

Oxygen Isotope Exchange

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Abstract

Seeking help to understand a 1 dimensional diffusion problem. Skip to section 3 for the maths!

1 Background

Oxygen isotope exchange is a technique for determining the surface exchange and bulk diffusivity of a material. These two properties are useful when designing solid oxide fuel cells (SOFCs), electrolyzers, oxygen sensors etc.. The experiment typically involves exposing a sample to an atmosphere enriched with ^{18}O for a known period of time and then measuring the relative concentration of the isotope to that of atmospheric oxygen. It is important to understand that the total concentration of oxygen is not changing, but rather the ratio of oxygen isotopes. The measurement is commonly made using secondary ion mass spectroscopy (SIMS). Once the empirical depth profile has been obtained, an analytically derived curve can be fitted using the least squares approach. This approach is successfully used in Manning et al. [1996], where the equations are restated, but not derived.

The diffusive behavior in the bulk is described by the eq. (1),

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \quad (1)$$

where C is the concentration of the ^{18}O in the semi-infinite medium at a distance, x , from the surface; t is the duration of the exposure to the ^{18}O enriched atmosphere; and D is the oxygen diffusivity of the material at the relevant temperature and pressure. The surface exchange boundary condition is stated in eq. (2),

$$k(C_{gas} - C(0, t)) = -D \left. \frac{\partial C}{\partial x} \right|_{x=0} \quad (2)$$

where C_{gas} is the ^{18}O concentration in the gas at the surface (considered to be constant) and k is the surface exchange coefficient. This can be rearranged to the following explicit form,

$$C(0, t) = \frac{1}{h} \left. \frac{\partial C}{\partial x} \right|_{x=0} + C_{gas} \quad (3)$$

where h is the ratio k/D .

Initially,

$$C(x, t) = C_{bg}, \quad x \geq 0, \quad t = 0 \quad (4)$$

where C_{bg} is the background concentration of ^{18}O in the material (typically c. 0.2 %).

Crank [1975] derives an analytical solution to this problem as shown in eq. (5),

$$C'(x, t) = \operatorname{erfc} \left\{ \frac{x}{2\sqrt{Dt}} \right\} - e^{(hx+h^2Dt)} \operatorname{erfc} \left\{ \frac{x}{2\sqrt{Dt}} + h\sqrt{Dt} \right\} \quad (5)$$

where C' is the normalised, relative ^{18}O concentration described by eq. (6).

$$C'(x, t) = \frac{C(x, t) - C_{bg}}{C_{gas} - C_{bg}} \quad (6)$$

The full derivation of this solution can be found in chapter 3 of Crank [1975] in the section on semi-infinite media with bulk diffusion and surface evaporation.

2 Test case

To clarify with an example, an experiment could involved two steps:

1. Exposure to ^{18}O enriched environment ($C_{gas} > C_{bg}$) for 6 hours: $t_1 = 6$ hours
2. Exposure to atmospheric oxygen ($C_{gas} = C_{bg}$) for 3 hours: $t_2 = 3$ hours

Assuming that D and h in eq. (5) do not change between the two steps, the only altered variable is the time, t . The solution that appears to work in the above case is:

$$C'_{bd}(x, t_1, t_2) = C'(x, (t_1 + t_2)) - C'(x, t_2) \quad (7)$$

where $C'_{bd}(x)$ is the normalized, relative concentration distribution for the back diffusion experiment after the two stages. This can be rearranged, using eq. (6), to the form,

$$C_{bd}(x, t_1, t_2) = (C'(x, (t_1 + t_2)) - C'(x, t_2)) * (C_{gas} - C_{bg}) + C_{bg} \quad (8)$$

So, in order to plot the back diffusion profile I simply used (5) twice, with two different times, and then subtracting one from the other.

Although I am not yet clear why this appears to work, the physical reasoning which led to eq. (7) was the following:

1. The solution must never be negative, even if step 2 is longer than step 1
 - (a) In eq. (7), step 1 contains step 2, so this condition is always satisfied
2. The initial conditions for the second step are wrong in the sense that it doesn't start as zero everywhere in reality

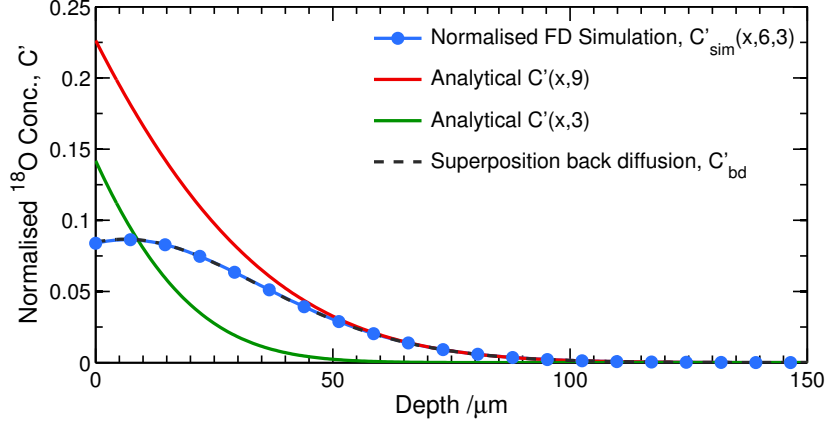


Figure 1: Normalised concentration against depth for the normalised FD simulation results, two analytical solutions and their superposition. The FD simulation results were normalised using eq. (9) for ease of comparison.

- (a) However, in my solution this error in the initial conditions of the second step appear to be accounted for by the extra exchange time allowed for in step 1

Figure (1) shows the normalised results of the FD simulation, as well as the analytical curves for 9 hours (i.e. 6+3), 3 hours, and the difference between the two. It is difficult to see the difference curve as it lies so closely (although not exactly) along that of the simulation. Equation (9) was used to convert the concentration profile from the simulation, C_{sim} , into its normalised, relative form, C'_{sim} .

$$C'_{sim}(x, t) = \frac{C_{sim}(x, t) - C_{bg}}{C_{gas} - C_{bg}} \quad (9)$$

3 The question

What is the analytical solution of eq. (10), with boundary condition eq. (11) and initial condition eq. (12)?

$$\frac{\partial C_{bd}}{\partial t} = D \frac{\partial^2 C_{bd}}{\partial x^2} \quad (10)$$

$$\begin{aligned} C_{bd}(0, t) &= \left. \frac{1}{h} \frac{\partial C}{\partial x} \right|_{x=0} + C_{gas}, & 0 < t \leq \phi_1 \\ C_{bd}(0, t) &= \left. \frac{1}{h} \frac{\partial C}{\partial x} \right|_{x=0} + C_{bg}, & \phi_1 < t \leq \phi_1 + \phi_2 \end{aligned} \quad (11)$$

$$C_{bd}(x, t) = C_{bg}, \quad t = 0, \quad x \geq 0 \quad (12)$$

Is it possible that it could be eq. (13), which is the substitution of eq. (5) into my hypothesis in eq. (7)?

$$\begin{aligned}
C'(x, t_1 + t_2) = & \dots \\
& \left(\operatorname{erfc} \left\{ \frac{x}{2\sqrt{D(t_1 + t_2)}} \right\} - e^{(hx+h^2D(t_1+t_2))} \operatorname{erfc} \left\{ \frac{x}{2\sqrt{D(t_1 + t_2)}} + h\sqrt{D(t_1 + t_2)} \right\} \right) \dots \\
& - \left(\operatorname{erfc} \left\{ \frac{x}{2\sqrt{D(t_2)}} \right\} - e^{(hx+h^2D(t_2))} \operatorname{erfc} \left\{ \frac{x}{2\sqrt{D(t_2)}} + h\sqrt{D(t_2)} \right\} \right) \quad (13)
\end{aligned}$$

where,

$$C'(x, t) = \frac{C(x, t_1, t_2) - C_{bg}}{C_{gas} - C_{bg}} \quad (14)$$

References

- J. Crank. *The Mathematics of Diffusion*. 1975.
- P. S. Manning, J. D. Sirman, and J. A. Kilner. Oxygen self-diffusion and surface exchange studies of oxide electrolytes having the fluorite structure. *Solid State Ionics*, 93(1-2):125–132, 1996.