

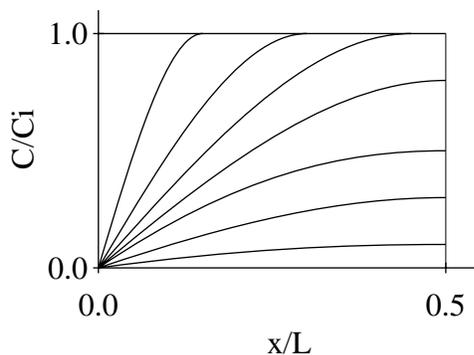
3.185 Problem Set 3

More diffusion

Solutions

1. W³C Problem 27.16: Outgassing from a silicone sheet in vacuum.

This is mathematically similar to problem set 2 problem 3, as long as you put $x = 0$ at the vacuum surface of the silicone sheet, with x measuring the distance into the sheet toward the steel. Except this time, the concentration of oxygen starts uniform and high, and at time $t = 0$ the surface concentration drops to zero. The concentrations will thus look something like this:



The oxygen concentration in the silicone will vary with time according to the Fourier series solution to the diffusion equation, using one-quarter period here since the flux is zero at the silicone-steel interface ($x = L/2$). After a relatively short time, only the $n = 1$ term is relevant, which is:

$$C = \frac{4C_i}{\pi} \exp\left(-\frac{\pi^2 Dt}{L^2}\right) \sin\left(\frac{\pi x}{L}\right).$$

We want to know when the concentration will reach 1% of C_i , indicating that nearly all of the oxygen has diffused out of the silicone and the vacuum quality will improve, so we set $C/C_i = 0.01$ at $x = L/2$. The sin of $\pi/2$ is one, which makes the rest easy:

$$\frac{C}{C_i} = 0.01 = \frac{4}{\pi} \exp\left(-\frac{\pi^2 Dt}{L^2}\right) \cdot 1,$$

$$\frac{\pi^2 Dt}{L^2} = -\ln\left(\frac{\pi}{4} \cdot 0.01\right)$$

$$t = \frac{L^2}{\pi^2 D} \ln\left(\frac{400}{\pi}\right) = 0.49 \frac{L^2}{D}.$$

For a 3mm (=0.3cm) thick sheet, $L = 0.6$ cm, and diffusivity given was 10^{-7} cm²/s, so $t = 1.76 \times 10^6$ seconds, or over 20 days! This is why polymers and oils are used very sparingly in high-vacuum equipment: dissolved gases in them seep out for a long time and keep the pressure from dropping to the very low levels needed, for example, in molecular beam epitaxy deposition of thin films.

2. Hydrogen diffusion through metal foil.

- (a) The flux in this diffusion-limited case is given by:

$$J_x = -\frac{P_0^* e^{-Q_p/RT}}{\delta} (\sqrt{p_1} - \sqrt{p_2}).$$

By way of explaining where this comes from (which is not part of the “solution”), we can simplify things by defining $P^* = P_0^* \exp(-Q_p/RT)$, then the equation becomes

$$J_x = -\frac{P^*}{\delta} (\sqrt{p_1} - \sqrt{p_2}),$$

and we can use the equilibrium constant for the reaction $\text{H}_2(\text{g}) \rightarrow 2\text{H}$:

$$K_{eq} = \frac{C_{\text{H}}^2}{p_{\text{H}_2}} \rightarrow C_{\text{H}} = \sqrt{K_{eq} p_{\text{H}_2}}$$

to fit it to the familiar diffusion flux equation:

$$J_x = -\frac{D}{\delta} (C_1 - C_2) = -\frac{D\sqrt{K_{eq}}}{\delta} (\sqrt{p_1} - \sqrt{p_2}).$$

So P^* is just $D\sqrt{K_{eq}}$.

This table summarizes the results of the hydrogen diffusion calculations:

Metal	P_0^* , $\frac{\text{cm}^3(\text{STP})}{\text{s}\cdot\text{cm}\sqrt{\text{atm}}}$	Q_p , $\frac{\text{cal}}{\text{mol}}$	P^* , $\frac{\text{cm}^3(\text{STP})}{\text{s}\cdot\text{cm}\sqrt{\text{atm}}}$	J , $\frac{\text{cm}^3(\text{STP})}{\text{s}\cdot\text{cm}^2}$
Nickel	1.2×10^{-3}	13850	3.8×10^{-8}	8.5×10^{-7}
Copper	1.9×10^{-4}	17350	4.4×10^{-10}	9.9×10^{-9}
Aluminum	0.37	30800	3.7×10^{-11}	8.2×10^{-10}

- (b) From the equation, we can look at the ratio of fluxes in two different situations, corresponding to parts *a* and *b* of this problem:

$$\frac{J_a}{J_b} = \frac{\frac{P_0^* e^{-Q_p/RT}}{\delta} (\sqrt{p_{1a}} - \sqrt{p_{2a}})}{\frac{P_0^* e^{-Q_p/RT}}{\delta} (\sqrt{p_{1b}} - \sqrt{p_{2b}})}$$

All of that $\frac{P_0^* e^{-Q_p/RT}}{\delta}$ stuff is constant, so it cancels. We were told that p_{2a} was zero, and we're only changing p_1 here, so p_{2b} is zero too. So we get:

$$\frac{J_a}{J_b} = \frac{\sqrt{p_{1a}}}{\sqrt{p_{1b}}}.$$

We want to get half the flux, so J_b is half of J_a , which when we square both sides gives us the pressure ratio:

$$\frac{J_a}{J_b} = 2 = \frac{\sqrt{p_{1a}}}{\sqrt{p_{1b}}}$$

$$\frac{p_{1a}}{p_{1b}} = 4.$$

So the new pressure must be one quarter of the old pressure, 0.05 atm.

Qualitatively, the **flux** is proportional to the **difference in concentrations** (kinetics). Both sides of the foil are at **equilibrium** (thermodynamics), so the equilibrium constant governs the concentration. That constant says that the **concentration** is proportional to the **square root of the pressure** because hydrogen is diatomic in the gas and monatomic in the metal $\text{H}_{2(\text{g})} \rightarrow 2\text{H}$ (thermodynamics), so the **flux** is proportional to the **difference in the square roots of the pressures** on the two sides (mixed thermo and kinetics).

3. The FFC-Cambridge process for titanium reduction

Our assumptions really didn't do justice to the complexity of the process, with its various electrochemical complications. The driving force of voltage drop, which produces an electric field, works against the chemistry which wants to produce oxide.

However, the basic principle of the sum of reaction and diffusion resistances still holds (plus an additional resistance to electron conduction through the oxide), and of particular importance to this process, the efficiency depends on the extent to which the diffusional resistance can be minimized so it comes close to using the minimum energy required to reduce the oxide. In that sense, the thickness of the resulting porous titanium layer (represented by Y here) is crucial; to maintain reaction limitation, its final value must be small enough to give a small Biot number.

- (a) The two mechanisms here are diffusion and heterogeneous chemical reaction at an interface; these operate in series. So the relevant dimensionless number is the ratio of the two resistances, which is the (mass transfer) Biot number given by

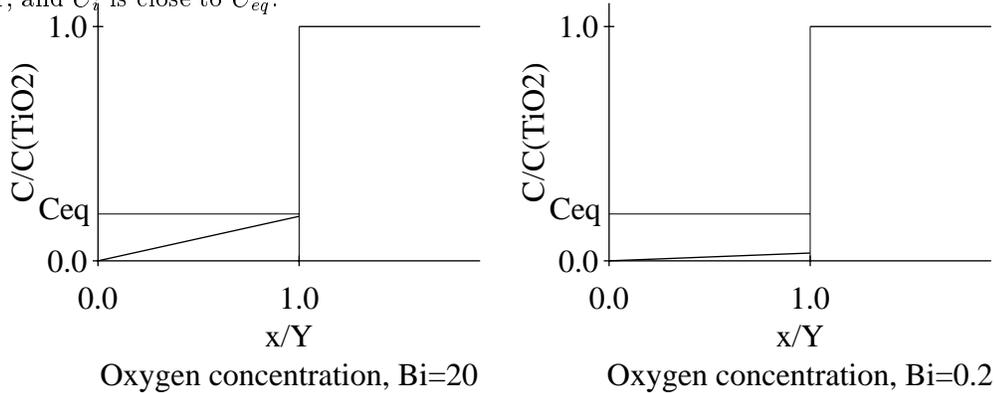
$$\text{Bi} = \frac{kY}{D};$$

when it is large, the reaction is fast and diffusion is slow, so the process is *diffusion-limited*.

- (b) The problem states that the oxygen concentration in the oxide is very uniform, and at the outer surface of the titanium it's zero. The maximum possible concentration in the titanium is C_{eq} , so C_i , the concentration in the titanium at the interface, must be between zero and C_{eq} .

The reaction rate is proportional to the difference between C_{eq} and C_i ; the diffusion flux is proportional to C_i (minus zero).

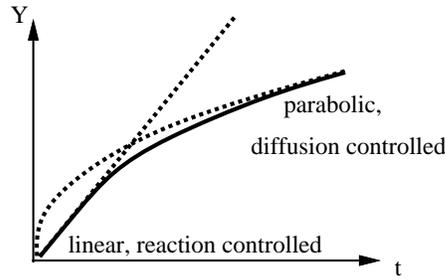
If the Biot number is small, then the reaction is slow and diffusion is fast, so C_i will be close to zero; the slow reaction results in very small C_i (you can think of this as: any oxygen which gets through the slow reaction gets rapidly diffused across the titanium, so its concentration in the titanium is low). Conversely, if the Biot number is large, then the reaction is fast and diffusion is slow, so there will be a big concentration difference between the two faces of the porous titanium layer, and C_i is close to C_{eq} .



- (c) The concentration at $x = Y$ is C_i , and the concentration at $x = 0$ is zero, so the flux is:

$$J_O = -D \frac{C_i - 0}{Y} = -\frac{DC_i}{Y}.$$

- (d) This is the classic linear \rightarrow parabolic reaction \rightarrow diffusion-limited growth curve:



This is a neat process, and has some advantages over the current Kroll process for making titanium (whose inventor was so disappointed with his process that he was certain something better would come along within 5-10 years—that was 50 years ago). The energy efficiency is enormously better, but any impurities in the TiO_2 are also present in the final titanium product. Furthermore, this requires expensive pre-processing to shape the titanium oxide into the little pellets which go on the electrodes, and post-processing to consolidate the bits of porous titanium (which need to be thin, see the solution preamble above) into a solid ingot.

My group is working with a group at Boston University to develop a process which purifies and consolidates at the same time as it reduces, going from cheap granular low-purity TiO_2 to dense high-purity Ti at high efficiency and all in one step. Several things could go wrong with various parts of the process, rendering it ineffective, but if it works, it will bring down the price of titanium enormously—and you will definitely hear about it...

4. Iron oxidation

(a) From the equation given:

$$\left(\frac{\Delta m}{A}\right)^2 = k_p t$$

For iron at 1000°C , the table provided gives k_p as $1.4 \times 10^{-4} \frac{(\text{kg O}_2)^2}{\text{m}^4 \cdot \text{s}}$, and t is 1800 seconds, so the mass gain is $0.50 \frac{\text{kg O}_2}{\text{m}^2}$, or $0.050 \frac{\text{g O}_2}{\text{cm}^2}$.

This is the amount of added oxygen, and there are two moles of iron oxide per three moles of oxygen molecules, so the mass of iron oxide is this times $\frac{2 \text{ moles Fe}_2\text{O}_3}{3 \text{ moles O}_2} \frac{159.6 \text{ g/mol}(\text{Fe}_2\text{O}_3)}{32.0 \text{ g/mol}(\text{O}_2)}$, which is $0.167 \frac{\text{g Fe}_2\text{O}_3}{\text{cm}^2}$.

The thickness is this divided by the density of $5.24 \frac{\text{g}}{\text{cm}^3}$, so the film is 0.032 cm thick, or about 1/3mm.

(b) The k_p for the Fe-1%Ti alloy is $1.6 \times 10^{-5} \frac{(\text{kg O}_2)^2}{\text{m}^4 \cdot \text{s}}$, and gives a mass gain of $0.17 \frac{\text{kg O}_2}{\text{m}^2}$, which is about 1/3 of that in part 4a. This is because the titanium is more reactive with the oxygen, so the oxide film contains a disproportionate amount of titanium oxide, which has lower interdiffusivity and grows more slowly than iron oxide.

5. Dimensional Analysis: the Shrinking Gaussian

The “Shrinking Gaussian” solution to the time-dependent diffusion equation:

$$C = \frac{\beta}{\sqrt{\pi D t}} \exp\left(-\frac{x^2}{4 D t}\right)$$

(a) Dimensions and units:

Dimension	Units
C	$\frac{\text{mol}}{\text{m}^3}$
β	$\frac{\text{mol}}{\text{m}^2}$
D	$\frac{\text{m}^2}{\text{s}}$
t	seconds
x	meters

Note: substitution of g or kg for mol works just as well.

- (b) As we can see above, there are five dimensions, and three base units (mol or g or kg, m, s), therefore, there are just two dimensionless parameters.
- (c) We want to construct π_C and π_x , eliminating β , D and t .

Dimension	mol	m	s	Dimension	mol	m	s
C	1	-3	0	x	0	1	0
β^{-1}	-1	2	0	β^0	0	0	0
$D^{1/2}$	0	1	$-\frac{1}{2}$	$D^{-1/2}$	0	-1	$\frac{1}{2}$
$t^{1/2}$	0	0	$\frac{1}{2}$	$t^{-1/2}$	0	0	$-\frac{1}{2}$
Total	0	0	0	Total	0	0	0

So we have:

$$\pi_C = \frac{C\sqrt{Dt}}{\beta}$$

$$\pi_x = \frac{x}{\sqrt{Dt}}$$

- (d) Start with the solution itself:

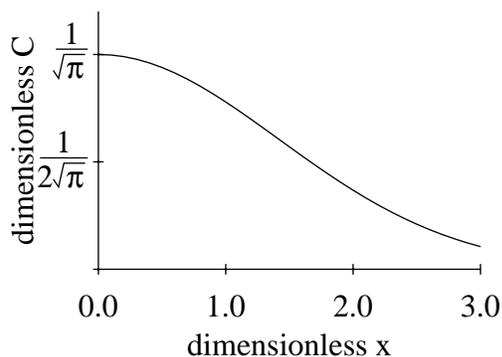
$$C = \frac{\beta}{\sqrt{\pi Dt}} \exp\left(-\frac{x^2}{4Dt}\right)$$

One rearrangement should do it:

$$\frac{C\sqrt{Dt}}{\beta} = \frac{1}{\sqrt{\pi}} \exp\left(-\frac{x^2}{4Dt}\right)$$

$$\pi_C = \frac{1}{\sqrt{\pi}} \exp\left(-\frac{\pi_x^2}{4}\right)$$

- (e) When made dimensionless like this, the “Shrinking Gaussian” becomes a simple Gaussian with a maximum value of $1/\sqrt{\pi}$:



As for the width, you could define any measure of it, and give the corresponding value. One such measure is where the Gaussian reaches $1/e$ of its maximum; this is relatively easy because you just set the exponent to -1 , so $-\pi_x^2/4 = -1$ and $\pi_x = 2$.

Another popular measure for Gaussian distributions is the “full width at half maximum” (FWHM). For this, you solve:

$$\exp\left(-\frac{\pi_x^2}{4}\right) = \frac{1}{2}$$

$$\pi_x = 2\sqrt{\ln 2} \simeq 1.39$$

Either of these measures was fine.