

# Chapter 2

## Diffusion

### 2.1 September 5, 2003: 1-D Cartesian and Cylindrical Steady-State

TODO:

- Check reading room to make sure texts are there.
- Bring: cards, class list.
- Check text to make sure chap 25 units are consistent with mine.

Opener: Colleen's facility with names... my advisee!

Mechanics:

- Diffusion handout typo: should be  $\operatorname{erfc}(y) = 1 - \operatorname{erf}(y)$ .
- Choose new recitation times!
- Finalize test dates.
- Invite example processes.
- Index cards for muddiest part.
- Try names.

**Diffusion** Stuff they've learned before, new twist. Steady state 1-D cartesian, cylindrical coordinates.

Steady-state: accumulation=0. In today's case, species isn't generated or consumed inside the glass, so in-out=0. (Monday: generation by homogeneous chemical reaction.)

1-D: concentration varies only in one direction.

My style: start with a motivating example, introduce the physics along the way. When we're done, we have the physics, and an example of how to use it.

Yesterday: 3.185 is about low-cost high-quality processes. Here a process, not for material but for helium, maximize productivity a.k.a. throughput subject to process constraints.

Example: helium diffusion through pyrex glass, enormously higher  $D$  than any other gas (25x hydrogen!). Some helium in natural gas, can flow through pyrex tubes to separate, 2mm OD 1mm ID. Generally diffusion-limited. Want to calculate the production rate, more important understand how works, because from understanding flows design recommendations. ASSUME diffusion-limited, so this is the slow-step, not adsorption/desorption etc.

Simple solution: unroll to a plate, with  $C_{in}$  on one side (equilibrium with partial pressure in natural gas) and  $C_{out}$  on the other (pumped away into tanks), be sure to use thickness  $\delta$ . We know how to do this:

Constitutive law: Fick's first, gradient points up, diffusion goes down, proportionality constant  $D$ :

$$\vec{J} = -D\nabla C, J_x = -D\frac{\partial C}{\partial x} \quad (2.1)$$

Units of each term.

1-D: no difference in  $y$ - or  $z$ -direction, so those partials are zero. When varies in only one direction and not time, not partial but total  $dC/dx$ .

Conservation with no accumulation or generation:  $dJ_x/dx = 0$ , substitute to get

$$\frac{d}{dx} \left( D\frac{dC}{dx} \right) = 0, \quad (2.2)$$

ASSUME constant  $D$  this is

$$\frac{d^2C}{dx^2} = 0. \quad (2.3)$$

General solution in 1-D:

$$C = Ax + B. \quad (2.4)$$

Boundary conditions (limited by diffusion):

$$x = 0 \Rightarrow C = C_{in}, x = \delta \Rightarrow C = C_{out}. \quad (2.5)$$

Result: flux

$$J = -DdC/dx = -D\frac{\Delta C}{\delta}. \quad (2.6)$$

At 500°C,  $D_{\text{He-pyrex}} = 2 \times 10^{-8} \frac{\text{cm}^2}{\text{s}}$ , for some steady gas/helium mixture  $C_{in} = 10^{-5} \frac{\text{g}}{\text{cm}^3}$ , say  $C_{out} \simeq 0$ . For  $\delta = 0.5\text{mm} = 0.05\text{cm}$ , this gives

$$J = 2 \times 10^{-8} \frac{\text{cm}^2}{\text{s}} \cdot \frac{10^{-5} \frac{\text{g}}{\text{cm}^3}}{0.05\text{cm}} = 4 \times 10^{-12} \frac{\text{g}}{\text{cm}^2 \cdot \text{s}}. \quad (2.7)$$

Tube array with total length 10m=1000cm (e.g. 100 tubes each 10 cm long),  $R_2 = \text{OD}/2 = 0.1\text{cm}$ , so throughput is

$$JA = 2\pi R_2 L J = 8 \times 10^{-10} \pi = 2.5 \times 10^{-9} \frac{\text{g}}{\text{s}} \quad (2.8)$$

Or do we use  $R_1$ ? That would give  $1.2 \times 10^9$ . How far off is the flux? A dilemma.

Timescale:  $\delta^2 \simeq Dt \Rightarrow$  steady state. Here  $t \simeq \delta^2/D = 125000$  seconds, about a day and a half.

Design: what to do to improve throughput?

- Smaller  $\delta$ : possible breakage
- Higher  $D$ : change glass, raise temperature
- Higher  $\Delta C$ : raise/lower temperature, change glass

Okay, that was the braindead 1-D solution. What about the real cylinder?

**Cylindrical coordinates** So,  $C_{out}$  at outside,  $C_{in}$  at inside, what to do between? Use  $R_1$  and  $R_2$  for inner, outer radii. Fick's first, assume 1-D, so  $C$  is function of  $r$  only.

$$J_r = -D\frac{dC}{dr} \quad (2.9)$$

Conservation: in at  $r + \Delta r$ , out at  $r$ , no gen or accum, area  $2\pi rL$ :

$$0 = [2\pi r L J_r]_r - [2\pi r L J_r]_{r+\Delta r}, \quad (2.10)$$

divide by  $2\pi L$ ,  $\Delta r \rightarrow 0$ :

$$0 = -\frac{d}{dr}[rJ_r] \quad (2.11)$$

Plug in flux:

$$0 = \frac{d}{dr} \left( rD \frac{dC}{dr} \right). \quad (2.12)$$

Now solve:

$$A' = rD \frac{dC}{dr} \quad (2.13)$$

$$\frac{A'}{Dr} = \frac{dC}{dr} \quad (2.14)$$

$$C = A \ln r + B \quad (2.15)$$

where  $A = A'/D$ . From BCs:

$$\frac{C - C_{in}}{C_{out} - C_{in}} = \frac{\ln(r/R_1)}{\ln(R_2/R_1)} \quad (2.16)$$

Check at  $R_1$  and  $R_2$ , units.

Flux =  $-DdC/dr$ :

$$J_r = -D \frac{dC}{dr} = -D \frac{d}{dr} \left[ C_{in} + (C_{out} - C_{in}) \frac{\ln(r/R_1)}{\ln(R_2/R_1)} \right] = D \frac{C_{in} - C_{out}}{\ln(R_2/R_1)} \frac{1}{r}. \quad (2.17)$$

Important result: not flux, but flux times area.

$$AJ_r = -2\pi rLD \frac{dC}{dr} = 2\pi rLD \frac{C_{in} - C_{out}}{\ln(R_2/R_1)} \frac{1}{r}. \quad (2.18)$$

Note  $rs$  cancel, so  $AJ_r$  is constant for all  $r$ . Make sure units work. Cool.

Numbers, result:  $1.8 \times 10^{-9}$ . Between the 1-D estimates. Overestimated flux, at  $R_2$  is really  $1.44 \times 10^{-12}$ , twice that at  $R_1$ , so  $R_1$  value is closer.

More important: cartesian gave *wrong design criterion!* Not minimize  $\delta$ , but minimize  $R_2/R_1$ ! Double production by going from 2 to  $\sqrt{2}$  because  $\ln(\sqrt{2}) = \frac{1}{2} \ln(2)$ , e.g. 3 mm OD with no change in thickness!

Other design issues: helium on inside or outside? Inside means glass is in tension, outside compression. But if gas is dirty, inside is easier to clean.

Note: on problem set 2, will derive this for a sphere for a drug delivery device. Pretty cool.

## 2.2 September 8, 2003: Steady-State with Homogeneous Chemical Reaction

Mechanics:

- New recitations: R12, F2, both in 8-306.
- Fri: very different lecture, ABET stuff.

Names.

Muddy stuff:

- Recitations. :-)
- Dislike cgs units.
- Clearer writing and neater presentation. (Big chalk...)
- Why both ways? One is simple but wrong, other is complex and right.
- Flux in cylindrical coordinates. Give full gradient. (Next time.)
- Integrating to get solution:  $d/dr(rdC/dr) = 0 \Rightarrow C = A' \ln r + B$ .
- General  $\rightarrow$  particular solution in cylindrical coords. Start with general, plug in BCs:

$$C = A \ln r + B \quad (2.19)$$

$$C_{in} = A' \ln R_1 + B \quad (2.20)$$

$$C_{out} = A' \ln R_2 + B \quad (2.21)$$

$$C_{out} - C_{in} = A'(\ln R_2 - \ln R_1) \quad (2.22)$$

$$A' = \frac{C_{out} - C_{in}}{\ln(R_2/R_1)} \quad (2.23)$$

$$C_{in} = \frac{C_{out} - C_{in}}{\ln(R_2/R_1)} \ln R_1 + B \quad (2.24)$$

$$B = C_{in} - \frac{C_{out} - C_{in}}{\ln(R_2/R_1)} \ln R_1 \quad (2.25)$$

$$C = \frac{C_{out} - C_{in}}{\ln(R_2/R_1)} \ln r + C_{in} - \frac{C_{out} - C_{in}}{\ln(R_2/R_1)} \ln R_1 \quad (2.26)$$

$$C - C_{in} = \frac{C_{out} - C_{in}}{\ln(R_2/R_1)} \ln(r/R_1) \quad (2.27)$$

$$\frac{C - C_{in}}{C_{out} - C_{in}} = \frac{\ln(r/R_1)}{\ln(R_1/R_2)} \quad (2.28)$$

- Didn't finish: timescale to steady-state  $\tau \sim L^2/D$ , in this case 125,000 seconds, about a day and a half. Will explore this more rigorously on Friday.

Summarize: illustrates 3.185 methodology

- Problem statement: maximize throughput = flux  $\times$  area
- Conservation equation
- Constitutive equation
- Combine to give (partial) differential equation

- General solution with integration constants
- Boundary conditions give values of integration constants
- Use solution to get problem objective: flux×area
- Design recommendation follows from solution

Like p. 465 of W<sup>3</sup>R.

**Generation** Homogeneous chemical reactions. RCC carbon fiber-reinforced graphite composite! Very high-temperature, high-strength. Carbon fiber preform, model as a porous material, diffusion of acetylene to the surfaces of the fibers, at high temp it decomposes and deposits graphite.

Problem: as it deposits, it seals off the entrances, non-constant diffusivity. Generation of acetylene  $G = -kC$ . UNITS!

Set up problem in center, symmetry, sheet of material. 1-D equation:

$$0 = D \frac{d^2 C}{dx^2} + G = D \frac{d^2 C}{dx^2} - kC \quad (2.29)$$

General solution, using polynomials  $e^{Rx}$ ,  $R = \pm\sqrt{k/D}$ , so

$$C = A \exp\left(x\sqrt{\frac{k}{D}}\right) + B \exp\left(-x\sqrt{\frac{k}{D}}\right) \quad (2.30)$$

BCs: at  $x = \pm\frac{L}{2}$ ,  $C = C_0$ , so  $A = B$ ,

$$C_0 = A \left[ \exp\left(\frac{L}{2}\sqrt{\frac{k}{D}}\right) + \exp\left(-\frac{L}{2}\sqrt{\frac{k}{D}}\right) \right] = A \cosh\left(\frac{L}{2}\sqrt{\frac{k}{D}}\right) \quad (2.31)$$

Result:

$$\frac{C}{C_0} = \frac{\cosh\left(x\sqrt{\frac{k}{D}}\right)}{\cosh\left(\frac{L}{2}\sqrt{\frac{k}{D}}\right)} \quad (2.32)$$

What does this look like? Pay attention to  $\frac{L}{2}\sqrt{\frac{k}{D}}$ , or more generally,  $\frac{L^2 k}{D}$ . Can either be sorta uniform, or VERY non-uniform, uniform if that number is small (thin sheet, slow reaction, fast diffusion), nonuniform if it's large (thick sheet, fast reaction, slow diffusion). Makes sense.

So, have process, want to double thickness with same uniformity, can't change  $D$  much, how much change  $k$ ? Drop by factor of 4. Problem: takes four times as long!!

The real solution: blow acetylene through it!

## 2.3 September 10, 2003: Unsteady-State Diffusion

TODO:

- Check reading room to make sure texts are there.
- Bring: cards, class list.
- Check W<sup>3</sup>R pages for this lecture.

NAMES!

Mechanics:

- Get office hours together.
- Pump the zephyr instance.
- Fri: very different lecture, ABET stuff.

Muddy stuff:

- Cylindrical gradient (W<sup>3</sup>R appendices A-B, p. 695–700):

$$\nabla C = \frac{\partial C}{\partial r} \hat{r} + \frac{1}{r} \frac{\partial C}{\partial \theta} \hat{\theta} + \frac{dC}{dz} \hat{z}, \quad (2.33)$$

$$\nabla^2 C = \frac{\partial^2 C}{\partial r^2} + \frac{1}{r} \frac{\partial C}{\partial r} + \frac{1}{r^2} \frac{\partial^2 C}{\partial \theta^2} + \frac{\partial^2 C}{\partial z^2}, \text{ or} \quad (2.34)$$

$$= \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial C}{\partial r} \right) + \frac{1}{r^2} \frac{\partial^2 C}{\partial \theta^2} + \frac{\partial^2 C}{\partial z^2}, \text{ or} \quad (2.35)$$

$$(2.36)$$

- During derivations, important points are obscured. “What we’ve learned” summaries help. Basically following outline mentioned before, on p. 465 of W<sup>3</sup>R. Also feel free to snoop around Athena directory...
- How to draw exponentials in concentration profile?
- Plotting hyperbolic trig functions—necessary? No. If needed, use calc/table.
- Too quick jump from integ consts to carbon fiber material, missed lots.
- Keep C<sub>2</sub>H<sub>2</sub> conc constant for constant rate? Not quite, keep it uniform.
- How to calculate C<sub>2</sub>H<sub>2</sub> consumption rate? Use concentration (or partial pressure) and reaction constant. But often don’t know reaction constant, need to try at various temperatures, or just do what we did—find something which works, and use this methodology to understand why and how to make work for new designs.
- How do we get:

$$\lim_{\Delta x \rightarrow 0} -D \frac{\frac{dC}{dx} \Big|_x - \frac{dC}{dx} \Big|_{x+\Delta x}}{\Delta x} + G = D \frac{d^2 C}{dx^2} + G? \quad (2.37)$$

Derivative of the derivative is the second derivative?

- Arrhenius plot: which part is diffusion-limited, which part reaction-limited? Can’t really compare because of different units. But can sort of make a plot of  $\log(kL^2/D)$  vs.  $1/T$ , look at different parts. Want: low-temperature reaction-limited case, with fast diffusion to wipe out conc gradients. Diffusion-limited means it doesn’t diffuse in very far.

Next Monday: reaction and diffusion in series, which dominates is more straightforward, can easily compare the different coefficient.

- How did  $\sqrt{k/D}L/2$  become  $kL^2/D$ ? What's important for design: if two designs have the same  $kL^2/D$ , then have the same  $\sqrt{k/D}L/2$ , same uniformity. So use the simpler one to guide design decisions. Get into further with dimensional analysis next week.
- Why no flux at  $x = 0$ ? Because of symmetry: on left, flux goes right; on right, flux goes left; in middle, flux goes... nowhere! Symmetry, or zero-flux boundary condition, like PS2 #3.

**Unsteady Diffusion** Last two times: stories to take home: increasing production rate of helium from natural gas, high-quality manufacturing of reinforced carbon-carbon for space shuttle wing, nose leading-edge tiles. This time: math first, examples later, because three different solutions to the diffusion equation, examples can use one or more.

Now accumulation  $\neq 0$ , rate also in mol/sec =  $V\partial C/\partial t$ . Chapter 27 material. Resulting equation in 1-D:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} + G. \quad (2.38)$$

Physical intuition: concentration curvature is either due to generation, or leads to time evolution, or both. Upward curvature means neighbors diffuse in, either  $G$  negative or  $C$  increases; downward means diffuse out, either  $G$  positive or  $C$  decreases.

Today focus on zero-generation solutions which you've seen before, to be used in this class (book derives them using Laplace transforms...):

- Error function:

$$C = \text{Aerf}(c) \left( \frac{x}{2\sqrt{Dt}} \right) + B, \quad (2.39)$$

$$\frac{\partial C}{\partial t} = -\frac{x}{2\sqrt{\pi Dt^3}} \exp\left(-\frac{x^2}{4Dt}\right), \quad (2.40)$$

$$\frac{\partial C}{\partial x} = \frac{2}{\sqrt{\pi}} \frac{1}{2\sqrt{Dt}} \exp\left(-\frac{x^2}{4Dt}\right), \quad (2.41)$$

$$\frac{\partial^2 C}{\partial x^2} = -\frac{1}{\sqrt{\pi Dt}} \frac{2x}{4Dt} \exp\left(-\frac{x^2}{4Dt}\right) \quad (2.42)$$

$$= -\frac{x}{2\sqrt{\pi D^3 t^3}} \exp\left(-\frac{x^2}{4Dt}\right). \quad (2.43)$$

So this satisfies equation 2.38.

What it looks like: graph erf, erfc; discuss constant C BC  $x = 0 \Rightarrow C = C_0$ , uniform C IC  $t = 0 \Rightarrow C = C_i$ . Results:

$$C_i > C_s \Rightarrow C = C_s + (C_i - C_s) \text{erf}\left(\frac{x}{2\sqrt{Dt}}\right) \quad (2.44)$$

$$C_s > C_i \Rightarrow C = C_i + (C_s - C_i) \text{erfc}\left(\frac{x}{2\sqrt{Dt}}\right) \quad (2.45)$$

Semi-infinite. But what if your part is not semi-infinite, but thickness  $L$ ? (Not many parts are semi-infinite...) Since  $\text{erf}(2)=0.995$  and  $\text{erfc}(2)=0.005$ , we can approximate  $\infty \simeq 2$ , if  $\frac{L}{2\sqrt{Dt}} > 2$ , then erf is about 1 and erfc about 0, can consider semi-infinite. Solve for  $t$ :

$$t < \frac{L^2}{16D} \Rightarrow \text{semi-infinite}. \quad (2.46)$$

(Recall  $t > L^2/D \Rightarrow$  steady-state...)

- “Shrinking Gaussian”:

$$C = \frac{A\delta}{\sqrt{\pi Dt}} \exp\left(-\frac{x^2}{4Dt}\right) + B \quad (2.47)$$

$$\frac{\partial C}{\partial t} = \dots \quad (2.48)$$

Graph: initial layer of height  $A + B$  in background of  $B$ , spreads out. Note: not valid for short times, only for

$$2\sqrt{Dt} > \delta \Rightarrow t > \frac{\delta^2}{4D}. \quad (2.49)$$

Note also (semi-)infinite, like erf valid for  $t < L^2/16D$ . Note one-sided, two-sided; either way, BC at  $x = 0 \Rightarrow \partial C/\partial x = 0$ .

Not necessarily square initial condition! Can even start with erf, drive in to shr Gaussian.



## 2.4 September 12, 2003: 9/11 remembered, ABET

TODO: Bring ABET handout!  
Schedule office hours.

September 11. The day meant a lot of things to a lot of people. Yesterday the occasion was commemorated in a number of ways, here in Boston, in my hometown of New York City, and around the country and the world. I can't hope to be as profound as some of the speakers at those services, but can talk about a few things it meant to me personally, in particular as I have reflected on my decision to become an engineer, and my purpose in the profession. Perhaps some of it will resonate with one or two of you; I invite your comments or questions, and we'll take as long for this as we have to.

I'd like to start nine days before the tragedy, when I was in New York for my sister-in-law's wedding. My wife's parents live in Brooklyn, which is where the ceremony was held, but we were staying with her aunt and uncle in Long Island. At least twice a day in the few days beforehand, we drove the Belt Parkway and Brooklyn-Queens Expressway, wrapping around Brooklyn, passing under the Verazzano bridge and entering New York Harbor, with the view of the Statue of Liberty and the majestic buildings rising ahead, the skyline dominated, of course, by the World Trade Center.

During those drives, I recalled the experience of my High School French teacher Mr. Schwartzbart, an Austrian Jew who survived World War II in a rural Belgian boys' camp which, unknown to him at the time, was made up entirely of Jewish boys, and in fact, was set up to keep them safe throughout the Nazi occupation. He described the terror he felt under the occupation, and then the arrival of the American soldiers, "All of them giants," he said, then pointed to me, "like Adam," they had come to set the continent free.

And he described the journey to America as a young teenager, a transforming experience. Most amazing was the entry of his ship carrying scores of poor immigrants like himself into New York Harbor, this impossibly enormous bridge which just got bigger and bigger as they approached (the Verazzano was the longest span in the world for about 50 years), the tranquility of the harbor within, with the great buildings visible ahead including the Empire State, and the Statue of Liberty to his left as they steamed toward Ellis Island (the World Trade Center's construction was still 20 years away). There was an awe-inspiring sense of the magnitude of this great nation of impossible size which had overwhelmed some of the greatest evil the world had ever known, and his heart swelled with joy at the thought that there was such power on the side of liberty.

These days in is fashionable to reflexively cringe at the identification of this country with freedom, and this teacher in particular very frequently commented cynically on the deficiencies in American culture and education. Having come to know this side of him, when we asked why he came to this country, Mr. Schwartzbart's reply surprised us: "The land of the free and the home of the brave." Then after a pause, "It really is true." His personal experience of this gave great weight to these words.

During these drives along the Belt Parkway, my thoughts also turned toward the fragility of the grand edifices, and in particular to the 1993 bombing of the underground parking lot of one of the Twin Towers. Fortunately the towers withstood that attempt to destroy them, but there would surely be more attempts, and no amount of devastation was too horrible for the perpetrators to dream up. Should anything happen, I was grateful for the opportunity to see this beauty, and even to feel a small piece of what Paul Schwartzbart had felt some fifty years earlier. I thought of how fortunate is his generation which came through the Depression, fought that terrible war, and lived to see the nation preside over such a long and prosperous peacetime as the world had perhaps never before known.

So you can imagine my shock when just nine days later, as I sat in my office, my wife called from home to say that while watching CNN, they announced that a plane had crashed into the World Trade Center. Well, I thought, about 60 years ago a small plane hit the Empire State building, I'm sure there was a lot of damage and many people killed, but the rest of the building should be fine. Just a few minutes later she called again to tell me about the second plane, and suddenly I was afraid. Then the Pentagon, and the missing plane in Pennsylvania. My thoughts turned to the Mid-East, and this administration's policy of deliberate neglect in the Israeli-Palestinian peace process. Then the last call, one tower had collapsed. With her voice choking from the tears, she described its fall as "like a house of cards," and could say little more.

Immediately, I logged out, got on my bike, and pedaled home as fast as I could.

I'm sure each of us can tell a story about where we were when it happened. Being from New York, I was immediately concerned for friends and family. My wife's grandmother went to the roof of her building in Queens, from where she saw the second plane hit the south tower, and that tower's collapse. I had shared this view every day growing up as I rode the Roosevelt Island tramway to school and saw these buildings which seemed as permanent as mountains. My wife's best friend in College, who lives in the Prospect Heights section of Brooklyn and works in the southern tip of Manhattan, noticed people in his neighborhood looking up and saw some smoke, but rushed into the subway as he was late for work; the packed subway stopped after it left Brooklyn and waited in the tunnel for about 20 minutes before it turned back and he got out and learned what had happened. My Elementary School best friend worked in the 17th floor of Tower 1, and had a bad back which would have made it painful and difficult to get out—if he hadn't been home sick that day.

Then there was my father's friend whom I know well and whose business had just finished moving into the 89th floor of Tower 1. His staff had been told not to come in that morning until 10 AM, because their carpets, freshly washed during the 1-7 AM shift, would need to finish drying. As he drove north on the New Jersey Turnpike, he saw the first plane crash right through the windows of his new office, then took the next exit and went right back to his daughter's kindergarten class.

The previous Spring and Summer I had a course 6 UROP student in my group. His brother worked above the 90th floor of Tower 2, and on the first and second day afterward without a word to anyone in his family, my student grew panicked, then desparate, then increasingly hopeless. His brother finally called to say that a friend had literally dragged him from the office after the first plane hit, and they ran out of the building together just as the second plane smashed into it. He described bits of the hell that was the area around him, but at the time had no other thought than to get away, go home and lie down in shock, not even thinking about his relatives who were trying to reach him. My student described the moment when they connected as one of the happiest of his life.

Another friend was not so fortunate. Her father worked in an upper floor of Tower 2, and was one of just two in his company who didn't make it out. To make matters worse, she was trapped in L.A. because of grounded planes, unable to get back and try to locate him, so day upon day she was not only uncertain and hurting but frustrated at being far from anyone who could help her. She is still grieving, as it's hard to accept that she lost the closest person to her in the world because a handful of maniacs decided to crash a plane into his building.

There are of course tens of thousands more stories like these, so many people were affected directly or knew someone who was. But even if you were not so directly involved, if you're like me, the tragedy didn't end on that day, but played out over and over again in your mind. I can't count how many mornings in the ensuing months I woke up at 3 AM thinking about the towers' collapse, feeling hurt, afraid, angry, and much as I hate to admit it, somewhat vindictive as we learned of the total destruction of the Al Qaeda camps and cave complexes in Afghanistan.

Then thoughts turned to my own life. What can I do, what's my role in the world, how can I help?

I turned to the motivations I had for entering science and engineering, and materials science in particular, which I came up with in High School. Motivations for studying these things vary greatly, from interest in the subject matter, elegance of the equations, beauty of nature etc., to being able to earn a stable income and support a household, or perhaps a large income, to serving society in some way. My own motivations fell somewhat in the first category, but if I had followed that alone I would have been 6-3 (computer science); it was the last of these categories, serving society, which steered me into Materials Science.

As a high school student, I verbalized this service as follows. As a scientist or engineer, I would be helping to solve the world's little problems, which I listed as:

- Agriculture, to feed a growing planet.
- Medicine, allowing people to lead longer, healthier lives.
- Transportation and communications, to bring people together and lessen the chances of conflict. For example, much of the reason war between France and Germany today is unthinkable is because there are so many more personal cross-border relationships now than in 1940 or 1914, it's very difficult for a propagandist to castigate an entire people as "the enemy" and it's becoming more difficult every year.

- Human interactions with the environment, for sustainable living.
- A recent addition, information access, with implications for democracy, as the biggest enemy of an authoritarian state is the truth.

All of these are important in themselves, but even more important, if we do our jobs well and make a difference in these areas, we help the artists, politicians, economists, philosophers and theologians to solve the big problems, which I would list as:

- World peace.
- Averting famines, and their relief. Almost all famines can be avoided without resort to international aid, and are the result of poor resource management or hoarding.
- Real public health, made available to those who need it around the world.
- Justice, including somewhat equitable economic distribution.
- Truth in journalism and history.
- Human happiness and fulfillment.
- Purpose and meaning for our lives.
- Artistic expression of emotions, of values, of that purpose and meaning.
- Last year Ross Benson added: Tolerance of differences.

An important consequence of this understanding of “little problems” and “big problems” is that being a scientist or engineer requires a lot of *faith*, faith that our knowledge and our inventions will be used wisely, for good and not for evil. The more “sciencey” our contributions, the more faith is necessary, with the ultimate example perhaps being nuclear science, which can be used to produce lots of cheap power or cure diseases, or destroy entire cities in an instant. If we work on weapons, they can of course be used for defense or for aggression.

But even if we’re not working on nuclear science or weaponry, one of the lessons of September 11 for me is that no matter how careful we are to focus on purely non-military technologies, this tragedy showed that even a civilian jetliner—built to bring people together—can be abused by people with sufficient hatred as a weapon of mass destruction. This is truly frightening for us, and requires us to have that much more faith in the people, institutions and systems surrounding the technology in whose development we participate.

So what should we do? Shall we abandon technology altogether and go back to rubbing sticks together? Perhaps we should join the peace corps? For some of us that will be the answer, but I think there’s a lot more that can be done with the little problems that can help to make a real impact on the big ones. So how can we put ourselves in positions to do as much good as possible?

I can think of a few ways, but at your age and even at mine, perhaps the most important is to take a step back and examine what we’re doing and why. I have an advisee taking this class now who took off all of last Spring for that very purpose, and ended up returning to MIT (and in fact to Materials Science) that much more focused than the previous December for the experience. Of course, you don’t have to take off a semester to do this, there are very good ways to do some of this right here.

First, the HASS and HASS-D subjects present outstanding opportunities for this kind of exploration. MIT is no longer just about training technology leaders, but also about training world leaders who know about technology, and this school has put enormous resources into building world class departments in the Humanities, Arts and Social Sciences. For example, I’ve heard tremendous things about our Anthropology department from a variety of external sources, and even within our department we offer a HASS subject called Materials in the Human Experience (3.094) every Spring.

Second, I’ve made a point of suggesting to all of my advisees that they get to know the MISTI programs (I think that stands for MIT Internships in Science, Technology and Industry), which do an outstanding job not just of sending students to companies, universities and government labs in foreign countries, but also preparing them for the trip, even culturally and psychologically.

Third, develop a habit of using your wealth to support organizations and causes which effectively promote what you view as positive values. You may not have much now, but you will later, and getting into this habit is not hard; furthermore, membership in many of these organizations requires a contribution of as little as \$30. If you like I can discuss offline some of the organizations I've given to since my undergraduate years, one even since high school.

Fourth, look for opportunities to participate in the process of improving lives yourselves. Whether tutoring or mentoring, or working in a social justice organization, or writing to Congress, participating in society in a meaningful way is important to making it all work, and I believe important to improving ourselves too. Believe it or not, time is actually one resource which you will *not* have more of later in life than you have now, particularly if children become part of your life.

Fifth and perhaps most importantly, get to know your fellow students. This buzzword is repeated over and over again, but it's worth repeating yet again: because MIT attracts the best and brightest from all over the world, the *diversity* of the students on this campus is truly extraordinary, it's almost certainly broader and deeper than anything you've experienced before college, and almost certainly broader and deeper than anything you will ever experience later in life. That goes for Cambridge as well, and many other universities, though much less so on the graduate level and beyond. And by getting to know your colleagues, I don't just mean hanging out and eating pizza, nor even getting to know what spices they use to cook lamb, though food is of course an important part of social interaction. I'd encourage you to learn something about your friends' lives, their families, their values—and be willing to discuss these aspects of yourselves too.

And given its importance, I'd encourage you to learn something about your friends' faith. Human institutions, organizations, systems and even nations are terrific, but never perfect, as we learned in a powerful way on September 11. Participating in and strengthening them is an important and honorable activity, but I believe that placing all of our hope on them is not viable in the long term. At some point they're going to let us down, as this country has in some ways let down my French teacher Mr. Schwartzbart. Furthermore, evidence abounds for forces at work in the universe beyond those of physics, and even grows with the increase of human knowledge about this universe; perhaps the most significant example is the Anthropic Principle in Cosmology, which some of you may have heard of and I'd be happy to discuss offline.

That concludes what I said last year: the tragedy reminds us that our work here is very important, but must be viewed in context, and done with faith that it will be used for the broad purposes for which we intend it. Since last year, time has passed and some of the emotions have subsided just a bit, also several important things have happened, or have not happened, causing my own feelings about this to be somewhat more complicated.

For one thing, the message from Washington continues to urge us to live out lives as if nothing had happened, because if we changed anything, we'd be giving the terrorists what they want. But this is foolishness, important things have changed, and as citizens there are things we can do on a daily basis to improve our country's security, and the silence from Washington has been deafening.

A few months ago I saw a book provocatively titled, "When you ride alone, you ride with bin Laden." The cover art was derived from a World War II poster, "When you ride alone, you ride with Hitler," whose point was that the practices of avoiding driving, carpooling, and using public transportation save gasoline needed for the war effort. In that vein, an important thing which has *not* happened is that there has been no effort whatsoever on a national level to reduce our dependence on imported oil, which has been a huge factor in our problems in the Middle East. In fact, we've seen the opposite in this administration's rollback in fuel economy standards, and heard talk about the costs to the auto manufacturers and consumers of requiring increases in efficiency, with no mention whatsoever of the multitude of costs of continuing to burn fossil fuels as extravagantly as we like.

Another thing which has changed my view of the world was the war in Iraq. For months, the administration hyped any evidence at all for Iraqi connections to Al Qaeda and possession or development of weapons of mass destruction. Then inspections were allowed (to be fair, largely due to U.S. pressure, and no thanks to the posturing of certain countries like France), and one-by-one the inspections eliminated every piece of purported WMD evidence save the rumor about uranium purchase from Niger. And so with that one rumor as justification, we sent an invasion force to Kuwait, and used technological superiority to destroy the Iraqi army in about four weeks.

I believe that the war was wrong for a number of reasons. First, as mentioned, it was completely

unjustified. There was no correlation to terrorism, none to weapons of mass destruction, and there are a dozen dictators around the world whose human rights violations could similarly motivate action. If violation of U.N. resolutions was the motive, then it's up to the U.N. to act.

Second, this war was an extremely imprudent waste of resources. It is unwise to spend a couple of hundred billion dollars on a flimsily-justified war in a time of record deficits, and even more imprudent to tie down fifteen of the U.S. Army's thirty-three combat brigades in that occupation during a time of multiple threats from WMD in North Korea and Iran, to shaky stability in Afghanistan, to low-level al Qaeda activity from Indonesia to Somalia. And most significant is the loss of hundreds of American and thousands of Iraqi lives, very nearly including that of my own brother, a Captain in the U.S. Army third infantry division's second brigade, whose unit was hit by an Iraqi missile just after their capture of downtown Baghdad. Like my Course 6 UROP student two years ago, the days between learning of the attack and confirming my brother's safety were some of the longest of my life. I cannot imagine the terror and grief of hundreds of thousands of loved ones of Iraqi soldiers who did not know for weeks or months whether their sons, brothers, husbands or fathers were dead or alive, nor the pain of those whose worst fears were in the end confirmed.

Finally, the war has cost us diplomatically, and will continue to cost us potentially for many generations. The arrogance with which the administration shrugged off overwhelming international opposition was shocking, particularly as it involved three of the five Security Council permanent members, some of our most important allies, and both of our neighbors. Even more shocking was the pathetically childish pettiness with which the administration spoke of "punishing" the opponents to the war—particularly the French—and then turned around to ask them to contribute money and troops to the occupation and reconstruction to reduce the resource burden on us. But in the long term, the most diplomatically destructive aspect of the war is the precedent it sets for accusing a nation of violations of one sort or another, putting aside international outcry for restraint, and using military superiority to crush the weaker victim. This precedent can easily be abused by, say, Turkey, Syria, Egypt, Jordan and Saudi Arabia against Israel, North Korea against the South, Russia against the former Soviet Republics, China against Taiwan—any nation with a fight to pick can say, "But of course it's been done before, by the Land of the Free and Home of the Brave!"

And so we are reminded of our duty as citizens to speak out about matters of importance to our country. And in particular, as scientists and engineers we have the duty to speak out with authority on certain issues such as the small cost of reducing energy consumption, and the enormous costs of not doing so. Most of all, in the changed world our need for faith is greater than ever, in our work as well as our outlook for the future. I welcome any comments, contributions, or questions.

**ABET Sheet Review** See the ABET sheet.

**Unsteady Diffusion Continued** Muddy stuff:

- Symbol conventions:  $C_i$  is initial,  $C_0$  I use as surface and sometimes other things;  $C_s$  always surface concentration.
- Physical meaning of graphs, interpretation of these things: coming soon.
- Exact criteria for each solution: will be summarized.
- Semi-infinite and erf validity. First, semi-infinite applies to one-sided erf and one-sided shrinking Gaussian. Fully infinite applies to two-sided both. Second, the criterion is derived from the error function:  $t < L^2/16D \Rightarrow \text{erf}(x/2\sqrt{Dt}) > 0.995$  and erfc is below 0.005. Same criterion for erf, erfc, shrinking Gaussian.
- How do the M and top-hat initial conditions give the same equation? Over a long time, the details of the initial condition smooth out and become Gaussian.

Continuing where we left off last time (did the erf and shrinking Gaussian):

- Fourier Series:

$$C = a \exp(-b^2 Dt) \sin(bx) \text{ (or } \cos), \quad (2.50)$$

$$\frac{\partial C}{\partial t} = -ab^2 D \exp(-b^2 Dt) \sin(bx), \quad (2.51)$$

$$\frac{\partial C}{\partial x} = ab \exp(-b^2 Dt) \cos(bx), \quad (2.52)$$

$$\frac{\partial^2 C}{\partial x^2} = -ab^2 \exp(-b^2 Dt) \sin(bx). \quad (2.53)$$

$$(2.54)$$

Elegant and simple. Separation of variables: all of the  $t$  in one term, all of the  $x$  in the other  $f(t)g(x)$ .  
[Eigenfunctions...]

Graph: sine wave decays with time.

## 2.5 September 15, 2003: Wrapup unsteady, boundary conditions

Muddy from last time:

- Appreciate 9/11 reflections, not political opinions. Apologies to those affected, particularly language. Forms a strong part of 9/11 feelings, particularly as administration has done its best to tie them together. Uncomfortable with talking about one side and not the other. War must always be a last resort when other means e.g. negotiation have been tried. Defining objectives as narrowly as “regime change” with neither aggression nor clear and present danger (Bush *and* Clinton) is as misguided and wrong as extremists in the region who call for destrurction of a certain state “by any means necessary”. Open for last words...

Continuing where we left off last time (did the erf and shrinking Gaussian):

- Fourier Series:

$$C = a \exp(-b^2 Dt) \sin(bx) \text{ (or } \cos), \quad (2.55)$$

$$\frac{\partial C}{\partial t} = -ab^2 D \exp(-b^2 Dt) \sin(bx), \quad (2.56)$$

$$\frac{\partial C}{\partial x} = ab \exp(-b^2 Dt) \cos(bx), \quad (2.57)$$

$$\frac{\partial^2 C}{\partial x^2} = -ab^2 \exp(-b^2 Dt) \sin(bx). \quad (2.58)$$

$$(2.59)$$

Elegant and simple. Separation of variables: all of the  $t$  in one term, all of the  $x$  in the other  $f(t)g(x)$ . [Eigenfunctions...]

Graph: sine wave decays with time. Like a sinusoidal layered material being annealed in time. If period =  $2L$ , then  $b = \pi/L$ , get:

$$C = a \exp\left(-\frac{\pi^2 Dt}{L^2}\right) \sin\left(\frac{\pi x}{L}\right). \quad (2.60)$$

But what use is a sine wave? Note linearity of diffusion equation: any sum of solutions is also a solution. So we can add sine waves to get something more useful, use that.

Fourier transform: express *any* initial condition as sum of sine waves. We'll do one: square wave of period  $2L$  for multilayer material annealing, each term has period  $2L/n$  so  $b_n = n\pi/L$ :

$$C = \sum_{n=0}^{\infty} a_n \exp\left(-\frac{n^2 \pi^2 Dt}{L^2}\right) \sin\left(\frac{n\pi x}{L}\right). \quad (2.61)$$

The Fourier transform:

$$a_n = \frac{4}{n\pi}, \quad n \text{ odd}, \quad 0, \quad n \text{ even}. \quad (2.62)$$

Illustrate different sine functions, how they add to a square wave. Result:

$$C = C_0 + (C_{max} - C_0) \sum_{n=1, n \text{ odd}}^{\infty} \frac{4}{n\pi} \exp\left(-\frac{n^2 \pi^2 Dt}{L^2}\right) \sin\left(\frac{n\pi x}{L}\right). \quad (2.63)$$

So we start with all these sine waves, then what happens? Higher-order terms shrink real fast. Graph amplitude vs. time, show  $n = 3$  drops out nine times faster,  $n = 5$  twenty-five times faster. Do it as  $t/\tau$ , where  $\tau = L^2/\pi^2 D$ , so first term is  $\exp(-t/\tau)$ , second  $\exp(-9t/\tau)$ . One term remains real fast.

Consider:  $t = L^2/D$ ... What is single-term max concentration at that time?  $4/\pi \times \exp(-\pi^2) = 6.5 \times 10^{-5}$ , quite close to zero!

Other application: finite system with thickness  $L$ , uniform IC, constant  $C$  boundary conditions. Graph, show the “virtual” wave outside. Note that at short times, erf is easier; long times, one-term sine wave is easy.

TA wanted to do 2-D and 3-D separation  $C = f(t)g(x)h(y)...$

Suppose something more like first lecture, section 2.1 (p. 6): initial flat, one side raised? Then linear plus Fourier series, with odd and even  $n$ ; even so, at  $t = L^2/D$ , first term, max conc is a tiny fraction of original. So, very close to steady-state!

**Which to use?** Summary of criteria:

- Error functions erf, erfc:
  - (Semi-)infinite
  - Uniform initial condition at  $t = 0$  equal to boundary condition at  $x = \infty$
  - Constant concentration boundary condition at  $x = 0$ , infinite source/sink backing it up.
- Shrinking Gaussian  $\frac{A\delta}{\sqrt{\pi Dt}}e^{-x^2/4Dt} + B$ :
  - (Semi-)infinite
  - Fixed amount of material already in solid and diffusing into infinity
  - Gaussian “width”  $2\sqrt{Dt}$  much larger than  $\delta$
- Fourier series:
  - Infinite 1-D sine or square wave initial condition, *or*
  - Finite layer thickness  $L$
  - Uniform initial condition at  $t = 0$
  - Constant concentration boundary conditions at  $x = 0, x = L$

Examples:

- Decarburizing steel sheet: initial concentration  $t = 0 \Rightarrow C = C_i$ , boundaries  $x = 0, L \Rightarrow C = C_s = 0$  due to oxidation. Start erf, go to Fourier.
- Semiconductor devices: initial treatment with phosphorous-containing gas, initially no phosphorous so  $t = 0 \Rightarrow C_P = 0$ ; fixed concentration at surface  $C = C_{eq}$  or  $C_s$  or  $C_0$ . Erf. Then seal the top, no more gas, drive-in diffusion gives shrinking Gaussian.
- Galvanizing steel: thin layer of zinc on iron. Initial:  $x < \delta \Rightarrow C = C_0, x > \delta \Rightarrow C = 0$ . Start erf (diffusion couple) but centered at  $x = \delta$

$$C = \frac{C_0}{2} \operatorname{erfc} \left( \frac{x - \delta}{2\sqrt{Dt}} \right). \quad (2.64)$$

This holds for as long as the zinc is semi-infinite, i.e.  $t < \delta^2/16D$ . For long times  $t > \delta^2/D$ , finite amount of zinc means shrinking Gaussian:

$$C = \frac{C_0\delta}{\sqrt{\pi Dt}} \exp \left( -\frac{x}{4Dt} \right). \quad (2.65)$$



## 2.6 September 17, 2003: Boundary conditions, layer growth

Fun opener: Michael Dixon on calculus in physics in Dorchester.

Muddy from last time:

- Square wave: why is  $a_n$  zero for even  $n$ ? That's the Fourier transform; would throw off symmetry.
- How erfs in infinite square wave IC? Like diffusion couple...
- What is plotted on the graph of amplitude vs. time?
- Steady Fourier:  $\frac{4}{\pi} \exp(-\pi^2)$  constant? No, wave with that amplitude at  $t = L^2/D$ ; for longer time asymptotically approaches  $C = C_{av}$ .
- In galvanizing situation, why erf for small times? Isn't it a finite amount of zinc? At very small times, can consider even the zinc as semi-infinite. Also, at small times  $t < \delta^2/D$ , shrinking Gaussian doesn't work, goes to infinitely tall and thin.
- What to use in example 3 between  $\delta^2/16D < t < \delta^2/D$ ? Nothing covered here; perhaps another Fourier transform...
- Write down initial conditions for examples... Added to lecture notes, in my home directory.

**Diffusion boundary conditions** Types:

- Constant  $C$ : what's that  $C$ ?
- Constant flux: sealed means zero, sometimes ion beams, etc. (not often)
- Flux vs.  $C$ , for chemical reaction or mass transfer coefficient.  $J = k(C - C_{eq})$  (note ChemEs'  $k''$ ...) Units:  $k$  in cm/s. Also mass transfer coefficient through fluid film:  $J = h_D(C - C_{eq})$ , where  $h_D = \delta/D$ .

Example: gas diffusion in metal. Oxygen, nitrogen, hydrogen in metals: diffuses monoatomically,  $2O(m) \rightleftharpoons O_2(g)$ , equation:

$$K_{eq} = \frac{p_{O_2}}{[O]^2}. \quad (2.66)$$

So oxygen concentration at equilibrium is proportional to the square root of pressure. (Not the same for helium, argon, etc.) Then if flux is proportional to difference in concentrations, it's proportional to square root of difference in partial pressures!

Misconception 1: Equilibrium is **NOT** steady-state. Global equilibrium here would be a brick of  $SiO_2$ . Local equilibrium gives concentrations at interface sometimes. Can be out of local equilibrium and at steady state too.

Misconception 2: kinetic reaction rate order is **NOT** thermodynamic order.

**Layer growth** Motivating example: silicon oxidation (example W<sup>3</sup>R pp. 487-489). Electronic components, this is the "gate oxide" in MOSFETs, draw p-n-p structure. Thickness must be tightly controlled for the FET to work—to switch at the right voltage. How to make the oxide? Expose it to air, and it just grows. Cool. Wet oxidation too: expose it to steam and it grows differently (slower?). How much does it grow, how long to leave it there?

Go to the phase diagram, this one is pretty simple. Start with equilibrium. Many times, can use the phase diagram. Others, with impure phases (like air), or partial pressure or total pressure dependency, need activity to get equilibrium concentration at interface.

Out of equilibrium, but interfaces at local equilibrium: diffusion-limited, explain the concept of pseudo-steady-state. Growth is really slow because, although  $D$  might be high leading to steady-state,  $C_3 - C_1$  is really small, leading to slow flux, really slow growth of the layer. Growth rate:

$$J_O = \frac{2 \text{ moles O}}{1 \text{ mole SiO}_2} \frac{\rho_{SiO_2}}{MW_{SiO_2}} \frac{dY}{dt}. \quad (2.67)$$

Why? Proportional to  $J_O$ , then it's just a matter of working out units.

No.  $J\Delta t$  is the amount over a certain amount of time,  $(C_1 - C_0)\Delta Y$  is the area on the graph needed to transform that much Si to  $\text{SiO}_2$ .

For equilibrium, set  $J = \Delta C/Y$ , solve for  $Y$ :

$$\frac{C_3 - C_1}{Y} = \frac{2 \text{ moles O}}{1 \text{ mole SiO}_2} \frac{\rho_{\text{SiO}_2}}{M_{\text{SiO}_2}} \frac{dY}{dt} \quad (2.68)$$

$$Y dY = \frac{1 \text{ mole SiO}_2}{2 \text{ moles O}} \frac{M_{\text{SiO}_2}(C_3 - C_1)}{\rho_{\text{SiO}_2}} dt \quad (2.69)$$

$$\frac{Y^2 - Y_0^2}{2} = \frac{1 \text{ mole SiO}_2}{2 \text{ moles O}} \frac{M_{\text{SiO}_2}(C_3 - C_1)}{\rho_{\text{SiO}_2}} (t - t_0). \quad (2.70)$$

Parabolic growth. Plotted in text, p. 489. But the plot doesn't quite work!

## 2.7 September 19, 2003: Layer Growth, Dimensional Analysis

Mechanics etc.

- Forgot last time: test 1 October 13?
- Monday: no class, but I will be here for office hours 2:30-3:30 as usual; Albert?
- Next Thurs 9/25: GE CEO Jeffrey Immelt at Bartos theater (downstairs Media Lab)...

Muddy from last time:

- Pseudo-steady-state of what? Diffusion: growth is slow, so conc profile reaches steady-state.
- Why  $J_0 = \frac{\Delta Y}{\Delta t}(C_1 - C_0)$ ? Explain:  $J_0 \Delta t$  is the amount of oxygen which the flux has fed through.  $(C_1 - C_0) \Delta Y$  is the amount of oxygen needed to transform  $\Delta Y$  worth of silicon into silicon dioxide.
- Why  $Y(t)$ ? Is all diffusion-limited growth proportional to  $\sqrt{t}$ ?

**Layer growth** Motivating example: silicon oxidation (example W<sup>3</sup>R pp. 487-489). How much does it grow, how long to leave it there?

Back to phase diagram:  $C_0$ ,  $C_1$  and  $C_3$  as three equilibrium concentrations at operating temperature. Out of equilibrium, but interfaces at local equilibrium: pseudo-steady-state.

For equilibrium, set  $J = \Delta C/Y$ , solve for  $Y$ :

$$\frac{Y^2 - Y_0^2}{2} = \frac{1 \text{ mole SiO}_2}{2 \text{ moles O}} \frac{M_{\text{SiO}_2}(C_3 - C_1)}{\rho_{\text{SiO}_2}}(t - t_0). \quad (2.71)$$

Parabolic growth. Plotted in text, p. 489. But the plot doesn't quite work!

Next out of local equilibrium: say 1st order chemical reaction as the slow step. (Note: kinetic order vs. thermodynamic equilibrium exponents!) Then introduce  $C_2$  between  $C_1$  and  $C_3$ , say the rate is proportional to  $C_2 - C_1$ , proportionality constant is the reaction rate coefficient which we call  $k$ . Very short times:

$$J = k(C_2 - C_1) \simeq k(C_3 - C_1),$$

constant growth rate, *linear* film growth.

Suppose  $C_3$  at oxide outer surface,  $C_2$  at back interface,  $C_1$  in equilibrium with silicon, reaction limit with constant  $k$ ,  $J = k(C_2 - C_1)$ . Want  $J(C_3, C_1)$ . Solve all together:

$$J = k(C_2 - C_1) = \frac{D}{Y}(C_3 - C_2) \left[ \Rightarrow \frac{C_3 - C_2}{C_2 - C_1} = \frac{kY}{D} \right]$$

$$\left( k + \frac{D}{Y} \right) C_2 = kC_1 + \frac{D}{Y} C_3$$

$$C_2 = \frac{kC_1 + \frac{D}{Y} C_3}{k + \frac{D}{Y}} = \frac{\frac{kY}{D} C_1 + C_3}{\frac{kY}{D} + 1}$$

Now get  $J$ :

$$J = k \left( \frac{kC_1 + \frac{D}{Y} C_3}{k + \frac{D}{Y}} - C_1 \right)$$

$$J = k \left( \frac{\frac{D}{Y} C_3 - \frac{D}{Y} C_1}{k + \frac{D}{Y}} \right)$$

$$J = \frac{C_3 - C_1}{\frac{Y}{D} + \frac{1}{k}} = \frac{k(C_3 - C_1)}{\frac{kY}{D} + 1}$$

Resistances in series. What dominates? Biot number!  $\frac{kY}{D}$  Ratio of resistances. Small times and small  $Y$  mean small Biot, reaction-limited. Long times and large  $Y$  mean large Biot, diffusion-limited.

**Dimensional analysis** W<sup>3</sup>R pp. 140–142. Definitions:

- Base units: m, s, mol
- Derived units: cm/s, N, mol/cm<sup>3</sup>
- Dimensions:  $L, t, C_O$

**Step 1** Postulate desired behavior as a function of the other variables, *e.g.*  $J_O = f(C_1 - C_3, k, D, Y)$ , or  $f(J_O, C_1 - C_3, k, D, Y) = 0$ . The number of parameters is the number of dimensions  $n$ , in this case  $n = 5$ .

This is done by intuition, and is very often the hardest step in the process.

**Step 2** Find the number of base units in the system  $r$ . Here: cm, s, mol, so  $r = 3$ .

**Step 3** Buckingham Pi theorem: number of dimensionless groups =  $n - r$ .

**Step 4** Choose  $r$  dimensionally-independent variables to eliminate, which will make the others dimensionless. Here we'll choose  $C_1 - C_3, D$ , and  $Y$ .

Counterexample: can't use  $k, D$  and  $Y$  because they're not independent! Very often there are multiple "right answers" (fluid dynamics), choose the one which is most convenient.

**Step 5** Form the  $\pi$  groups from what's left, which are unitless versions of the parameters. Dimensionless  $J$ , called  $\pi_J$ , is  $J \cdot [C_3 - C_1]^a \cdot [D]^b \cdot [Y]^c$ . Easy way: make a table with base units across the top, start with dimensions of  $J$ . Which of the eliminated units have moles?  $C_3 - C_1$ , so we can say  $a = -1$  and moles are cancelled. Then which have seconds?  $D$ , so we can say  $b = -1$  and seconds are cancelled. Now there's just  $\text{cm}^{-1}$ , so  $c = 1$  and we're done:

$$\pi_J = \frac{J_O Y}{(C_3 - C_1) D}$$

Likewise,  $\pi_k$  starts with  $k$  in m/s, so  $a = 0, b = -1, c = 1$ . Look, it's the mass transfer Biot number!

**Step 6** Rewrite Step 1 in dimensionless terms, and we're done:

$$\pi_J = f(\pi_k).$$

What's this? So simple? Can't be.

Let's test:

$$J_O = \frac{C_3 - C_1}{\frac{1}{k} + \frac{Y}{D}}$$

Mult by  $\frac{Y}{(C_3 - C_1) D}$  to give

$$\frac{J_O Y}{(C_3 - C_1) D} = \frac{1}{\frac{D}{kY} + 1} = \frac{1 + \frac{D}{kY} - \frac{D}{kY}}{\frac{D}{kY} + 1} = 1 - \frac{1}{1 + \frac{kY}{D}}$$

So,

$$\pi_J = 1 - \frac{1}{1 + \pi_k}$$

Limiting cases: large  $\pi_k$  means  $\pi_J = 1 - 0 = 1$ , so  $J_O = \frac{D}{Y}(C_3 - C_1)$ .

For small  $\pi_k$ , use  $\frac{1}{1+x} \simeq 1 - x$  near  $x = 0$ , so  $\pi_J = \pi_k, J_O = \frac{D}{Y}(C_3 - C_1) \frac{kY}{D} = k(C_3 - C_1)$ . Excellent!

Purpose: simplify down to an easier expression, single graph. If couldn't solve equation, single graph could be obtained from one experiment, generalized to any other reaction-diffusion problem of the same nature. Physical modeling, *e.g.* wind tunnel: get the dimensionless numbers right, every detail of flow is the same, dimensionless drag force is identical!

This ends diffusion, next week heat conduction!