C interstitials are mobile. Si & Fe immobile

\[ \mathbf{J}_1 = -4_1 \nabla u_1 \quad \text{(1)} \]

\[ u_1 = u_1^0 + kT \ln a_1 \quad \text{(2)} \]

\[ a_1 = \gamma_1 x_1 \quad \text{(activity of carbon)} \]

\[ \mathbf{J}_1 = -L_{11} \nabla (kT \ln a_1) \]

\[ \Rightarrow \mathbf{J}_1 = -\frac{L_{11} k T \nabla a_1}{a_1} \quad \text{(4)} \]

We know \( L_{11} > 0 \)

so from (4) we see that diffusional flux is in a direction opposite to the gradient in activity of carbon. Gradient in activity is from left to right. Thus, diffusion of carbon is from Si-rich to Si-poor side.
(2) \[ \vec{J}_1 = -D_1 \left( \nabla c_1 + \frac{c_1 \nabla \ln \theta}{K_T} \right) \]

There is no concentration gradient in the material

\[ \Rightarrow \vec{J}_1 = -\frac{D_1 c_1 \nabla \ln \theta}{K_T} \]

\[ = -\frac{D_1 c_1 \omega_1}{K_T} \left[ \frac{\partial \theta}{\partial r} \hat{r} + \frac{1}{r} \frac{\partial \theta}{\partial \theta} \hat{\theta} \right] \]

\*Eq 7.49

\[ \Rightarrow \theta = \frac{\mu (1+v) \theta \sin \theta}{3 \pi (1-v)} \]

\[ \Rightarrow \vec{J}_1 = -\frac{D_1 c_1 \omega_1 \mu (1+v) \theta}{3 \pi K_T (1-v)} \left[ -\frac{\sin \theta \hat{r} + \cos \theta \hat{\theta}}{r^2} \right] \]

Total flux

\[ J_{\text{Tot}} = \int_{\theta = 0}^{2\pi} \vec{J}_1 \cdot d\theta = 0 \]

(\( \hat{e}_\theta \) component does not contribute to flux)

\[ = -\frac{A}{R} \int_{0}^{2\pi} \sin \theta \sin \theta \, d\theta = 0 \]
\[ c_{1*} = c_i \exp \left( \frac{-\omega_1 p}{kT} \right) \]

\[ J_i = -D_1 \left( \nabla c_i + c_i \frac{\omega_1}{kT} \nabla p \right) \]

\[ J_i = 0 \]

\[ \nabla c_i = -c_i \frac{\omega_1}{kT} \nabla p \]

\[
\begin{pmatrix}
\partial c_1 \\
\partial x \\
\partial y \\
\partial z
\end{pmatrix}
\] + \[
\begin{pmatrix}
\partial c_1 \\
\partial y \\
\partial z
\end{pmatrix}
\] = - c_i \omega_1 \frac{\partial p}{kT} \left( \begin{pmatrix}
\partial P x \\
P y \\
\partial z
\end{pmatrix}
\] + \[
\begin{pmatrix}
\partial P y \\
\partial P z
\end{pmatrix}
\]

Comparing coefficients on both sides.

\[
\begin{align*}
\frac{\partial c_1}{\partial x} &= -c_i \omega_1 \frac{\partial p}{kT} \frac{\partial P_1}{\partial x} \\
\end{align*}
\]

\[ \int \frac{\partial c_1}{c_i} = \int -\frac{\partial_1 \partial P_1}{kT} \]

\[ c_i^0 \]

\[ \ln \left( \frac{c_{eq}}{c_i^0} \right) = -\frac{\omega_1 p}{kT} \]

\[ c_{1*} = c_i^0 \exp \left( -\frac{\omega_1 p}{kT} \right) \]
\[
Solve[\partial_x (J[x]) = 0, \sigma'[x]] \quad // \quad Simplify // Flatten
\]
\[
\begin{align*}
\{ \sigma'[x] \to & (3 \left( 3 \beta^{1/3} \frac{\partial}{\partial \xi} \left( \sin \frac{1}{2} \pi \text{Conc}[x] \right) \right)^2 \gamma_{x}^{2/3} \text{Conc}'[x] + \\
& 2 \pi^{4/3} \text{Conc}[x] \sin \left( \frac{1}{2} \pi \text{Conc}[x] \right) \gamma_{x}^{5/3} \sigma''[x] \right) \\
& (2 \pi^{4/3} (-1 + \cos \pi \text{Conc}[x])) (3 - 3 \cos \pi \text{Conc}[x]) + 4 \pi \text{Conc}[x] \sin \pi \text{Conc}[x] ) \gamma_{x}^{6} \text{Conc}'[x]) \}
\end{align*}
\]

**Part 3**

In this section, we will try to solve the system using a much simpler relationship between volume and pore size.

\[
\begin{align*}
Q[x_\_] & := 2 \gamma_{x} A \\
\text{Em} & = 110^3; \quad k = 110^{-21}; \quad l = 10; \quad T = 300; \quad \gamma_{x} = 0.05; \\
J[x_\_] & := -D_1 \left( \text{Conc}'[x] + \frac{\text{Conc}[x] Q[x_\_] \sqrt{k T \text{Em} l}}{\kappa T \text{Em} l} \sigma'[x] \right) \\
\text{DSolve[}[J''[x] == 0], \text{Conc}[x], x]
\end{align*}
\]

**G2-4. The Sponge Problem**

The first part of the sponge problem asks us to determine the stress-free volume expansion of the sponge as a function of humidity. This is NOT a realistic question as the sponge is not hydroscopic and will not absorb water unless the humidity is locally 100%. Water will only travel through the sponge as a condensed phase, so there will be a saturated vapor pressure of water where ever the sponge expands. However, if "humidity" is defined as the fraction of water in the pores of the sponge, then other approximations for volume expansion as a function of humidity can be considered. In this case, we assume the relationship between volume expansion and concentration is linear. (We will discuss the merits of this assumption later).

\[
\begin{align*}
v[x_\_] & := B \text{Conc}[x]
\end{align*}
\]

The constant B must relate the volumetric strain of the sponge (estimated to be 0.3 at full saturation) to the concentration of water ("humidity") and \( \Omega \) is the pore volume.
For the purposes of this problem, we assume the hydrostatic pressure in the material to be essentially the stress times the strain. In a real isotropic material, pressure is actually 3 times this value. The sponge can probably be approximated as an isotropic material, but to first order this is the same value.

\[ p'[\mathbf{x}] = \Delta \varepsilon \sigma'[\mathbf{x}] \]

The pressure itself is minus the reciprocal of the isothermal compressibility times the volume expansion.

\[ p[\mathbf{x}_+] := -\frac{dV[\mathbf{x}]}{V \beta} \]

We assume at steady state there is a constant, one dimensional flux through the sponge. (Derivatives are with respect to distance \( \mathbf{x} \))

\[ J[\mathbf{x}] = -D_1 \left( c'[\mathbf{x}] + \frac{c[\mathbf{x}] \Delta \varepsilon \sigma'[\mathbf{x}]}{k T} \right) \]

The above equation is taken from KOM 3.82, except the relationship for a stress and strain used in the footnote was used rather than the pressure itself. Dimensional analysis showed that the units of the terms in the braces are \( 1/m^4 \). \( D \) therefore is \( m^2/s \).

Since the pressure is essentially the stress in the system times the strain, the above equation can be rewritten in terms of pressures:

\[ J[\mathbf{x}_+] := -D_1 \left( c'[\mathbf{x}] + \frac{\Omega c[\mathbf{x}]}{k T} p'[\mathbf{x}] \right) \]

When the gradient of the flux is 0, steady state conditions have been achieved.

\[
\text{DSolve}[[J'[\mathbf{x}] = 0], \{c[\mathbf{x}], \mathbf{x}\}]
\]

\[ \{ \{ c[\mathbf{x}] \rightarrow \frac{k T V \beta - \sqrt{k^2 T^2 V^2 \beta^2 - 2 B x \Omega^2 C[1]} - 2 B \Omega^2 C[1] C[2]}{B \Omega^2} \}, \{ c[\mathbf{x}] \rightarrow \frac{k T V \beta + \sqrt{k^2 T^2 V^2 \beta^2 - 2 B x \Omega^2 C[1]} - 2 B \Omega^2 C[1] C[2]}{B \Omega^2} \} \} \]

A priori, it is difficult to determine which solution is more real. Presumably, the positive concentration gradient makes more physical sense (the flux goes down the concentration gradient).

\[ c[\mathbf{x}_+] := \frac{k T V \beta + \sqrt{k^2 T^2 V^2 \beta^2 - 2 B x \Omega^2 C[1]} - 2 B \Omega^2 C[1] C[2]}{B \Omega^2} \]

The constants of integration \( C[1] \) and \( C[2] \) must now be found. Boundary conditions are employed, including the condition that \( B = \frac{0.3}{\pi} \), as determined from experiment.

\[
\text{Solve}[[c[0] = 1, c[0.1] = 0], \{C[1], C[2]\}]
\]

\[ \{ \{ C[2] \rightarrow \frac{-2 k T V \beta + 1 B \Omega^2}{20 k T V \beta - 10 B \Omega^2}, C[1] \rightarrow -10 k T V \beta + 5 B \Omega^2 \} \} \]
\[ c[x] \rightarrow \left( \frac{-2. \cdot k \cdot T \cdot V \cdot \beta + 1. \cdot \beta \cdot \Omega^2}{20. \cdot k \cdot T \cdot V \cdot \beta - 10. \cdot \beta \cdot \Omega^2} \right) \]  

\[ C[1] \rightarrow -10. \cdot k \cdot T \cdot V \beta + 5. \cdot \beta \cdot \Omega^2 \]

Simplify

Rationalize // Flatten

\[ k \cdot T \cdot V \beta + \sqrt{\frac{20 \cdot k^2 \cdot T^2 \cdot V^2 \cdot \beta^2 \cdot \rho^2 \cdot \Omega^2 \cdot B^2 \cdot k \cdot T \cdot V \cdot (40 \cdot 400 \times \beta^2 \cdot \rho^2 \cdot \Omega^2 \cdot B^2 \cdot k \cdot T \cdot V \cdot (-10 \cdot 100 \times \beta^2 \cdot \rho^2 \cdot \Omega^2 \cdot B^2 \cdot k \cdot T \cdot V)}{20 \cdot k \cdot T \cdot V \beta - 10 \cdot \beta \cdot \Omega^2}} \]

\[ c[x_] := \frac{k \cdot T \cdot V \beta + \sqrt{20 \cdot k^2 \cdot T^2 \cdot V^2 \cdot \beta^2 \cdot \rho^2 \cdot \Omega^2 \cdot B^2 \cdot k \cdot T \cdot V \cdot (40 \cdot 400 \times \beta^2 \cdot \rho^2 \cdot \Omega^2 \cdot B^2 \cdot k \cdot T \cdot V \cdot (-10 \cdot 100 \times \beta^2 \cdot \rho^2 \cdot \Omega^2 \cdot B^2 \cdot k \cdot T \cdot V)}}{20 \cdot k \cdot T \cdot V \beta - 10 \cdot \beta \cdot \Omega^2} \]

\[ E \text{ was determined experimentally to be } 5 \text{ kPa. } \beta = 3 / E. \text{ } D_1 \text{ was determined directly by measuring the time for water to wick up a } 5 \text{ cm long, } 1 \text{ cm}^2 \text{ section of a Cell - 0 sponge. Pore size was guessed to be about } 1 \text{ mm. } B \text{ was guessed based on estimates of volume expansion of a sponge found online (0.2) and experimentally (0.4).} \]

\[ \beta = -6 \times 10^{-4}; k = 1.38 \times 10^{-23}; T = 300; r_p = 1 \times 10^{-3}; D_1 = 10^{-4} / 60; \]

\[ \Omega := \frac{4 \pi}{3} r_p^3; V = 10^2 10 10^{-2} 5 10^{-2}; B = \frac{0.3}{\Omega}; \]

In our first model, we will consider a constant volumetric expansion.

\[ \text{Plot}[c[x], \{x, 0, 0.1\}, \text{PlotLabel} \rightarrow \text{"Humidity vs. Distance"}, \text{AxesLabel} \rightarrow \{\text{"x, in m"}, \text{"Humidity"}\}] \]

- Graphics -

To find the pressure gradient we need to plug into the expression for the pressure.
Plot[p[x], {x, 0, 0.1}, PlotLabel -> "Pressure on Container vs. Distance",
AxesLabel -> {"x, in m", "P, in Pa"}]

Obviously, using the assumption of a linear relationship between concentration and volume expansion the plots of pressure and concentration versus distance will be identical, save for a scaling factor. The pressures described above seem quite large—upwards of 10 MPa, enough to break most polymer molds that this experiment would likely be performed in, but the model assumed that the amount of water absorbed by the sponge would not be limited by the pressure applied to the sponge—that is, 100% humidity means the sponge will contain as much water as if it were not constrained. With that in mind, these numbers actually seem low—water is barely compressible and a fully saturated sponge is almost all water, so the pressure from the water on the walls would be intense. The polymer matrix can modify that somewhat, however. The above assessment is therefore somewhat reasonable.

**Part 1 Redux: Another look at pore filling**

One of the most glaring assumptions of the first part of this problem is the mathematically simplifying assumption that there is a linear dependence on pore filling with respect to volume expansion. This is clearly not correct. Pore filling is a function of the dihedral angle of contact between the water coming into the pore (this dictates the driving force for wetting of the pore) and therefore the shape of the pore. Modeling the pores as spheres it could be possible to more accurately describe the rate of pore filling, which to first order should go quickly at first, slow down in the center (as the wetting angle gets wider), and finish fast (as the surface of the spherical pore comes back on the filling water). To this end, the "humidity" dependence would be better approximated by assuming the pores are spheres and integrating the volume of the sphere with respect to an angle $\phi$ that varies from 0 to $\pi$ for no filling to total filling. This is one method for determining the volume of a partially filled sphere. Redefining $dV$:

$$dV[x_] := \frac{r_p^3}{3} \cdot 2 \cdot \pi \cdot (1 - \cos[c[x]\pi])$$
\[ p[x_] := \frac{-dV[x]}{\nu \beta} \]

The pressure relationship doesn't change as it is dictated by the relationship between volume expansion (strain) and the isothermal compressibility. Plugging into the flux equation:

\[ J[x_] := -D \left( \frac{c'[x]}{\kappa T} \right) p'[x] \]

\[ \text{DSolve}[[J'[x] == 0, c[x], x]] \]

The equations appear to involve the variables to be solved for in an essentially non-algebraic way. More...

\[
\{ [c[x] \rightarrow \text{InverseFunction}[\frac{-3 k T V \beta \#1}{C[1]} + \frac{2 \pi \text{Sin}[\pi \#1]}{C[1]} - \frac{2 \pi \text{Cos}[\pi \#1] \#1 r_p^3 \&}[x + C[2]]] \}
\]

The function appears to be too difficult to solve.
Measuring the Diffusivity of sponge with moisture

- We cut a piece of dry sponge roughly 5cm long with one centimeter square cross section
- It took about 300 seconds for the water to travel 5 cm
- We supplied one end with a saturating supply of water and timed the water's propagation through the sponge.
Searching the literature led us to revise our volume change to 30%.

This translated into a 40% volume change.

We found the linear expansion to be 12%.

After saturating it with water, we measured the sponge's dimensions before adding water and again.

Measuring the expansion of sponge with moisture.
The literature suggests using an approximate value of $f = \frac{3}{E}$ for isotropic materials. Measured compression distance found the Young’s modulus. Knowing the area of contact we calculated the pressure applied and with the weight added the initial sponge thickness with only the height wood block in place.

We measured the compressibility of wet sponge.

Measuring the compressibility of wet sponge.