20). The term  $n$  is the set of integers: 0,1,2,3,...,etc. The constant  $\alpha$  is assumed to equal 1 in a similar fashion as the pre-exponential constant in the time-dependant solution. The position-dependant solution is

$$\phi_n(z) = \text{Cos}(\lambda_n z) \quad (22)$$

Each value of  $n$  gives rise to a solution. The collection of possible solutions can be collected into one function by using an infinite summation

$$\phi(z) = \sum_{n=0}^{\infty} a_n \phi_n(z) \quad (23)$$

Combining equations (13) and (23) the overall solution becomes

$$X_A(z, t) = \sum_{n=0}^{\infty} a_n \phi_n(z) e^{-\lambda_n^2 D_{ab} t} \quad (24)$$

This solution is in the form of a Fourier series. This form allows the summation coefficients  $a_n$  to be determined. The initial condition (4) is used to determine these coefficients

$$a_0 = \frac{1}{2L} \int_0^{2L} f(z) dz = \frac{1}{2L} \int_0^L dz \rightarrow a_0 = \frac{1}{2} \quad (25)$$

$$a_n = \frac{2}{2L} \int_0^{2L} f(z) \text{Cos}(\lambda_n z) dz = \frac{1}{L} \int_0^L \text{Cos}(\lambda_n z) dz \rightarrow a_n = \frac{\text{Sin}(\lambda_n L)}{\lambda_n L} \quad (26)$$

The overall solution is then

$$X_A(z,t) = a_0 + \sum_{n=1}^{\infty} a_n \text{Cos}(\lambda_n z) e^{-\lambda_n D_{ab} t} = \frac{1}{2} + \sum_{n=1}^{\infty} \frac{\text{Sin}(\lambda_n L)}{\lambda_n L} \text{Cos}(\lambda_n z) e^{-\lambda_n D_{ab} t} \quad (27)$$

This expression gives the molar fraction at a specific point in space and time. An average molar fraction in the lower cell can be expressed as:

$$\overline{X}_{A,L}(t) = \frac{\int_0^L X_A(z,t) dz}{L} = \frac{1}{2} + \sum_{n=1}^{\infty} \left( \frac{\text{Sin}(\lambda_n L)}{\lambda_n L} \right)^2 e^{-\lambda_n^2 D_{ab} t} \quad (24)$$

The sine term contains the argument  $\lambda_n L = n\pi/2$  which is a multiple of  $\pi/2$  on odd values of  $n$  and a multiple of  $\pi$  on even values. Therefore, the even summation terms in equation (27) equal zero. In order to discard them, a change in summation index is required. Since only the odd terms are desired, i.e. the  $2k+1$  terms, any term  $n$  is replaced by  $2k+1$  and the starting index value becomes  $k=0$ . The expression for molar fraction in the lower cell then is

$$\overline{X}_A(t) = \frac{1}{2} + \frac{4}{\pi^2} \sum_{k=0}^{\infty} \frac{1}{(2k+1)^2} e^{-\left(\frac{(2k+1)\pi}{2L}\right)^2 D_{ab} t} \quad (29)$$

For the upper cell, the expression for average molar fraction is identical except the “+” after the “1/2” term is replaced with a “-“ sign.

A more general description of the initial molar fractions in the cells doesn't assume pure gases in the cells; the initial condition (Eq (4)) becomes:

$$X_A(z) = \begin{cases} x_{L,0} & 0 < z < L \\ x_{U,0} & L < z < 2L \end{cases} \quad (30)$$

where the lower and upper cell molar fractions of carbon dioxide are  $x_{L,0}$  and  $x_{U,0}$ , respectively. Since the boundary conditions remain homogenous the method of Separation of Variables can be used in a similar manner as applied to the previous initial condition. The overall solution is:

$$X_A(z,t) = \frac{1}{2}(x_{L,0} + x_{U,0}) + \sum_{n=1}^{\infty} (x_{L,0} - x_{U,0}) \frac{\text{Sin}(\lambda_n L)}{\lambda_n L} \text{Cos}(\lambda_n z) e^{-\lambda_n D_{ab} t} \quad (31)$$

Using this result, the average molar fraction in each cell is given by:

$$\overline{X}_A(t) = \frac{1}{2}(x_{L,0} + x_{U,0}) \pm \frac{4}{\pi^2} (x_{L,0} - x_{U,0}) \sum_{k=0}^{\infty} \frac{1}{(2k+1)^2} e^{-\left(\frac{(2k+1)\pi}{2L}\right)^2 D_{ab} t} \quad (32)$$

## MODELING OF THE CELL FLUSHING MECHANISM

The amount of time necessary to flush a diffusion cell of a specified percentage of carbon dioxide initially present depends on the molar fraction of CO<sub>2</sub> in the gas exiting the cell being flushed as a function of time. In mathematical terms,

$$\alpha = \frac{1}{\overline{X}_{A,o}} \int_0^{t_A} X_o(t) dt \quad (33)$$

where the desired percentage is  $\alpha$ , the initial overall molar fraction of species A is  $\overline{X}_{A,o}$ , and  $X_o(t)$  is the molar fraction of species A in the exiting gas. The purpose of this section is to derive an expression for  $X_o(t)$ . Differential methods differ in the chosen control volume.

## METHOD #1: CONTROL VOLUME IS THE ENTIRE DIFFUSION CELL

If the entire diffusion cell is chosen as the control volume, then imagine a box drawn around the cell. The change in the amount of carbon dioxide in the cell equals the inflow  $M_{IN}$  minus the outflow  $M_{OUT}$  of carbon dioxide. In differential form

$$\frac{\partial M_{A,C}}{\partial t} = M_{IN} - M_{OUT} \quad (34)$$

where  $M_{A,C}$  is the amount of CO<sub>2</sub> in the cell. Assuming the gases act ideally, the masses of carbon dioxide equal

$$M_{A,C} = \frac{MW_A PV_T}{RT} \bar{X}_A \quad (35)$$

$$M_{IN} = \frac{MW_A PV_F}{RT} X_{A,IN} \quad (36)$$

$$M_{OUT} = \frac{MW_A PV_F}{RT} X_{A,OUT} \quad (37)$$

the terms are

$MW_A$  = molecular weight of species A (CO<sub>2</sub>)

$P$  = absolute pressure

$V_T$  = cell volume

$V_F$  = volumetric flow rate of flushing stream

$\bar{X}_A$  = average molar fraction of species A in cell

$X_{A,IN}$  = molar fraction of species A in inlet stream

$X_{A,OUT}$  = molar fraction of species A in outlet stream

$R$  = ideal gas constant

$T$  = absolute temperature

If the pressures and temperatures of the cell and both streams are equal and the flushing flow rate is constant then equations (35-37) can be used to reduce equation (34) to:

$$V_T \frac{\partial \bar{X}_A}{\partial t} = V_F X_{A,IN} - V_F X_{A,OUT} \quad (38)$$

In this experiment the flushing gas is pure nitrogen. Therefore equation (38) simplifies to

$$\frac{\partial \bar{X}_A}{\partial t} = -\frac{V_F}{V_T} X_{A,OUT} \quad (39)$$

If it assumed that perfect mixing occurs during the flushing process then the exiting gas has the same molar fraction of species A as the entire cell. This is stated as

$$X_{A,OUT} = \bar{X}_A \quad (40)$$

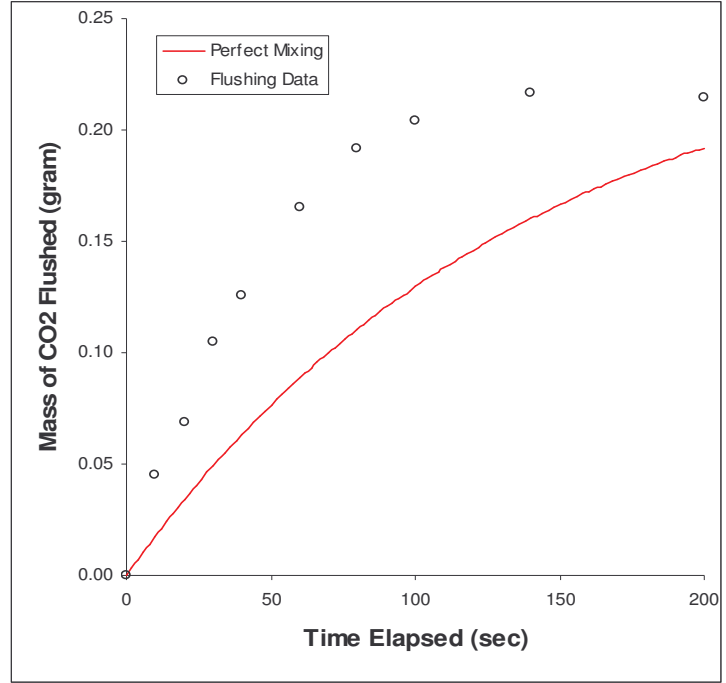
Substitution of equation (40) into equation (39) produces the differential equation

$$\frac{\partial \bar{X}_A}{\partial t} = -\frac{V_F}{V_T} \bar{X}_A \quad (41)$$

An accepted solution to equation (41) is

$$\bar{X}_A(t) = \bar{X}_{A,o} e^{-\frac{V_F t}{V_T}} \quad (42)$$

Experimental data of amount of CO<sub>2</sub> flushed versus elapsed flushing time is graphed in Figure 2. The amount of CO<sub>2</sub> flushed as predicted by equation (42) is also plotted. Comparison of the model predictions to the experimental data indicates the model to be inaccurate. It is likely that assumption (40) is invalid.



## METHOD #2: CONTROL VOLUME IS AN INFINITESIMAL VOLUME

This method uses a disk of area  $A_C$  and infinitesimal thickness  $\Delta z$ . In this method, nitrogen will be chosen as species A. The accumulation in the control volume is

$$\frac{\partial M_{A,C}}{\partial t} = A_C \frac{\partial C_A}{\partial t} \Delta z \quad (43)$$

with overall concentration of species A as  $C_A$ . The flow of species A into and out of the control volume are. Respectively,

$$M_{IN} = X_{A,IN} N_{IN} - D_{AB} A_C \left. \frac{\partial C_A}{\partial z} \right|_z \quad (44)$$

$$M_{OUT} = X_{A,OUT} N_{OUT} - D_{AB} A_C \left. \frac{\partial C_A}{\partial z} \right|_{z+\Delta z} \quad (45)$$

where  $D_{AB}$  is the binary diffusivity and  $X_{A,i}$  is the molar fraction of species A in stream  $i$ . Combining equations (43-45) in a mass balance produces

$$A_C \frac{\partial C_A}{\partial t} \Delta z = X_{A,IN} N_{IN} - D_{AB} A_C \left. \frac{\partial C_A}{\partial z} \right|_z - X_{A,OUT} N_{OUT} + D_{AB} A_C \left. \frac{\partial C_A}{\partial z} \right|_{z+\Delta z} \quad (46)$$

If it assumed that the gases behave ideally, the pressures and temperatures of all streams are equal, and the flushing flow rate is constant, then equation (46) becomes

$$A_C \frac{\partial X_A}{\partial t} \Delta z = V_F (X_{A,IN} - X_{A,OUT}) + D_{AB} A_C \left( \left. \frac{\partial X_A}{\partial z} \right|_{z+\Delta z} - \left. \frac{\partial X_A}{\partial z} \right|_z \right) \quad (47)$$

Dividing both sides of equation (47) by  $A_C \Delta z$  results in

$$\frac{\partial X_A}{\partial t} = \frac{V_F}{A_C} \frac{(X_{A,IN} - X_{A,OUT})}{\Delta z} + D_{AB} \frac{1}{\Delta z} \left( \frac{\partial X_A}{\partial z} \Big|_{z+\Delta z} - \frac{\partial X_A}{\partial z} \Big|_z \right) \quad (48)$$

As  $\Delta z \rightarrow 0$  equation (48) becomes the partial differential equation

$$D_{AB} \frac{\partial^2 X_A}{\partial z^2} + \frac{V_F}{A_C} \frac{\partial X_A}{\partial z} = \frac{\partial X_A}{\partial t} \quad (49)$$

Solution of this PDE requires two boundary conditions and an initial condition. If it is assumed that the exiting gas has the same molar fraction as the infinitesimal disk of gas at the exit then the change in molar fraction at the exit is zero. In symbolic terms,

$$\frac{\partial X_A}{\partial z} \Big|_{z=L} = 0 \quad (50)$$

At the cell entrance the inlet gas is assumed to be pure nitrogen ( $X_A = 1$ ). The change in molar fraction at the entrance is the difference between the inlet gas and the molar fraction at the entrance at that point in time.

$$\frac{\partial X_A}{\partial z} \Big|_{z=0} = 1 - X_A(L, t) \quad (51)$$

These boundary conditions are classified as Robin boundary conditions. If flushing occurs soon enough after diffusion between the cells is stopped then the initial condition is given by

$$X_A(z, 0) = 1 - X_{ACO_2}(z) \quad (52)$$

where  $X_{ACO_2}(z)$  is the expression given in equation (27). Conditions (50-52) cause the solution to equation (49) to be a series of eigenfunctions with eigenvalues that are solutions to a transcendental function. Consequently, the simplest solution method is numerical. Predictions of this model in comparison to experimental flushing data is plotted in Figure 3. This model appears to agree with experimental data quite well.

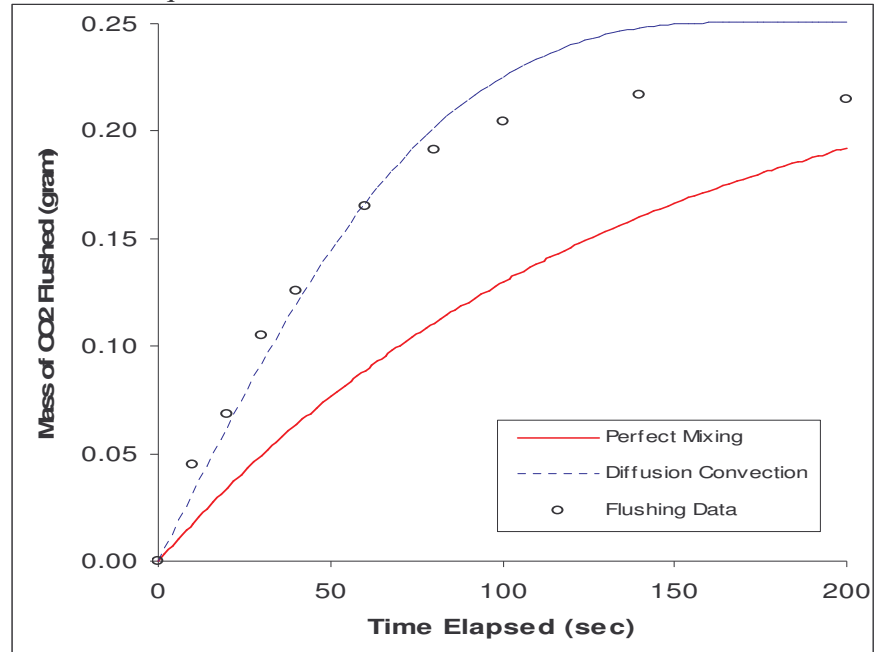


Figure 3: Comparison of Flushing Models and Experimental Data

## ABSORPTION CONSIDERATIONS

A final item to consider is the ability of the absorbent to adequately absorb the flushed gas. A comparison of absorption versus time for two different flushing flow rates (all other factors being equal) is shown in Figure 4. Apparently, as the flushing rate increases from 0.25 SCFH to 0.50 SCFH the absorption mechanism becomes nonlinear. Consequently, this experiment is conducted at flushing rates of 0.25 SCFH or less.

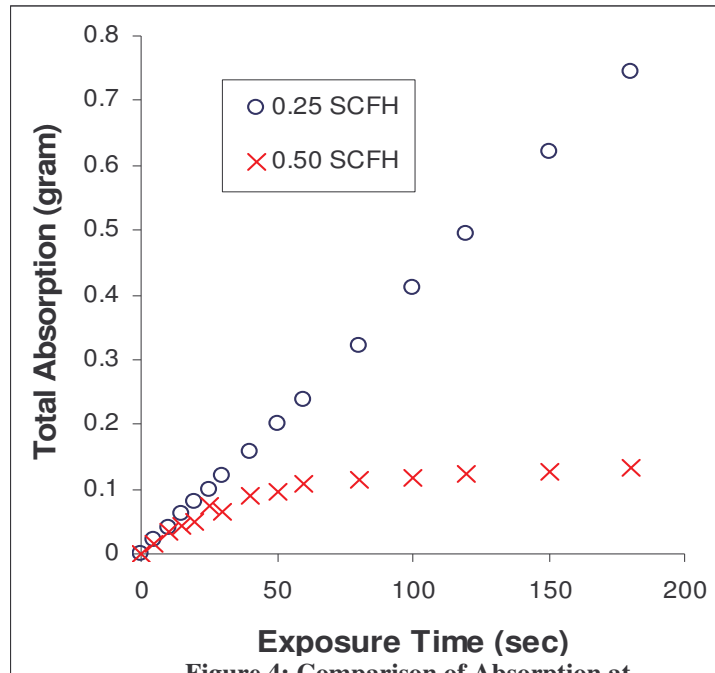


Figure 4: Comparison of Absorption at Different Flushing Rates