1 Nonlinear system

1.1 Discretization

From Eq. **??**,

$$0 = D_i \frac{\partial^2 C_i}{\partial z^2} - \frac{\partial (x_i \mathbf{N})}{\partial z} + \frac{4 s_i \nu}{\Phi}.$$

Recall that the molar fraction x_i is a function of gas concentration C_i. Particularly

$$x_i = \frac{C_i}{\sum_j C_j} = \frac{C_i}{C_i + \sum_{j \neq i} C_j}. \tag{1}$$

Substituting,

$$\frac{\partial^2 C_i}{\partial z^2} - \frac{1}{D_i} \frac{\partial}{\partial z} \left(\frac{C_i}{C_i + \sum_{j \neq i} C_j} \mathbf{N} \right) + \frac{4 s_i \nu}{D_i \Phi} = 0. \tag{2}$$

Expanding,

$$0 = \frac{C_{i,j-1} - 2C_{i,j} + C_{i,j+1}}{h^2} - \frac{1}{D_{i,j}} \left(\frac{\frac{C_{i,j+1}\mathbf{N}_{j+1}}{C_{i,j+1} + \sum_{k \neq i} C_{k,j+1}} - \frac{C_{i,j-1}\mathbf{N}_{j-1}}{C_{i,j-1} + \sum_{k \neq i} C_{k,j-1}}}{2h} \right) + \frac{4 s_i \nu_j}{D_{i,j} \Phi_j} \tag{3}$$

$$= \frac{1}{h^2} \left(C_{i,j-1} - 2C_{i,j} + C_{i,j+1} \right) - \frac{1}{2 D_{i,j} h} \left(\frac{C_{i,j+1}\mathbf{N}_{j+1}}{C_{i,j+1} + \sum_{k \neq i} C_{k,j+1}} - \frac{C_{i,j-1}\mathbf{N}_{j-1}}{C_{i,j-1} + \sum_{k \neq i} C_{k,j-1}} \right) + \frac{4 s_i \nu_j}{D_{i,j} \Phi_j}. \tag{4}$$

This is the equation used to solve for the concentration of gas $i \in [0, 2]$ at grid point $j \in [0, n+1]$.

1.2 BCs

The three gases in this application are $\{C_{0,j},\ C_{1,j},\ C_{2,j}\} = \{C_{MTS,j},\ C_{H2,j},\ C_{HCl,j}\}$. This means $i = \{0, 1, 2\} = \{MTS, H2, HCl\}$. Boundary conditions are

$$C_{0,0} = P/RT(1+\alpha) = \overline{C_{MTS0}},\ \ C_{1,0} = \alpha P/RT(1+\alpha) = \overline{C_{H20}},\ \ C_{2,0} = 0 = \overline{C_{HCl0}},\ \text{Left side}, \tag{5}$$

$$C_{0,n+1} = C_{0,n},\ \ C_{1,n+1} = C_{1,n},\ \ C_{2,n+1} = C_{2,n},\ \ \text{Right side}. \tag{6}$$

Here, $\alpha = C_1/C_0$ is the gas ratio of the reactants H2 and MTS, and the CVI chamber has isobaric and isothermal conditions P and T. We assemble the constituent vector

quantities in Eq. 4 as

$$\{C_{i,j}\} = \begin{Bmatrix} C_{0,0} \\ C_{1,0} \\ C_{2,0} \\ C_{0,1} \\ C_{1,1} \\ C_{2,1} \\ \cdots \\ C_{0,n} \\ C_{1,n} \\ C_{2,n} \\ C_{0,n+1} \\ C_{1,n+1} \\ C_{2,n+1} \end{Bmatrix}, \{D_{i,j}\} = \begin{Bmatrix} D_{0,0} \\ D_{1,0} \\ D_{2,0} \\ D_{0,1} \\ D_{1,1} \\ D_{2,1} \\ \cdots \\ D_{0,n} \\ D_{1,n} \\ D_{2,n} \\ D_{0,n+1} \\ D_{1,n+1} \\ D_{2,n+1} \end{Bmatrix}, \{\mathbf{N}_j\} = \begin{Bmatrix} \mathbf{N}_0 \\ \mathbf{N}_1 \\ \mathbf{N}_2 \\ \cdots \\ \mathbf{N}_{n-1} \\ \mathbf{N}_n \\ \mathbf{N}_{n+1} \end{Bmatrix}, \{\nu_j\} = \begin{Bmatrix} \nu_0 \\ \nu_1 \\ \nu_2 \\ \cdots \\ \nu_{n-1} \\ \nu_n \\ \nu_{n+1} \end{Bmatrix}, \{\Phi_j\} = \begin{Bmatrix} \Phi_0 \\ \Phi_1 \\ \Phi_2 \\ \cdots \\ \Phi_{n-1} \\ \Phi_n \\ \Phi_{n+1} \end{Bmatrix}, \tag{7}$$

$$\{s_i\} = \begin{Bmatrix} s_0 \\ s_1 \\ s_2 \end{Bmatrix}. \tag{8}$$

This way, the location of points $C_{i,j}$ and $D_{i,j}$ are $C[3j+i]$ and $D[3j+i]$, the locations of $\mathbf{N}_j, \nu_j, \Phi_j$ are $\mathbf{N}[j], \nu[j], \Phi[j]$, and the location of s_i is $s[i]$.

Applying boundary conditions,

$$\{C_{i,j}\} = \begin{Bmatrix} \overline{C_{MTS0}} \\ \overline{C_{H20}} \\ \overline{C_{HCl0}} \\ C_{0,1} \\ C_{1,1} \\ C_{2,1} \\ \cdots \\ C_{0,n} \\ C_{1,n} \\ C_{2,n} \\ C_{0,n} \\ C_{1,n} \\ C_{2,n} \end{Bmatrix}. \tag{9}$$

The total number of entries in each vector are the following: $\{C_{i,j}\} = \{D_{i,j}\} = 3(n+2)$, $\{\mathbf{N}_j\} = \{\nu_j\} = \{\Phi_j\} = n+2$, $\{s_i\} = 3$. However, notice that 6 of the gas concentration values $C_{i,0}$ and $C_{i,n+1}$ are no longer unknowns. Then to find a solution we reduce to a

system of $3n$ equations solving for $3n$ unknowns at n grid points, or

$$\{C_{i,j}\} = \begin{Bmatrix} C_{0,1} \\ C_{1,1} \\ C_{2,1} \\ \cdots \\ C_{0,n} \\ C_{1,n} \\ C_{2,n} \end{Bmatrix}, \{D_{i,j}\} = \begin{Bmatrix} D_{0,1} \\ D_{1,1} \\ D_{2,1} \\ \cdots \\ D_{0,n} \\ D_{1,n} \\ D_{2,n} \end{Bmatrix}, \{\mathbf{N}_j\} = \begin{Bmatrix} \mathbf{N}_0 \\ \mathbf{N}_1 \\ \mathbf{N}_2 \\ \cdots \\ \mathbf{N}_{n-1} \\ \mathbf{N}_n \\ \mathbf{N}_{n+1} \end{Bmatrix}, \{\nu_j\} = \begin{Bmatrix} \nu_1 \\ \nu_2 \\ \cdots \\ \nu_{n-1} \\ \nu_n \end{Bmatrix}, \{\Phi_j\} = \begin{Bmatrix} \Phi_1 \\ \Phi_2 \\ \cdots \\ \Phi_{n-1} \\ \Phi_n \end{Bmatrix}, \tag{10}$$

$$\{s_i\} = \begin{Bmatrix} s_0 \\ s_1 \\ s_2 \end{Bmatrix}. \tag{11}$$

Now, the locations of the entries $C_{i,j}$ and $D_{i,j}$ are $C[3(j-1)+i]$ and $D[3(j-1)+i]$, the locations of $\mathbf{N}_j, \nu_j, \Phi_j$ are $\mathbf{N}[j], \nu[j-1], \Phi[j-1]$, and the location of s_i is $s[i]$. This means the new lengths of each vector are $\{C_{i,j}\} = \{D_{i,j}\} = 3n$, $\{\nu_j\} = \{\Phi_j\} = n$, $\{\mathbf{N}_j\} = n+2$, and $\{s_i\} = 3$. (Notice that $\mathbf{N}$ does not change. This is because the entries at the endpoints $j = 0, n+1$ are needed as part of the central difference approximations for $j = 1, n$.)

1.3 j in [2,n-1]

Substituting this into the nonlinear solution to the concentration of gas i at point $j \in [1, n]$,

$$0 = \frac{1}{h^2}\Big(C[3(j-2)+i] - 2C[3(j-1)+i] + C[3j+i]\Big) + \frac{4s[i]\nu[j-1]}{D[3(j-1)+i]\Phi[j-1]}$$

$$-\frac{1}{2D[3(j-1)+i]]h}\left(\frac{C[3j+i]\mathbf{N}[j+1]}{C[3j+i]+\sum_{k\neq i}C[3j+k]} - \frac{C[3(j-2)+i]\mathbf{N}[j-1]}{C[3(j-2)+i]+\sum_{k\neq i}C[3(j-2)+k]}\right). \tag{12}$$

In terms of the code, the expression $\sum_{k\neq i} C[3j+k]$ is different depending on i. Particularly,

$$i = 0 \to \sum_{k\neq i} C[3j+k] = C[3j+1] + C[3j+2], \tag{13}$$

$$i = 1 \to \sum_{k\neq i} C[3j+k] = C[3j+2] + C[3j], \tag{14}$$

$$i = 2 \to \sum_{k\neq i} C[3j+k] = C[3j+1] + C[3j]. \tag{15}$$

The analogous is true for $\sum_{k\neq i} C[3(j-2)+k]$:

$$i = 0 \to \sum_{k\neq i} C[3(j-2)+k] = C[3(j-2)+1] + C[3(j-2)+2], \tag{16}$$

$$i = 1 \rightarrow \sum_{k \neq i} C[3(j-2)+k] = C[3(j-2)+2] + C[3(j-2)], \tag{17}$$

$$i = 2 \rightarrow \sum_{k \neq i} C[3(j-2)+k] = C[3(j-2)+1] + C[3(j-2)]. \tag{18}$$

Substituting this in,

1.3.1 i=0

$$0 = \frac{1}{h^2}\Big(C[3(j-2)] - 2C[3(j-1)] + C[3j]\Big) + \frac{4s[0]\nu[j-1]}{D[3(j-1)]\Phi[j-1]}$$
$$-\frac{1}{2D[3(j-1)]h}\left(\frac{C[3j]\mathbf{N}[j+1]}{C[3j]+C[3j+1]+C[3j+2]} - \frac{C[3(j-2)]\mathbf{N}[j-1]}{C[3(j-2)]+C[3(j-2)+1]+C[3(j-2)+2]}\right). \tag{19}$$

1.3.2 i=1

$$0 = \frac{1}{h^2}\Big(C[3(j-2)+1] - 2C[3(j-1)+1] + C[3j+1]\Big) + \frac{4s[1]\nu[j-1]}{D[3(j-1)+1]\Phi[j-1]}$$
$$-\frac{1}{2D[3(j-1)+1]h}\left(\frac{C[3j+1]\mathbf{N}[j+1]}{C[3j+1]+C[3j+2]+C[3j]} - \frac{C[3(j-2)+1]\mathbf{N}[j-1]}{C[3(j-2)+1]+C[3(j-2)+2]+C[3(j-2)]}\right) \tag{20}$$

1.3.3 i=2

$$0 = \frac{1}{h^2}\Big(C[3(j-2)+2] - 2C[3(j-1)+2] + C[3j+2]\Big) + \frac{4s[2]\nu[j-1]}{D[3(j-1)+1]\Phi[j-1]}$$
$$-\frac{1}{2D[3(j-1)+2]h}\left(\frac{C[3j+2]\mathbf{N}[j+1]}{C[3j+2]+C[3j+1]+C[3j]} - \frac{C[3(j-2)+2]\mathbf{N}[j-1]}{C[3(j-2)+2]+C[3(j-2)+1]+C[3(j-2)]}\right) \tag{21}$$

For $j \in [2, n-1]$, Eq. 12 is a permissible input into the nonlinear solver. However, adjustments need to made for points $j = 1, n$. This is because the equations which solve for the concentrations at those points do not contain as many unknowns.

1.4 j=1

For example, consider the case $j = 1$. Then

$$0 = \frac{1}{h^2}\Big(C[-3+i] - 2C[i] + C[3+i]\Big) + \frac{4s[i]\nu[0]}{D[i]\Phi[0]}$$
$$-\frac{1}{2D[i]]h}\left(\frac{C[3+i]\mathbf{N}[2]}{C[3+i]+\sum_{k\neq i}C[3+k]} - \frac{C[-3+i]\mathbf{N}[0]}{C[-3+i]+\sum_{k\neq i}C[-3+k]}\right). \tag{22}$$

Because $i \in [0, 2]$, there is no such index as $[-3+i]$. However the values at these ghost points are known; they are the left side boundary conditions. So we must manually substitute in $C_{i,0} = \{\overline{C_{MTS0}}, \overline{C_{H20}}, \overline{C_{HCl0}}\}$. Particularly,

1.4.1 i=0

$$i=0 \Longrightarrow \frac{1}{h^2}\left(\overline{C_{MTS0}}-2C[0]+C[3]\right)+\frac{4s[0]\nu[0]}{D[0]\Phi[0]}$$
$$-\frac{1}{2D[0]]h}\left(\frac{C[3]\mathbf{N}[2]}{C[3]+C[4]+C[5]}-\frac{\overline{C_{MTS0}}\mathbf{N}[0]}{\overline{C_{MTS0}}+\overline{C_{H20}}+\overline{C_{HCl0}}}\right)=0, \tag{23}$$

1.4.2 i=1

$$i=1 \Longrightarrow \frac{1}{h^2}\left(\overline{C_{H20}}-2C[1]+C[4]\right)+\frac{4s[1]\nu[0]}{D[1]\Phi[0]}$$
$$-\frac{1}{2D[1]]h}\left(\frac{C[4]\mathbf{N}[2]}{C[4]+C[5]+C[3]}-\frac{\overline{C_{H20}}\mathbf{N}[0]}{\overline{C_{H20}}+\overline{C_{HCl0}}+\overline{C_{MTS0}}}\right)=0, \tag{24}$$

1.4.3 i=2

$$i=2 \Longrightarrow \frac{1}{h^2}\left(\overline{C_{HCl0}}-2C[2]+C[5]\right)+\frac{4s[2]\nu[0]}{D[2]\Phi[0]}$$
$$-\frac{1}{2D[2]]h}\left(\frac{C[5]\mathbf{N}[2]}{C[5]+C[4]+C[3]}-\frac{\overline{C_{HCl0}}\mathbf{N}[0]}{\overline{C_{HCl0}}+\overline{C_{H20}}+\overline{C_{MTS0}}}\right)=0. \tag{25}$$

1.5 j=n

If $j=n$, then Eq. 12 leads to

$$0=\frac{1}{h^2}\left(C[3(n-2)+i]-2C[3(n-1)+i]+C[3n+i]\right)+\frac{4s[i]\nu[n-1]}{D[3(n-1)+i]\Phi[n-1]}$$
$$-\frac{1}{2D[3(n-1)+i]]h}\left(\frac{C[3n+i]\mathbf{N}[n+1]}{C[3n+i]+\sum_{k\neq i}C[3n+k]}-\frac{C[3(n-2)+i]\mathbf{N}[n-1]}{C[3(n-2)+i]+\sum_{k\neq i}C[3(n-2)+k]}\right). \tag{26}$$

However, there is no such index as $C[3n+i]$ for a vector with length $3n$, which was established at the very end of Sec. 1.2. However these values are known as the right side boundary condition. Particularly, $C_{i,n+1}=C_{i,n} \leftrightarrow C[3n+i]=C[3(n-1)+i]$. Substituting this in,

$$0=\frac{1}{h^2}\left(C[3(n-2)+i]-C[3(n-1)+i]\right)+\frac{4s[i]\nu[n-1]}{D[3(n-1)+i]\Phi[n-1]}$$
$$-\frac{1}{2D[3(n-1)+i]]h}\left(\frac{C[3(n-1)+i]\mathbf{N}[n+1]}{C[3(n-1)+i]+\sum_{k\neq i}C[3(n-1)+k]}-\frac{C[3(n-2)+i]\mathbf{N}[n-1]}{C[3(n-2)+i]+\sum_{k\neq i}C[3(n-2)+k]}\right. \tag{27}$$

1.5.1 i=0

$$i=0 \implies 0=\frac{1}{h^2}\Big(C[3(n-2)]-C[3(n-1)]\Big)+\frac{4s[0]\nu[n-1]}{D[3(n-1)]\Phi[n-1]}$$
$$-\frac{1}{2D[3(n-1)]]h}\Bigg(\frac{C[3(n-1)]\mathbf{N}[n+1]}{C[3(n-1)]+\underbrace{\sum_{k\neq i}C[3(n-1)+k]}_{C[3(n-1)+1]+C[3(n-1)+2]}}-\frac{C[3(n-2)]\mathbf{N}[n-1]}{C[3(n-2)]+\underbrace{\sum_{k\neq i}C[3(n-2)+k]}_{C[3(n-2)+1]+C[3(n-2)+2]}}\Bigg). \tag{28}$$

1.5.2 i=1

$$i=1 \implies 0=\frac{1}{h^2}\Big(C[3(n-2)+1]-C[3(n-1)+1]\Big)+\frac{4s[1]\nu[n-1]}{D[3(n-1)+1]\Phi[n-1]}$$
$$-\frac{1}{2D[3(n-1)+1]]h}\Bigg(\frac{C[3(n-1)+1]\mathbf{N}[n+1]}{C[3(n-1)+1]+\underbrace{\sum_{k\neq i}C[3(n-1)+k]}_{C[3(n-1)+2]+C[3(n-1)]}}-\frac{C[3(n-2)+1]\mathbf{N}[n-1]}{C[3(n-2)+1]+\underbrace{\sum_{k\neq i}C[3(n-2)+k]}_{C[3(n-2)+2]+C[3(n-2)]}}\Bigg). \tag{29}$$

1.5.3 i=2

$$i=2 \implies 0=\frac{1}{h^2}\Big(C[3(n-2)+2]-C[3(n-1)+2]\Big)+\frac{4s[2]\nu[n-1]}{D[3(n-1)+2]\Phi[n-1]}$$
$$-\frac{1}{2D[3(n-1)+2]]h}\Bigg(\frac{C[3(n-1)+2]\mathbf{N}[n+1]}{C[3(n-1)+2]+\underbrace{\sum_{k\neq i}C[3(n-1)+k]}_{C[3(n-1)+1]+C[3(n-1)]}}-\frac{C[3(n-2)+2]\mathbf{N}[n-1]}{C[3(n-2)+2]+\underbrace{\sum_{k\neq i}C[3(n-2)+k]}_{C[3(n-2)+1]+C[3(n-2)]}}\Bigg). \tag{30}$$

1.6 Implementation

The nonlinear solver fsolve finds the m roots of a set of m functions with m unknowns. For our application, $m = 3n$. This is because there are 3 equations - one for each gas - being solved for at n grid points (where those of $j = 0, n+1$ are already known). fsolve requires the system of equations rearranged such that the LHS equals zero, as well as an initial guess, and other arguments.

For our application, the expressions are given in this order: (Eq. 23, Eq. 24, Eq. 25, { Eq. 19, Eq. 20, Eq. 21 }, Eq. 28, Eq. 29, Eq. 30). That is the set of equations corresponding to $j = 1$, those corresponding to $j \in [2, n-1]$, and those corresponding to $j = n$. The initial guess is $\{C_{MTS0}, C_{H20}, C_{HCl0},\ C_{MTS0}, C_{H20}, C_{HCl0}, \dots\}$ and supplementary arguments are $\{D, h, \mathbf{N}, s, \nu, \Phi\}$.

Again, fsolve solves for $C_{i,j}$ where $j \in [1, n]$. Then, the boundary conditions $C_{i,0}, C_{i,n+1}$ are manually inserted/appended to the beginning/end of the vector. Then, gas concentrations for each of the gases are extracted out of the common vecotr. That is,

$$C_{MTS} = C[0 :: 3], \quad C_{H2} = C[1 :: 3], \quad C_{HCl} = C[2 :: 3]. \tag{31}$$

This means that, for example, C_{MTS} takes every third entry of C starting from the first position 0; C_{H2} does the same, starting from 1; C_{HCl} does the same, starting from 2. This is because of how the common vector $\{C_{i,j}\} = \{C_{0,0}, C_{1,0}, C_{2,0}, C_{0,1}, C_{1,1}, C_{2,1}, \dots\}^T$ is arranged. Then, pore radius updates as

$$\frac{\partial}{\partial t}\Phi = -2\nu V_{SiC}, \tag{32}$$

where

$$\nu = kC_{MTS}. \tag{33}$$

Diffusivity updates as

$$D_{i,j} = \left(\frac{1}{D_K} + \frac{1}{D_F}\right)^{-1} \tag{34}$$

where

$$D_{i,F} = \left[\frac{1}{1 - x_i}\sum_j \frac{x_j}{D_{b,ij}}\right]^{-1}, \qquad D_{i,K} = d_{i,K}\Phi T^{1/2}, \tag{35}$$

where the molar fraction of species i is

$$x_i = \frac{C_i}{\sum_j C_j}. \tag{36}$$

$\mathbf{N}$ updates as

$$\mathbf{N} = \nu \Delta s. \tag{37}$$

A new time step occurs and the algorithm is repeated until t_f, where $\Phi(z, t_f) < \Phi(z, 0)/100$.