# TRANSPORT

Alan Berger
<u>Graves and Muller</u>
- Consider a fluid in a stationary cavity. The cavity is infinite in one dimension, rather long in another dimension, and relatively short in the third. The cavity is closed on all sides except the top, which is in contact with fluid moving with a speed V.   Find the velocity profile for the fluid somewhere near the middle of the cavity. (Hint: I was allowed to use steady state, constant density, Newtonian fluid, and constant viscosity approximations in the derivation.)
    o My guess at the answer is given below. I basically wrote down Navier-Stokes and crossed out terms. No slip boundaries at the top and bottom. Another condition is that the mass flux across a line of constant x should be zero. I argued this from the perspective of steady state – it should be the same everywhere and it's zero at the walls. You might think of a better argument.
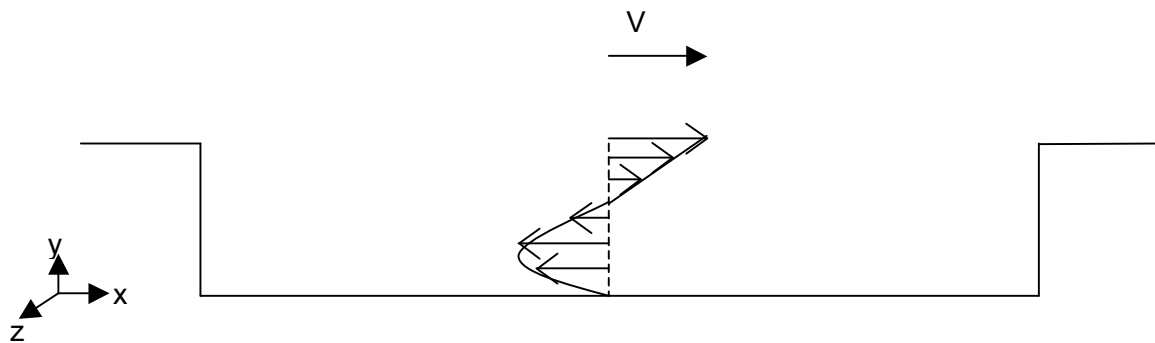
- A large, thin plate is heated until it reaches constant temperature T_H. This plate is then dumped into a bucket of cold water at temperature T_C. Find the temperature profile across the thickness of the plate.
    o Typical heat conduction in a solid problem. Muller and Graves asked about important parameters in the problem – I took this to mean dimensionless numbers. I strongly suggest that you know dimensionless groups (know both how to write them down symbolically and also physically what they describe). The one question that tricked me right at the end was "is there ever a time when the temperature profile in the rod remains flat, but just goes from T_H to T_C?" Although the governing equation for diffusion mandates that there will always be some curvature/slope, the answer they were looking for is that when diffusion is not limiting (low Biot number), the curvature is negligible and the temperature seems to drop uniformly.

Joe Chen

<u>Graves/Muller</u>
Again, the prelim began with Graves and Muller asking about my undergraduate education in transport. Graves asked the first question (a new one he said) by asking about a stirred reactor with two feeds of water and spherical solid pellets respectively. The solid dissolves in the water (it is not known whether the solid is completely dissolved or not). He wanted to know the exit concentration assuming a given fixed reactor volume and a given feed rate. I fumbled around a bit, not knowing exactly where to start. I drew a single particle and wrote down a mole flux of the component with a mass transfer coefficient multiplied by the concentration difference between the surface and the bulk. I first stated that the radius (and thus area) was a function of time, but actually it's not, since the reactor is at exit conditions (assuming a CSTR), so the radius basically instantaneously becomes the what it should be at the exit (assuming the sphere's don't completely dissolve). This was kind of counter-intuitive and I struggled with it for a little bit. Graves asked me how to get the mass transfer coefficient, and I gave him some spiel about the relevant dimensionless numbers (Sherwood and Schmidt). He also asked how to get the surface concentration, and I told him from an equilibrium relationship (though he seemed to not hear that, and he answered himself later). Either way, Graves seemed to be happy at this point, but Muller wanted me to continue on and find the reactor concentration. I wasn't exactly sure how to do this, but I said that you could combine the residence time, the molar flux, and the total area of all the spheres to get how much material would dissolve in the reactor. Then, dividing the total amount of material dissolved by the reactor volume would give the concentration. I really circled around this for a while, and I don't think Graves or Muller really knew how to do it exactly either. Graves had me write the mole flux in terms of Fick's law, but that was about it. This problem ended kind of unfinished, but Muller wanted to ask me a Bernoulli's equation problem. She essentially gave me a pipe with an expansion and told me to find the pressure drop given the inlet velocity. I wrote Bernoulli's law, found the velocity difference through a mass balance, and found the pressure difference from the change in velocity. I neglected to write down any frictional loss terms (from the expansion or from the wall), so Muller asked me whether those should be included (they should). I stated that they could be included using a friction factor. After that, they let me go.

Laurie Drews
<u>Graves/Cairns</u>
1. You have a box of water with a plate on top of it. The plate moves at velocity v. Show the pressure and velocity profiles in the center (far away from the edges). Start with Navier-Stokes and also prove why dp/dz is constant (if z is in the direction the plate is moving). Draw the profiles and be as accurate as possible. Discuss all boundary conditions.
2. Wet bulb temperature- show the governing equations. Never solved anything, just set up the equations and discussed how the experiment is run. Why does it not matter the velocity at which the thermometer is spun? Look at all governing dimensionless numbers. What is the j factor? Discuss the Chilton-Colburn analogy.

3. Say you have a metal sphere in moving air (I don't think it was stagnant). What is the characteristic time? In other words, what happens to the characteristic time as you double the radius of the sphere. Do a shell balance and again talk about all relevant dimensionless numbers (convection vs. conduction, heat transfer between the metal sphere and the air). Find tau and see how it relates to the radius. Does the heat transfer coefficient have a dependence on the radius (look at the correlations for forced convection)?

Erin Gallagher
Graves and Cairns
This pair took the exams seriously and quickly got down to business. After asking what I covered in my undergraduate curriculum, Graves asked me to draw a pipe that gradually widens, and to describe how pressure changes along the pipe. This is a classic problem that applies Bernoulli's equation, relating change in pressure to a change in velocity. The volumetric flow rate is constant, so by knowing one velocity, the other can be calculated, so pressure drop can be calculated. They wanted me to list all of the assumptions I made in order to use Bernoulli's equation. I eventually came up with them, by thinking about how Bernoulli's is a simplified form of Navier-stokes, but I took longer than they wanted. Next, Cairns asked me why the speed of rotation for a wet-bulb psychrometer did not affect the measured humidity. I had to think about this one for a few minutes, but managed to prove that the h/k_x ratio was the same no matter who spun the psychrometer. Next, they asked how I would estimate the time it should take to cool a metal sphere, which launched a discussion of the biot number, nusselt number, and order of magnitude estimates. Know your dimensionless numbers, where they come from, and the units of all of your variables. It was also helpful to know how to derive dimensionless numbers from the energy balance equation, as they asked for a few relationships that I hadn't heard of before, but was able to derive from scratch.

Josh Howe
Chu/Radke
This was undoubtedly my favorite of my prelims in addition to being my first and the one on which I performed the best. Before asking any questions, Radke asked about my previous background in transport (course title, credits, text, instructor), and asked what book I used to study for the prelim (BSL). Perhaps the last question was there because the only undergraduate transport text I used was Cussler, and only for half of a semester. Regardless, I was thereafter asked to step to the board.

You have a copper ball and you drop it into water. What is its temperature when it hits the bottom?

Awesome, this problem was not exactly what I had studied, but was similar enough to some combination of practice problems I'd done that I was happy about it (even happier than having the box of fluid and plate problem… but study that one, too). I started by wasting about 15 seconds by drawing a very general figure of what I thought such a setup might look like and verifying that the problem was defined correctly in my head. We decided to use a hot sphere and a tank of water at height "h." At this point I started

to set up the problem, setting the initial temperature of the sphere, the initial temperature of the water, and then prior to setting up my boundary conditions, I asked if it was reasonable to treat the problem as a "lumped capacitance" problem (a term some of my more transport-savvy study-buddies had taught me over the previous 10 days). Radke responded with, "well, can you? Justify it." I stated that if the Biot number was small, then I could. Radke: "What's the Biot Number? … write it down." I wrote down the Biot number definition ($Bi = h*L/k$, $L = d$) and then talked about what it meant physically when prompted (convective HT/conductive HT, so when conductive HT dominates, $Bi < 1$). Radke had me draw a temperature profile from the center of the falling sphere out to $T_{infinity}$ for the water for the low Bi case. Then we moved on with the problem as lumped capacitance.

Next, I set up a balance using Fourier's Law and Newton's Law of Cooling to set the fluxes equal and obtain a differential equation for the problem to solve to the surface temperature of the sphere (which was also the temperature throughout). At some point in this, I had asked Radke about $T_{infinity}$ in the water and whether to consider it a constant and he said "[you can if you need to or it makes the problem solvable]" to which I replied that it should be a good assumption, but the problem can be solved without that assumption. His reply: "then let's do it without assuming that, just for fun." So when I got my final differential equation, Radke asked, "so can you solve this now?" I said, "Yeah, separate it and integrate." He replied "I see two independent variables… you told me the temperature of the water was variable." Oops. So I quickly scrawled up $m*Cp*dT/dt=m*Cp*dT/dt$ to demonstrate that the rates would be proportional to one another by a constant for the system, and that I could express the differential equation just as the temperature of the sphere in time. He accepted this, and so I moved on to the next part of the problem: limits of time integration.

I started solving for the time by drawing a free body force diagram on the sphere in water while it is falling at a terminal velocity (buoyant force, gravitational force, drag force.) Chu asked "why is your F_d vector much smaller than your F_b vector?" Because water is fairly dense, as compared to, say, air, and so it provides a significant buoyant force, while the drag force from the water is likely to be of a lower magnitude. Luckily, he didn't press much more on that one or we would have been off to another 10-minute aside. After writing the force balance and lumping the buoyant and gravitational forces together in terms of delta-rho*g*V and setting them equal to the drag force (the lumped buoyant force would be used to explain a low transient regime to the velocity in the tank, as you can solve the transient equation of motion and get a very small characteristic time for the system… they didn't make me actually go through this one… another 15-minute aside avoided). For the drag force, I stated that it was going to be low Reynolds number flow (write the Reynolds number) and so I should use Stokes' Law for flow around a sphere, which expresses the drag force as linear in velocity (which I just put as the terminal velocity, neglecting the transient regime): $F_d = 6*\pi*\mu*R*v_{terminal}$. I solved for $v_{terminal}$, and used $h/v_{terminal}$ = delta-t to set an upper limit for my time integration, thus finishing the main problem. After this, it was on to a few questions where Radke and Chu picked apart my understanding of flow around spheres and drag forces. First, they asked for the friction factor as a function of Reynolds Number… and I drew up the

Moody Diagram for pipes… Oops! I corrected it, drawing instead the one for spheres, making sure to include the little transition bump (check BSL, know how to draw it). Radke asked me to locate the regime for Stokes flow, as well as asked why the plot got flat for large Re (apparently it's because F_d is a function of v^2 and f is something like F_d/KE, so it goes to a constant… I missed this part). Finally, my understanding of why Stokes flow drag is often attributed 1/3 to one type of drag and 2/3 to another was probed (2/3 form drag, 1/3 skin drag). Skin drag is the tangential force of the momentum transfer resulting from friction between streamlines, while form drag is "from the shape of the object." Of course, the form drag explanation wasn't cutting it for Radke, and I got to flounder around on the board for a bit while he asked me to draw the two types of drag on my sphere and it took me about 3 tries to finally draw the form drag as a normal vector pointing in toward the surface of the sphere. And then of course it became obvious the form drag is a result of the pressure difference in front of and behind the sphere. This concluded this prelim, so I erased the board and left.

Both Chu and Radke were jovial and maintained a positive atmosphere throughout. Despite expecting Radke to ask rapid-fire questions through the whole thing (which he did at times, nit-picking notations or other small things), it wasn't nearly as bad as I thought it might have been and I was very happy to have these two for my first prelim.

Andrew Jones
Graves/Radke
This test was pretty easy with the exception of a few oddball questions. I have a big mouth and made the mistake of saying Sturm-Louisville at the beginning. I then had to describe the operator and problem constraints, oops. On to the problem – flow on an incline plane! Very textbook question at the beginning of BSL. I started with a momentum balance but was told I could move to Navier Stokes if I wanted. A few oddball questions like that the Re < 2 for laminar flow and boundary condition questions. I also had to calculate the average velocity, which I am pretty sure they led me in the wrong direction integrating over the length and not the thickness. The problem was then formulated to have evaporation and I started the mole balance but we ran out of time.

Yongkwan Kim
Radke/Graves
This prelim was also one giant problem, and Radke did almost all the talking. There is an inclined plate with a film of liquid flowing on it. The top of the liquid is in contact with air. They made me draw velocity profiles for two cases, when you neglect the resistance of the air and when you don't. This was done without solving the Navier-Stokes equations first, thinking about the boundary conditions at each interface (no-slip at the plate, and continuity of velocity/shear at the liquid/air interface). One important note is that when you don't neglect the viscosity of air, the air forms a developing boundary layer on top of the liquid film, as more and more air is dragged along with the liquid down the plate. Then they asked me to solve the Navier-Stokes equations for the case when you neglect the viscosity of air. I ended up having to write the equation not just for

the direction along the flow, but also direction normal to the flow in order to get the information about the pressure gradient.

I think this is a standard problem you can find in any fluid or transport text, but I haven't solved it in years, which made it really difficult for me to do it on the board. Both Radke and Graves were very helpful in guiding me, though.

Matt Pavlovich
<u>Chu and Radke</u>
You'll probably read that these two are one of the most fun pairs you can get for a prelim, and that's pretty true. We start by having the standard chat about where I'm from and what my transport background is. Radke and I talk football for a little bit when he finds out I'm from Georgia Tech (Tech had just won the ACC and played in their first Orange Bowl in 40 years). I take this as a good sign, and it helps put me at ease for my first prelim. After that, Chu has me go to the board, and sets what must be a record for "consecutive words spoken by Jhih-Wei Chu in a prelim". He tells me "Let's start with a warm-up problem. We have a copper sphere at 50 C and we put it in a water bath at 25 C. How can we describe the sphere temperature as a function of time?" This so-called "warm-up problem" then proceeds to take up 30 of the 40 minutes I was in the room. I start by writing a transient heat balance on the sphere, and of course I proceed to royally screw up the spatial variables, throwing A's and r's and l's around like there's no tomorrow. Chu and Radke walk me through the unit analysis to show me how stupid I was, but they don't seem too broken up over it, and I eventually get it all in the right place. Radke asks me what assumption I'd made in order to write the dT/dt equation, and I tell him that I'm neglecting spatial variations of temperature in the sphere. This seems to be the correct answer, and Radke asks me to justify it. I toss out the Biot number, explain that the thermal conductivity k is expected to be large for copper, and that justifies the assumption. Radke agrees but asks me to "quantify the Biot number." Me: "well, it's the ratio of…" Radke: "No. Quantify it." Me: "It's hl/k, right?" Radke, unimpressed with my ability to regurgitate exactly what I've already written on the board: "we'll come back to this." He asks me to draw the temperature profile T(r) vs. r, which looks like a horizontal line until R (radius of the sphere), then exponential decay to the water temperature. Then Radke says we're going to change the sphere from copper to wood. I ask him if we can assume the other limiting case, i.e. ignore temporal variations in the sphere and assume temperature is only a function of radius. He says "no, we're going to look at the intermediate Biot number case," but I think he liked that I knew the other limiting case. I start doing a shell balance with heat flux in the r direction, and in classic Radke style, he tells me "you can just write down the answer." I don't actually *know* the answer, so I proceed with my shell balance, and eventually get a partial differential equation with a dT/dt term and a d^2T/dr^2 term. At some point, Jhih-Wei asks me to "fish out the Biot number" from one of the heat balances I'd written by rearranging variables, and I end up with some ratio of temperature differences (Ts - Tw)/(T0 - Tw). Apparently this is what Radke had meant by "quantify the Biot number." Now he asks me to revise my temperature profile, and I forget the famous boundary condition that the derivative at the center must be zero, so I draw some inane sloped line. Radke tells me "let's write some boundary conditions and see if that makes sense. First, write Fourier's

law." I know this one; $q = -k\, dT/dr$. Then the boundary conditions are 1) dT/dr ($r=0$) = 0 ("oh, I see what you mean"; I proceed to fix my temperature profile so that it has zero slope at $r=0$ and increasingly negative slope toward R); 2) $-k\, dT/dr$ ($r=R$) = hA (Ts - Tw), the Robin condition relating conduction at the surface to the convection involving temperature difference between the surface and the bulk water; 3) T ($t=0$) = 298 K, the initial condition for the dT/dt part. Now he asks me to classify this differential equation. "It's a partial differential equation?" "Well, yes, but tell me more. Is it parabolic? Hyperbolic? Elliptical?" "I honestly have no idea." "You took 230, right? You didn't cover this in there?" "No, we didn't. But… you could use Sturm-Liouville theory to solve it." (Sturm-Liouville theory is a method of solving PDE's that my class covered pretty extensively in 230; I'm not sure if it's standard curriculum or just a special "treat" we got from a visiting professor.) This was a bad thing to say, because of course Radke now assumes I know what I'm talking about. He grills me about boundary conditions and homogeneity and self-adjointness for a bit, and I totally get it wrong. By this point, there are about five minutes left in the exam, so Radke says "let's move on to a problem that'll really put some hair on your chest." Great. He says now the sphere is falling in the water bath, which is long in the z-direction, and we want to know the temperature when the sphere hits the bottom. He doesn't want me to solve the problem, just walk him through it. I say I'd do a force balance on the sphere to find terminal velocity, use that to find Reynolds number, use that plus the Prandtl number in a correlation for the Nusselt number, then find the heat transfer coefficient h. This all seems to go over well, and Radke lets me go a few minutes early.

Thoughts: know your units (the part that messed me up the most was when I got all the business with k, l, and A wrong at the beginning), and be sure your terminology and symbols are correct. I got yelled at at least three times for using r (the spherical coordinate axis) and R (the physical radius of the sphere) interchangeably. Radke and Chu were demanding but friendly, and they were very good at walking through your mistakes so that you could catch them yourself. Memorizing Navier-Stokes is a waste of time if you have these guys, but basic transport laws (Fick's, Fourier's, etc.) are good, as are basic dimensionless numbers (Re, Pr, Nu, Bi, etc.). I passed but not as convincingly as I thought I would.

Laura Quock
Graves: Fluid in a container with a plate moving with velocity, $\vec{v}$, over the top. Use Navier Stokes to find an expression for the velocity. Draw the velocity profile.
Cairns: Wet bulb problem. Describe situation and use of wet bulb thermometer in detail. Set up energy balance and mass balances. Use dimensionless numbers. Describe what the concentration at the surface of the wet bulb thermometer is.

Barry Shang
Radke/Newman
This was the first prelim for me. Originally, I was scheduled for Graves/Muller, but due to a scheduling conflict with one of the professors, Prof. Newman was asked to step in. This resulted in me switching with Alan Berger since Prof. Newman was his advisor. Anyway, I was certain they were just trying to trip us up right before the exams but I wasn't going to let this prevent me from staying on top of my game.

I walked in and the professors were friendly as expected. We went through the usual chit-chat about previous courses and textbooks. I mentioned Wilkes for fluid mechanics, and Geankoplis for heat/mass transfer. I knew Geankoplis had a poor reputation for being a "transport-lite" text so I made fun of it and glorified BSL instead, which Prof. Radke and Newman enjoyed since BSL is basically the transport Bible around here. Naturally, this led to Prof. Radke proposing that we do a BSL problem, namely, flow of a falling film.

I wrote down the NS equations in their simplified form and Prof. Radke asked me about why certain terms were zero. I had trouble proving that the pressure gradient in the direction of flow was zero. This led to me writing down the momentum balance in the other two directions, integrating the pressure gradients in the other two directions, and noting that the integration "constants" were functions of the other two variables. Then, I applied the boundary conditions, namely, that pressure was atmospheric at some specified height, which leads to the pressure gradient in the direction of flow being zero.

After all that, they asked me to find the velocity profile. Basically, you have no slip at the solid surface and zero shear stress at the air/water interface (since viscosity of air is low and the shear stress magnitudes are equated at the interface by Newton's third law. Also, you can assume the flow is laminar since the film height is small. Then, I was asked to find the mean velocity. You end up finding that it scales with (film height)^2, which we used later on.

Next, Prof. Radke says the water is evaporating as it flows down and asks me to find the film height as a function of distance down the film. This is similar to his previous problems (I think from 2009) where an infinitely long plate is moving with a film of evaporating water above. You set up a shell balance, with varying cross-sectional area (or film height) and use a convective mass transfer coefficient to describe the evaporative flux. Keep in mind that the mean velocity is a function of film height, which is a function of distance, so you can't take it out of the derivative when you take the limit.

Lastly, Prof. Radke asked some Radke-esque questions about relative humidity, etc., and how to find the evaporative flux given this information.

Overall, I think I did all right considering it was my first prelim and I didn't know what to expect. As long as you understand Radke's questions and follow his hints, you'll be fine. He'll rarely let you do the problem your way. Whenever I got some momentum going, the professors would shoot me down ("let's use x instead of y", "is that a function of x or y?", "you have three symbols up there that represent the same thing", etc.). This is not a poor thing though since Prof. Radke really tries to keep you on track. Prof. Newman didn't say much, other than arguing with Radke sometimes, and making fun of my poor math skills. He also suggested my board work was terrible, and likened me to a professor who was known for writing with one hand and quickly erasing with the other - but I'm gonna take that as a compliment instead :-0.

Alan Yiu
<u>Radke and Newman</u>
They asked me to consider a fluid flowing down an inclined plane, which is a classic
BSL problem. Radke did pretty much all the talking.
- They had me sketch what I expected the velocity profile to look like and have me justify it with boundary conditions.
- They asked me how I knew the flow was laminar, and I said you could look at the Reynolds number (<2300). Turns out that 2300 is the magic number for a pipe— for falling film, it's more like 4. Oops. They asked what characteristic velocity and length to use in the Reynolds number, and I chose the average velocity and the film thickness (δ).
- I used Navier-Stokes to solve for the velocity profile. Pretty straightforward, you can find this in BSL.
- Then he wanted me to express the Reynolds number in terms of only δ. You can find the average velocity by integrating velocity from 0 to δ and dividing by δ, which gives something proportional to δ^2. So Reynolds goes as δ^3.
- Then Radke asked me what happens if the water starts evaporating as it flows down the film. I said the film should get thinner as you move farther down the plate. He had me set up the mass and energy balances governing the system. At the end I had 3 couple equations, and he and Newman chuckled, "We aren't afraid of coupled equations though, are we?" I crapped my pants a little thinking that they would make me solve the system… but then they said I was done and let me out 5 minutes early.

They were pretty cheerful and helpful. They were pretty picky about specifics and notation, though, so just stay on your toes.

Zheng Zhai
<u>Radke and Newman</u>
They are both very nice.
The problems are:
1. The velocity profile of a falling water film. I used the continuity equation, N-S equation and set up the correct boundary condition to solve the velocity profile. Radke asked about one of the B.C.: Why $dVx/dy=0$ at $y=H$. Because the shear force in the gas phase = shear force in the liquid phase; $(-\mu_{gas})^* (dVx/dy)_{gas}= (-\mu_{liquid})^* (dVx/dy)_{liquid}$ When $y=H$, $(dVx/dy)_{liquid}= (\mu_{gas} /\mu_{liquid})^* (dVx/dy)_{gas}=\sim0$.
2. When the water film are falling, the height of the film is a function of x. Write out the shell balance.

KINETICS

Alan Berger
Clark and Reimer
- You have a long cylindrical furnace, and you intend to grow layers of silicon by passing silane gas over stacks of Si wafers. They gave me the reaction as follows:

  $SiCl_4$ (g) + $2H_2$ (g) → Si (s) + 4 HCl (g)
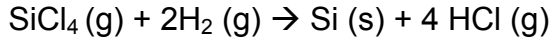
- Find the thickness of each wafer as a function of wafer number going down the reactor (assume equal spacing so wafer number is similar to length).
  - o I tried to think about the problem like a PFR with a changing molar flow rate. Unfortunately, I got sent down the wrong path because I just wrote the design equation for a PFR on the board from memory. The reason I did this was that in reading previous questions while studying, I came across an instance where Clark praised someone for "not wasting 10 mins on deriving a design equation." Sadly, in this case I think it would have been better to start from scratch with mass conservation. They both asked a lot of questions that threw me off track ("Why do we choose to operate reactors at steady state?" is the only one I can remember clearly now).
  - o When I wanted to calculate reaction rate as a function of conversion, they were kind enough to give me a rate law.
  - o They seemed almost angry that I was doing the problem in terms of volume instead of length down the reactor, even though a simple dV = AdL conversion works for constant cross-sectional area. I mention this because I think it's important to note that if your approach to the problem is not exactly what they have in mind, they might pick you apart. Be prepared for that and don't let it fluster you.
- Did you get that the wafers are all the same thickness, or is there variation? Is that desirable? If not, how would you fix that?
  - o No, they are fatter toward the front of the reactor where the concentration of reactants is highest. This is undesirable, we want them all the same. How to fix it is a reactor design question and I've never taken any design courses (I'm not even a ChemE) so needless to say I just spat out a whole lot of answers and hoped for the best. Reimer called most of my responses "Gerdonkin," not sure how to spell it but he explained it as a euphemism for "you don't know anything about chemical engineering." Moral of the story: even though the design prelim is a thing of the past, you might get asked design questions in one of the other exams.
  - o Despite the fact that I was able to go along with most of their ideas and corrections to what I was doing, they still failed me so hard that I had to take a remedial undergrad kinetics course (should have seen it coming

since I never had any kinetics before and told them that outright at the beginning of the exam).

Joe Chen
<u>Smit/Katz</u>

As I entered the room, Smit and Katz mentioned that it was the first year that thermo and kinetics were separated for prelims. I made a comment that I thought that thermo and kinetics tended to overlap, and so Smit asks for the connection between kinetic s and thermodynamics. I wrote down a simple unimolecular equilibrium reaction along with the overall reaction rate with the forward and reverse rate expressions. Then, using the definition of equilibrium, I derived the expression for the equilibrium constant in terms of the rate constants (kforward/kreverse). Smit and Katz then asked me a bunch of confusing questions about a part of my equation that included the concentration of the products over the reactants. They basically wanted me to generalize the expression for the equilibrium constant for all stoichiometries. Then, Smit asked me how to find the rate constant. I mentioned that they were usually found empirically, though you could estimate the rate constants from transition state theory or collision theory. Smit followed by asking me about transition state theory, asking me to draw a reaction coordinate vs. energy diagram. I drew one for the A/B reaction, with the transition state at the top of the hill along with an activation energy. Smit then asked if the activation energy was a constant. I replied I wasn't sure, but I thought it was a characteristic of the reaction. Smit replied that it did change in transition state theory depending on the definition of the transition state/reaction coordinate. He proceeded to draw on the board a picture of a particle passing through a narrow opening and defining two different reaction coordinates, one straight through the opening, and one at an angle. He asked a bunch of confusing questions about what the transition state was, which would have more activation energy, and a little bit about the partition functions for each case. He helped me through a lot of this part, since I really didn't know that much about TST.

After Smit finished his spiel about TST, Katz asked me a really open ended/ill-defined question about reactors. You were given the inlet exit temperature, the feed concentration, and the reaction (A goes to 3B). You had to try to find the conversion and exit temperature without knowing what kind of reactor it would be. Without knowing the internals, all you can really do is a mass and energy balance (assuming steady state). I started writing a mass balance, and Katz asked me if that would tell me anything. I replied no, not really. Then I moved to a mole balance, except I didn't know the exit concentration. Finally, I moved to the energy balance, and assuming that I knew the heat of reaction and the reactor was adiabatic. After a bunch of weird questions, they asked me to describe the energy balance in words (heat in by fluid minus head out by fluid plus heat of reaction generated). Both Smit and Katz nodded huge nods and then told me time was up.

Smit and Katz are not bad. They're nice, but they don't smile too much. Note that it was the first prelim on the first day, so they must have been in a pretty good mood.

Laurie Drews
Reimer/Clark
1. You have a batch reactor, A -> B zero order, and it has a cooling jacket. Find the temperature at which the reaction runs away (start with a heat balance).
2. Now change it to a CSTR, adiabatic, and first order. Draw X vs. T and discuss the stability of steady states. What are your assumptions? What if we don't assume constant density? Is this a good assumption for 2A -> B? How does the design equation change?
3. Packed bed reactor- write down the design equation and talk about assumptions.

Erin Gallagher
 Smit/Katz
I entered Prof. Smit's office, to find that Smit had been replaced by someone else (I didn't catch her name). She started off by asking me, on a fundamental level, what is activation energy and how can it be calculated? She wasn't looking for a description of the Arrhenius equation, or how you experimentally determine the value, but rather, via transition state theory, how one determines a reaction rate constant. I attempted to describe the Eyring equation while making it very obvious that I had no idea what I was talking about. Thankfully, Katz stepped in after a while and changed the subject. He asked me a bit about the Thiele modulus, what it represents, and how it changes for second order reactions. Then he asked me to draw an unknown reactor system at steady state, for A->B, where the final conversion, initial and final temperatures and total flow rate is known. The reaction mechanism is unknown, but basic thermodynamic data for the products and reactants are known. How do you figure out the actual concentrations of the inlet and outlet streams? I said to couple an energy balance with a mass balance, and use tabulated data to find the enthalpy of reaction. Then rate and initial concentration are the only two unknowns, which can be solved with two equations. I was stopped several times by the question "why" but eventually came up with reasonable answers. After this question, there was some time left, so our unknown tester brought me back to the original activation energy question, and watched me struggle to explain the limitations of transitions state theory for a while longer. Eventually, I simply admitted defeat and asked if they could recommend a good resource for me to brush up on my kinetic theory (McQuarrie & Simon).

Josh Howe
Clark/Bell
This was the last time slot on Friday, so, based on previous experiences, I was expecting Clark to be of a less-than-happy demeanor. I was pleasantly surprised, and both faculty were helpful and pleasant through most of the exam, excepting one point toward the end. We started off by talking about my kinetics background (fairly poor, but I used Fogler as an undergraduate) and got quickly into questions.

For some reason, I had a complete failure of all logical thought processes for the 40 minutes of this exam, and I find it to be mostly indefensible. This was, however, my third prelim of the day, so I suspect I was mentally fatigued. Regardless, I won't try to answer the questions too much, but will present them for reference.

"I have a reactor. It's a tube, and I've got some catalyst in there. I start with a known concentration… tell me what concentration I get out of the other end." Once we'd established it was a PBR and I started to work on the balance to find the design equation, the following things became relevant:
- gas phase reaction, A $\rightarrow$ 2B
- how do I know if my catalyst is all being used?
While I was deriving the design equation, Clark stated that "[I didn't] need to do that." Unfortunately, I am terrible at memorizing things, and I asserted that I did actually need to work through the derivation to obtain the design equation. Unfortunately, there were some errors along the way, but I eventually got everything into a reasonable form and worked out the volume change in terms of conversion. We talked a bit about Thiele modulus, and Bell asked how the equation for Thiele modulus would change for different orders of reaction. I thrashed around a bit and really didn't get too terribly far working on effectiveness factors sadly, and we'd spent quite a bit of time and Bell decided we'd just have to move on.

The second part of the exam (the last 15 minutes) was on how I'd obtain a rate constant. First, I started by stating that we could take experimental data and work from there, but this was apparently not what was being sought. I then suggested using Transition State Theory, which seemed to be the target. Then the question I didn't really want… "how?"
So I wrote down: $k = k_B*T/h*exp(-\Delta G^{\dagger}/(RT))$, Eyring's equation. Now it got even worse and more awkward: "Sure, that's Eyring's equation. Tell me more about it, where did Eyring get that equation… it came from somewhere." After a couple minutes of me standing there and trying to think about it, I was asked for the assumptions used in TST. I stated that the reactants and transition state were in equilibrium, but really didn't have anywhere to go from there, and thankfully this ended shortly thereafter, as neither Clark nor Bell were seeming too pleased at this point.

I barely failed this one, but felt like the "barely fail" was just a really nice way of delivering a failing grade for a performance that deserved to fail.

Andrew Jones
Bell/Smit
This was my first and by far my worst of the day. Bell and Smit did not smile the entire time and my weak attempts at humor were lost on them. The format was also very unorthodox. My exam started right away, after learning my first name, with them asking me my favorite kinetics topic. I landed on catalysis, but now realize I should have said something more like gas phase homogenous reactions of A goes to B of ideal gases. They then asked what my favorite catalytic reaction was, the Haber process. I proceeded to write the chemical reaction and describe how it probably proceeds

through a Langmuir-Hinshelwood mechanism. They asked me how I would setup an experiment to check my rate expression. They had me derive the rate expression as a function of conversion (very ugly because this is not an equimolar reaction). I was supposed to realize that at low conversions the PFR can be modeled using CSTR design equations. The equations become really easy then. I then walked through a Langmuir-Hinshelwood derivation and then onto questions about the pre-exponential and transition state theory. I proceeded to give a spotty description of the variables which I had learned from Wikipedia and my previous kinetics book, of which they did not agree with and became quite hot and bothered when I brought it up. Looking back at our kinetics class notes with Prof. Smit there really was not much in there. I stumbled quite a bit and didn't receive any help from the professors. In hindsight, I really had a lot of power in the direction the test was going.

Yongkwan Kim
Smit/Bell
They started out by asking me what was my favorite kinetics problem. I said isomerization problems where A $\rightarrow$ B. We ended up doing a problem where ortho-xylene becomes meta-xylene. They asked me how I would investigate the reaction rate. Eventually, what they wanted was for me to derive the design equation for the reaction in a PFR.

Then, they told me to suppose that this reaction is acid-catalyzed. They asked for a possible mechanism for this isomerization, and I had to guess at what the intermediate species would look like, where H^+ attaches to the methyl branch of o-xylene. Then the catalyzed branch moves from ortho position to the new meta position, and the H^+ ion detaches. They didn't expect me to know exactly how this happened, just a reasonable guess at the mechanism. I had to derive the rate law for this system in terms of concentrations of o- and m-xylene. It was important to recognize that since the H^+ is the catalyst for this reaction, they are equivalent to the reaction sites in more familiar mechanisms like Langmuir-Hinshelwood.

Then came the questions about Transition State Theory. Smit asked me, assuming I had all the quantum and statistical thermodynamics tools I needed, how I would go on about calculating the rate constant. I said that you assume the transition state and the reactant state is in equilibrium, and that the step from transition state to the product state is irreversible. Smit asked me what order parameters I would look at, and I said I would look at the distance the attached H^+ was from the new site. He added that the angle of the methyl branch is also an important parameter to look at. He also added that the velocity at the top of the transition hill has a Boltzmann distribution.

This was a very confusing prelim. Unlike thermo, it was a long discussion of one problem, where they both asked questions and corrected my answers. Smit's questions were very confusing, and Bell had to clarify at times.

Matt Pavlovich
Kinetics—Smit and Iglesia

The "usual chat" doesn't last more than thirty seconds, these two don't even try to make small talk, and I know this is going to be miserable from the start. Smit was on a kick this year where he'd ask a completely ridiculous question to start off: "what's your favorite reaction?" I pick, for God knows what reason, glucose-fructose isomerase. *Terrible idea*. First Smit asks me to draw it—I stumble through drawing the molecules, but I doubt Smit or Iglesia has enough of a biochem background to correct any error if in fact I made one. Then he asks me how I'd determine the reaction rate. I say that you could set up a packed-bed reactor with catalyst pellets, run glucose solution through at varying flow rates and temperatures, measure outlet fructose concentration with a polarimeter, and plot concentration versus time to try and fit a rate expression. I think this is a hell of a good answer (and it was actually a unit ops lab I did back in undergrad), but Smit tells me that that only finds concentration versus time, not a rate. This is true, and obviously I don't know how to do what he's asking me to do, but damned if he's going to give me a hint. After some time of awkwardly looking at him and Iglesia (who has done literally nothing so far), Smit asks me to write out the elementary steps in the reaction. I write $G + E \Leftrightarrow GE \Leftrightarrow F + E$ and say this naturally leads to using the Michaelis-Menten rate expression. They didn't ask me to derive it (which is nice—even though I probably could have done it, it's tedious), but they asked how I *would* derive it (assume GE -> F + E is irreversible and apply the pseudo-steady state assumption to GE), what Vmax is a function of (k2 and the number of enzyme active sites), and what Km is a function of (k1, k-1, and k2). Now Smit wants to find these k's theoretically. Naturally, the magic words there are "transition state theory", which is of course a complete mystery to me as it involves stat mech. I write up an equation relating k to ΔG (I accidentally write G on the left-hand side of the equation rather than k, and Iglesia pipes up for the first time, clearly angry with me that I've made a forgetful error), and Smit says that's fine, but how do you measure ΔG? This is sounding eerily like thermo, except he wants me to calculate it based on energies of reaction intermediates. I have no idea what Smit is talking about, so I spend the next three minutes drawing E before the reaction, GE complex, E after the reaction, and the famous G vs. reaction coordinate plot. None of this is what Smit is looking for, apparently. Iglesia says "we're not going to finish this. We need to move on." His question is a usual Iglesia-style problem: 2A -> B in a PFR, gas phase, and he wants to find concentration at the end of the PFR. I write the differential form of the PFR design equation, and he tells me to work in conversion instead of concentration. Sure thing. Except that I define the conversion in terms of concentration, which is apparently not okay. He wants it in moles. I change it, and now Iglesia wants me to put molar flow in terms of conversion. This sounds like a pretty stupid idea, really, because if I'd just left everything in concentration and related volumetric flow to molar flow by the ideal gas law, I'd be pretty much done by now. But I start throwing out the ideal gas law, and Iglesia cuts me off. "Why are you using this?" "I'm assuming ideal gas." "Did I tell you to make that assumption?" "I don't know—can I assume ideal gas?" "Yes." I don't really see the purpose of that exchange, except for Iglesia to try and assert his dominance over my solution, but I try and move on. I'm trying to relate the molar flow of B to the conversion of A, and after a bit of blankly staring at the board, I get something that looks halfway right except for the stoichiometry being off. After Iglesia points that out, I fix it. Iglesia makes another comment about not finishing this and moving on, and says that

there are two cases of non-ideality in a PFR: laminar flow and axial dispersion. I really wish he'd asked me that rather than telling me, because I know it, and by this point, I really need to prove that I know something. First, he asks me what sort of experiment you could run to validate plug flow. I say a tracer experiment, which I think is the only thing I've said that Iglesia has responded favorably toward. That favor is short-lived, though, as Iglesia asks some business about the Dirac delta function and how much the output would have to deviate from the input for the plug-flow assumption to hold. I understand the concept, but I have no idea how to answer his question. Then he asks how to correct my mass balance if there's laminar flow, and I say you'd solve the coupled momentum and mass transfer equations, or just get the velocity profile so you could find an average velocity. That's not what Iglesia is looking for, and he doesn't give me a hint about what he wants. Instead, he moves on to the axial dispersion part. After a lot of prodding and an exasperated look or two, I eventually realize that he wants me to put diffusion terms in my mass balance. I do that. No sooner than I finish writing Fick's law does Iglesia announce "That's all; you're finished." I reply "Thanks, have a good day!" trying to end on a high note. Neither Smit nor Iglesia acknowledges me. Thoughts: this one is painful. Neither Smit nor Iglesia smiled once for the entire 45 minutes. I've heard reports that both Smit and Iglesia, on different committees, are fine to have. Together, they're awkward and obtuse at best and unhelpful to downright mean at worst. Pick a reaction and know it inside and out in case Smit pulls this stunt again. Learn all your design equations in terms of conversion if you don't know them already—even if you're not accustomed to working in conversion, apparently Iglesia feels that you need to be. I did by far the worst on this prelim, even though I feel confident in kinetics and I did very well in Smit's 244 class the previous semester.

Laura Quock
Bell/Clark: What is your favorite reaction? Write the rate of reaction. Describe how you would experimentally find the order of reaction. Find temperature as a function of conversion for CSTR. Talked about falsified kinetics. Drew a plot of effectiveness factor vs. thiele modulus. Talked about what factors one could change in order to get a situation where internal diffusion is not limited. Asked about transition state theory.

Barry Shang
Reimer/Clark
By far the most unpleasant academic experience I've ever had, even worse than the 25% I got on the final exam way back in my Intro to ChemE class in undergrad. Anyway, Prof. Reimer asked most of the questions, and Prof. Clark occasionally made a few comments to further lower my self-esteem.

You are making silicon wafers in a tubular reactor. The reaction is $SiH_4(g) \rightarrow Si(s) + 2H_2(g)$. It occurs only at circular plates spaced evenly throughout the tube. Find the wafer height distribution as a function of distance down the reactor.

The key to this was making the very suspect assumption that the reactor was essentially a PFR. We can then find conversion as a function of length down the reactor (don't forget changing volumetric flow rate) and the reaction rate down the length of the

reactor. Therefore, you can find local reaction rate at each plate, and perform a "batch" reactor mass balance on Si(s), where rho*A*dh/dt = local rate. Anyway, I got a poor grade on this one, and for good reason, since I just did not like their way of modeling the problem as a PFR.

In the end, I kept on trying to do it my way (solve it sequentially as a series of "2-D" CSTR's, then generalize it for arbitrary n plates), and pretty much ignored their hints. The conventional idea of modeling this as a PFR is based on analogy to a PBR. However, in a PBR, the catalyst surface area/volume ratio is roughly constant down the length of the reactor, so it is fine to use differential PFR equations (since the reaction rate is constant throughout deltaV, in Fogler language in the differential mass balance). For the wafer problem though, the tube needs to be very long, and you need many plates packed relatively closely, so that deltaV is small in relation to the tube size, but large enough so that each deltaV contains a similar amount of wafer surface area (this is very similar to the scaling arguments that justify continuum mechanics). The problem here is that all the surface area is not spread out throughout deltaV, but concentrated at specific interval lengths down the reactor, so it's not quite like a packed bed. However, the analogy to a PBR was the "conceptual leap" they were looking for, and unfortunately, I just found that assumption to be way too suspect.
Anyway, the lesson here is not to try to do the problem your way, but just listen very carefully to what the professors ask you to do, and do the problem their way. It's probably the safest bet, or else the exam just becomes a huge mess of miscommunication for 40 min.

They also asked some small design questions, mainly, how to keep the wafer thickness roughly constant. You can cool the reactor near the entrance lowering the rate in this region. You can also add inerts, so that concentration of SiH4 remains roughly constant, keeping the rate relatively constant. By this time though, my self-esteem was already so low that all I was thinking about was going to the corner of my room to cry.

Alan Yiu
Reimer & Clark
They asked me to consider a catalytic converter as a CSTR. It was for a reaction of type A + B → C + D.
- First, Reimer had me set up the mass balance for a CSTR at steady state:
  - $F_{A0} - F_A = r_A$ (where r_A is the rate of disappearance of A)
- Then had me draw a plot of the two sides of this equation vs. F_A:
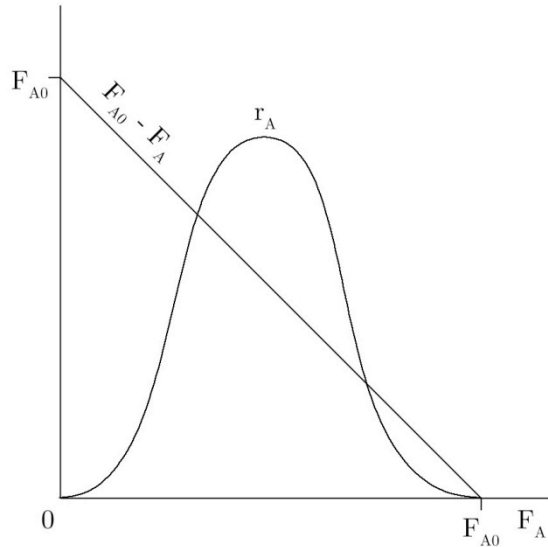
- o
  - o At first, I wasn't sure what r_A looked like, so he asked me to consider A and B reacting on a surface through a Langmuir-Hinshelwood mechanism. He asked what r_A would look like as a function of C_A, and I said it would increase then decrease (too much A means no surface sites for B to bind).
- Then he asked me where the steady states were on this plot (at the intersections of the curves) and whether each was stable. If $F_{A0} - F_A$ is greater than r_A, there's accumulation, which pushes you to the right on the F_A axis (x-axis). So the left and right steady states are stable, while the middle one is unstable.

Then, Clark asked for me to consider this reaction as occurring in a porous catalyst bead. For this scenario:

- He wanted to know what representative number described the situation, and I said the Thiele modulus.
  - o He asked what the Thiele modulus is, and I said that it's the characteristic reaction rate over characteristic diffusion rate, given by the formula:
  - o He asked how I got the formula, so I derived it:
- He asked for the effectiveness factor as a function of Thiele modulus. I said that it would depend on the order of the reaction, and drew something like:
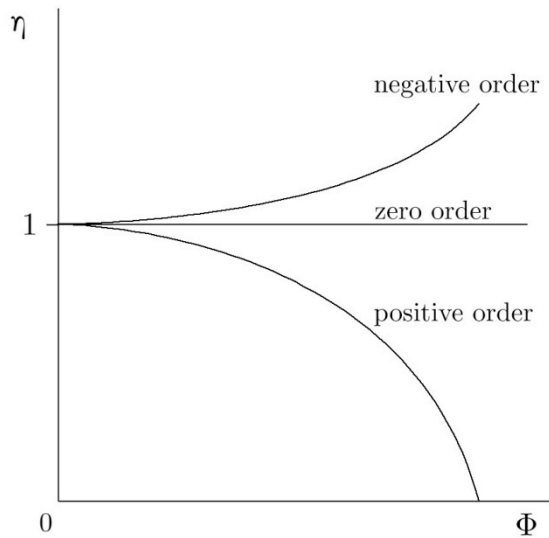
-
- He asked if there was a way, other than a negative-order reaction, to have effectiveness factor be greater than 1. I wasn't sure, so he asked how else I could increase reaction rate. I said you could increase temperature, which led me to the answer: an exothermic reaction could raise temperature, driving up reaction rate.

Then, at the very end, Clark asked about using a PBR instead.
- He asked what assumptions I would have to make, and I said it's like a PFR: radially well-mixed, no axial mixing.
- He asked how I would know that these assumptions are correct. I wasn't sure, so I brought up things like measure concentrations, look at Reynolds number, etc. He wanted me to say tracer studies.

Overall, they weren't very responsive and would wait for you to seem very certain of your answer before telling you it was right and that you could move on. Reimer was a little ambiguous but cheerful and pretty helpful. Clark seemed very unhappy to be there.

Zheng Zhai
Reimer and Clark
Reimer:
1.Gas SiH4 flow into the tube and this reaction happens: SiH4(g)-->Si+2H2(g). Si deposits on the disks in the tube (the disks are placed one after another in the cross section of the tube; and the distances between the disks are the same). Whether the thickness of the deposit silica changes along the tube?
This is a volume change PFR design.
2. Can you find out several methods making all the disks the same thickness? Changing temperature (changing the reaction rate) along the reactor; Adding a large amount of inert gas to the reaction system.
Clark:
1.Draw a plot: Conversion X versus temperature and explain.

THERMODYNAMICS

Alan Berger
<u>Alexander and Reimer</u>
- What is the maximum useful work we can extract out of a stream of high temperature steam? Take the steam to be at 1000K, the surroundings to be at 300K, and the "energy content" of the steam is 1000kJ.
    o I started talking about availability and useful work, but in the end I perceived that he just wanted me to do a Carnot engine efficiency calculation.
- Reimer asked me about an equilibrium reaction. He framed it around solar cells again (he must have realized it was an interest of mine), something about forming tin oxide. I can't remember the exact reaction, but there were two gas phase reactants forming tin oxide (solid) and another gaseous product.   He asked me all about equilibrium constants, activity, fugacity, and so on. If you want to pose the question to yourself or someone else for practice, try this:
- You have a reaction A (g) + B (g) $\leftrightarrow$ C (s) + D (g). The solid will form in a thin film layer on a glass substrate. How can we predict the thickness of the film? What is the equilibrium constant? How would you measure it?
    o This reminds me that when I started writing A + B $\leftrightarrow$ C + D underneath the actual products and reactants to save myself time, Reimer got upset and told me not to do that. I wrote everything out in full from there on. When he asked how I would calculate the entropy and enthalpy of reaction to in turn calculate ΔG^o_{rxn}, I mentioned 3rd law (I think this was okay) and standard heats of formation that can be looked up. He didn't like that second answer because apparently those numbers wouldn't be listed for something like tin oxide. Although I don't think he held me accountable for not realizing that, I don't remember coming up with a satisfactory answer.
- Draw a P-T diagram for a pure substance and explain each feature of the graph in detail.


Joe Chen
 <u>Cairns/Tullman-Ercek</u>

       They started by asking me where I went to undergrad and about my thermo background. Then, Cairns begins by talking about hydrogen production and asking me if I knew what the steam methane reforming reaction was. I said that I wasn't sure, so he tells me it's a reaction between methane and steam to make carbon monoxide and hydrogen. Then, he tells me to put up the water gas shift reaction (which I'm a little more familiar with). He then asks me about the temperature dependence of the equilibrium constant. Afterwards, he asks if the reforming reaction is exothermic and WGS reaction is endothermic, then what reaction condition should you operate at. I at first answer that it should operate at an intermediate temperature, but after some

prodding, I say that it should be a two stage process (hotter for the reforming reaction, colder for the WGS reaction).

Tullman-Ercek then asks if I know what a heat pump is. After a bit of thinking, I told her it was basically a refrigerator. Then, she asked me to draw the process for refrigeration. I fumbled around this one pretty badly, since I hadn't studied refrigeration cycles. After a ton of help and lots of awkward silences, I manage to put up the process (evaporator, compressor, condenser, throttle valve) along with a TS diagram of the refrigeration. This took a long time, so Tullman-Ercek said just to move on.

Cairns then asked how to calculate the maximum work of a fuel cell. This problem was straight out of Smith and Van Ness in Chapter 13, so this was easy (work is equal to the free energy change of the reaction). Then, he asked me how to find the reversible heat (T*deltaS). Next, he drew a voltage/current density characteristic (see below, this is much easier to understand with a graph). for a fuel cell and asked me to find the difference between the maximum work and the real work of a fuel cell. Since the work was G = nFE (Nernst equation), and n (number of electrons) could be related to the current, work was the x-axis value and y-axis value multiplied together (in essence). Since the voltage of the cell decreased with increasing current, the difference in the reversible/irreversible voltages (deltaE) multiplied by the differences in open circuit/operating current (delta I) resulted in the work lost due to irreversibilities (basically a shaded box). Next, he put the voltage from just the enthalpy change of the reaction (H = nFE I think?), which is higher than the voltage from the free energy change due to the heat lost. He asked me to draw what represented the reversible heat. This is just the difference in area between the free energy voltage and the enthalpy voltage multiplied by the current density (T*deltas = deltaH – deltaG). Finally, he drew the characteristic for a fuel cell in reverse (electricity in to split water). He told me there was a point where there was zero net heat. It turned out to be where the reversible and irreversible heat losses cancel. Cairns helped me throughout this graphical analysis, which was completely new to me. The finally let me go after going 15 minutes over the allotted time (although the extra time let me make up for my mishaps with refrigeration cycles).
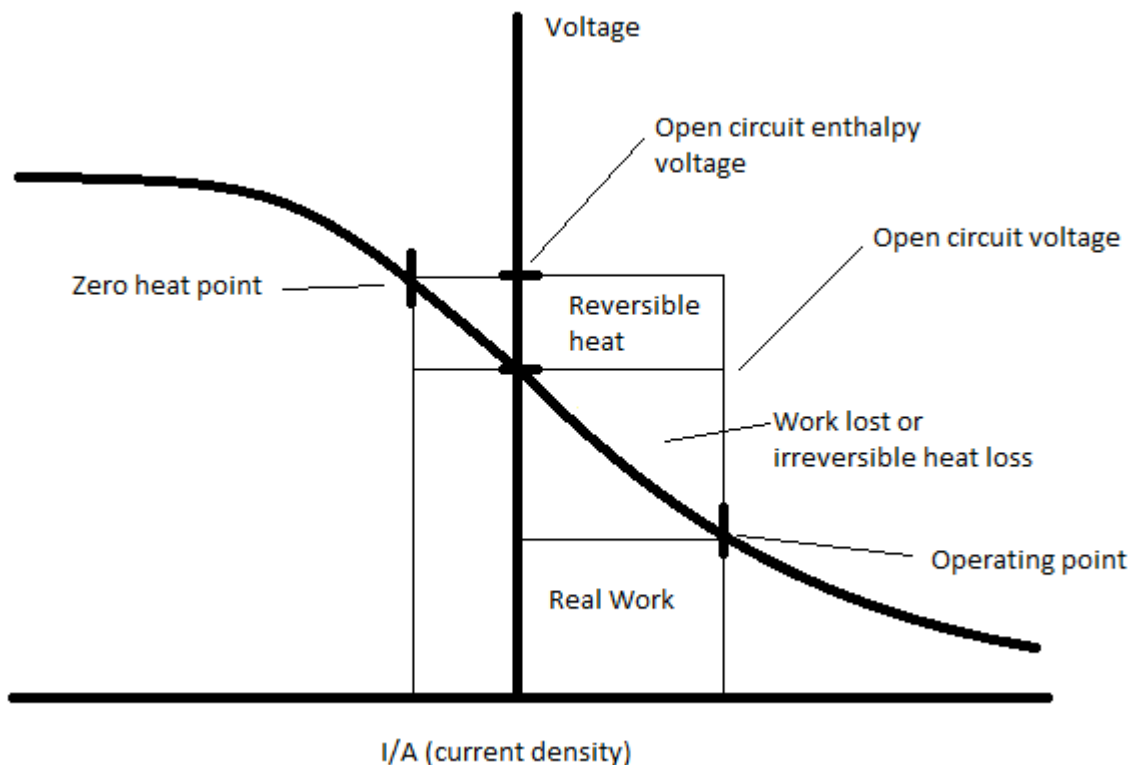
Laurie Drews
Chu/Alexander
1. You have a flash drum with an ideal mixture. Write down Raoult's Law and discuss how you derive it.
2. Consider a container of water with two hydrophobic plates in it. They are parallel, each with an area A. Find the critical distance these plates are held apart so that there is no water in between them. Use Gibbs Free Energy and don't forget surface tension and chemical potentials.

Erin Gallagher
Chu/Alexander
1) What is the maximum amount of work I can get out of transferring heat from a hot well to a cold well? They were looking for a discussion of Carnot efficiency, and wanted to know why this is the maximum possible efficiency. 2) You hold two hydrophobic plates underwater, what happens when you bring them really close together? The water is repelled from between the plates. Why? How close are they when water is no longer between the plates? Chu was aiming for a discussion of phase equilibrium, where the Gibb's free energy of the system between the plates is equal for water between the plates and no water between the plates. He wanted me to ignore all surface effects along the edge of the plates, and the fact that nothing would be between the plates after the water was repelled (assumptions I never would have made), so that

it was just a matter of balancing surface tension with chemical potential (mu*N = rho*Area), and using molar density of water to find the volume of water between the gap at this "equilibrium". Know your signs, units, and what chemical potential is. After finding the final equation for the distance between the plates, Chu asked me to estimate how wide that distance actually is. I guessed a micrometer, but the chuckles coming from Chu and Alexander informed me that I was several orders of magnitude off. They then thanked me, said goodbye (real friendly pair), and I was halfway out the door before they realized that they had another 15 minutes to quiz me. So, Alexander stepped in with 3) how would I separate two components in a flash chamber. I wrote down the basic (ideal) phase equilibrium equations, described assumptions for an ideal system, and was then allowed to leave.

Josh Howe
Prausnitz, Tullman-Ercek

This was Tullman-Ercek's first time doing prelims, so I wasn't sure what to expect from her. I spent a bunch of time studying Joule-Thompson coefficients, the Linde process, fugacity, activity coefficients, and other things Prausnitz has been known to ask (and was not disappointed). I expected something bio-influenced from Tullman-Ercek, so I glanced over Protein folding and a few other subjects just so that if they came up I'd have any idea at all how they worked (I am not a biology-fluent person). We started with the standard "what courses have you had and what texts did you use?" stuff and moved quickly from there. Notably, this one started late by a few minutes while I stood outside of Prausnitz's office waiting to be called in. When Tullman-Ercek came out to get me, I was told that I ought to have knocked (Prausnitz agreed).

First, Prausnitz began by asking me to write up the Gibbs-Duhem equation and explain how it is useful (it leads to Gibbs' phase rule, provides an equation to reduce degrees of freedom in problems, etc). He then restated his question "how is it useful if I'm an experimentalist." So I talked a bit about being able to know how chemical potentials would change relative to one another, but I wasn't really getting where he was going with it. Eventually, he asked "well, if my data doesn't agree with the Gibbs-Duhem equation, what can you tell me?" Well, your data's wrong. "Ok, but what if it does agree? Is my data right?" Hmm… it might be right. I want to say it's right, but I have a feeling I'm missing something… there's a trick here and I am not seeing it. Thankfully, he bailed me out: multiple sets of data may appear consistent with the Gibbs-Duhem equation and still be wrong, so my data might be right, but it might not. Oops. Then he asked me to write Henry's Law on the board. Unfortunately, I knew what Henry coefficients were, but couldn't write Henry's Law (I had forgotten to study this part of thermodynamics). He helped me through this one a bit, but mostly I just struggled while he told me what to write. Thankfully, we didn't stay on this topic too long, and we moved on to "What is oxygen used for?"

Apparently, the correct answer is "steel" and not "so people with respiratory problems can breathe, and also to feed into combustion reactions to supplement air if necessary." Either way, with this we began a journey through the Linde process and talked about

how to get oxygen (from the air). First, compress, then cool, then throttle to liquefy. Then, take liquid air and distill off N_2, leaving mostly O_2. So he followed up with "well, now I've got liquid O_2, but what if I want a gas?" You can use the liquid O_2 to cool the process stream in your Linde process to vaporize the stream and not lose the work you put into cooling. Somewhere in here we also talked about the Haber process and what we could use all the N_2 for (making ammonia, reaction over an iron oxide catalyst). We talked about why we'd pick the reaction pressure and temperature, what I'd think about the heat of reaction, activation energy, et cetera. In here we also discussed Le Chatlier's Principle.

After this, it was Tullman-Ercek's turn. She started off with "Ibuprofen is chiral and made as a racemic mixture. The S-enantiomer is the only active one, and people don't really like to put things into their bodies that don't do anything. What is the minimum amount of work necessary in order to get the S- and R-enantiomers separated?" Thankfully, I immediately knew that the answer had to be the Gibbs free energy of mixing, and so I wrote up the equation for that on the board (Work = $\text{delta}G_{mixing}$ = $n*R*T*(x_1 \ln x_1 + x_2 \ln x_2)$. She asked what the significance of the work was… why were those the terms that appeared? I stated that the work being undone were the entropic gains of mixing the particles. dG = dH – TdS, and if we're mixing two species, there won't be enthalpic changes, so the enthalpies cancel and we end up with only entropic terms. She continued to ask me things about this, but it was kind of confusing and so I asked what she meant, and she replied that she wasn't really sure and didn't think she was articulating it well because she hadn't gotten this far along with this question yet, and so we'd move onto the next question – a more practical one.

"My sister lives in a cold place, and her house gets cold because her heat doesn't work too well. Design a heat pump to heat her house." I started by stating that I wanted to pull heat in from a cold reservoir and exhaust it into a hot reservoir (outside and the house, respectively). I took the opportunity to draw some heat exchangers on the board, but for some reason couldn't really think of how I wanted to move between the points, so I threw a T-S diagram on the board, drew up the phase envelope, and started to diagram where I wanted to operate. Fortunately, it became fairly obvious that I wanted to adiabatically compress and expand (and Tullman-Ercek allowed me to do this), so I threw a compressor and expander into my diagram and felt like a real idiot for having to move to a T-S diagram to figure that out. Thankfully, she said something to the effect that she was going to ask for a T-S diagram, but that I voluntarily drew it while solving the problem, and we could just move on.

And so it was back to Prausnitz for round 2. We didn't have a lot of time left, so he asked me about relative volatility (I again struggled to write a definition but was helped through it), and we talked about azeotropes. Then he asked how we'd get past the azeotrope point in a separation. He wanted "extractive distillation." I didn't have this answer, but (we were talking about water/ethanol) I recommended using a dessicant and filtering, and then using the pure ethanol on other samples at the azeotrope point to take them past that point by adding pure ethanol. While it's messy, it would work.

Finally, he wanted me to talk a bit about osmotic pressure and what it meant, but we didn't really get too far into this one.

While it seemed like a complete disaster while I worked through everything and the only good point was that I nailed the ibuprofen question and everything else was just mental flailing while I tried to remember how to do anything in thermodynamics, I got a pretty solid grade on this one.

Andrew Jones
Prausnitz/Maboudian
This test was kind of fun. Looking at past questions I was expecting a lot of first law and fugacity questions of which I had none. The test was instead all process related questions. First question: "what is the relative volatility"? I had no idea but I guessed and got it right. Then I was led down the rabbit hole into the world of cryogenic distillation to make liquid O2 and N2 from air. I used the O2 to make H2 and the H2 to make liquid He. I was asked some process questions along the way. They also asked about the Joule-Thompson coefficient and the inversion temperature. I also had to describe the Rankine cycle, the gibbs-duhem relation and how to make the Rankine cycle more efficient. Is the Rankine efficiency the same for real gases and ideal gases as it is for the Carnot cycle? I also had to show how to find the entropy of a process.

Yongkwan Kim
Reimer/Alexander

Reimer:

There is a pipe that carries a toxic liquid. The pipe breaks and the liquid is in contact with atmospheric air, and the toxic chemical is now in liquid/vapor equilibrium. What chemical engineering process is similar to this situation? He was looking for a flash tank.

How would you go about solving for the numbers in the system? All he wanted was for me to write down the Raoult's Law.

Alexander:

A pipe carries a hot gas at a constant temperature. If you wanted to get work out of this gas and reject heat to the atmosphere, how would you calculate the maximum work that you can get out of this system? He was satisfied with me drawing a Carnot engine connecting the two temperature reservoir producing work and writing down the equations for efficiency.

Reimer:

There is a burning candle. How would you calculate the temperature? Adiabatic flame temperature calculation. The heat of combustion is obtained from writing down the

complete combustion reaction of a generic hydrocarbon (C_nH_m) using the heats of formation.

In reality, the temperature is actually lower than what you would get from calculation. Why? Energy is required for the molecules to transition between different energy levels so that we can actually observe the emitting light.

Explain to a sophomore (I forgot if he said high school or college sophomore) what it means to say that a process is entropically driven. He wanted the simplest example of a process where entropy was increasing: mixing of two gases.

You have a silicon wafer, and you're producing silicon carbide from it. How would you calculate the equilibrium constant of the reaction? He first wanted the equilibrium constant in terms of the activities of the products and reactants. Then he wanted them replaced with the product of activity coefficient and concentration of each species. All species in solid phase are crossed out.

Where would you get the activity coefficients? We ran out of time during this one, but he seemed ok with me saying that first the fugacity coefficients were obtained from an EOS ($\ln f = \int (Z - 1) \, dP/P$), then activity coefficients obtained. This made no sense to me, but he didn't seem to like the answer that I would get it from methods such as Van Laar.

Overall, there were a lot of different questions, or puzzles as Reimer called them. I tried to remember as many as I could, and only wrote the answers that Reimer seemed satisfied with. In reality, I fumbled through many of the questions and sometimes frustrated them. None of the questions were in-depth calculations.

Matt Pavlovich
Prausnitz and Maboudian
Typical chat ensues. Prausnitz asks who my favorite professor at Georgia Tech was. I laugh—his son teaches chemical engineering at Tech. 2010 was the first year that there wasn't a separate process design prelim, and Papa Prausnitz doesn't seem to have gotten the memo. The first half of this exam might as well have been "Prausnitz's chemical engineering trivia quiz", and I think he's been using these same trivia questions for the past three decades. He starts in predictable fashion by asking about separating the components of air. I tell him that it's 78% N_2, 21% O_2, and 1% trace elements, and he seems happy that I know that. Then, because I've read this answer in each of the last five years' write-ups, I say that to separate air, you use the Linde process, which involves cryogenic distillation. He asks me about how to get liquid air, and I say you can exploit the Joule-Thomson effect by compressing, pre-cooling, and throttling air to get it to liquefy (the Wikipedia pages about the Linde process and the Joule-Thomson effect are must-reads if you have Prausnitz). Then you feed this to a distillation column and separate the components. He asks what the bottoms and distillate streams will be; I don't know, but I guess N_2 will be the distillate because it's lighter (and therefore more volatile), and this turns out to be right. Then he asks the phase of O_2 when it exits the column (liquid), and what the main use of O_2 is industrially

(uh…). Turns out it's making steel. Sure, like I would have known that. Then he moves onto N_2—what's the phase coming out of the column (gas), how do you get it liquid again (use Joule-Thomson once again), and what's the use of N_2 (ammonia). This segues nicely into the other classic Prausnitz problem, the Haber process (a third excellent Wikipedia page), which makes ammonia by the reaction $N_2 + 3H_2 \Leftrightarrow 2NH_3$. He wants to know the operating conditions, specifically temperature and pressure. I know that you run at high pressure to favor the right side of the equilibrium, and I know that you run at high temperature, but I can't quite figure out that it's because you need lots of energy to break triple bonds in N_2. Next, he asks what we'd do if we needed the ammonia to get extra-cold. I recommended cooling with liquid helium (of course, produced by cooling hydrogen below its inversion temperature, throttling to get liquid hydrogen, using that to cool helium below its inversion temperature, then throttling again). He says that's fine, but what if we want to cool to a fraction of a Kelvin instead of 3 or 4 K? I have no idea, so I facetiously suggest putting it in space. Maboudian gets a kick out of it, but Prausnitz seems more eager to wow me with another obscure chemical factoid: apparently you use magnets. It has to do with aligning the spins of the atoms, or something quantum-y that I couldn't really understand, and it was invented at Berkeley which automatically makes it awesome. Then Prausnitz suddenly remembers this is a thermo exam and asks about how to calculate the equilibrium constant. I write $K_{eq} = [NH_3]^2/[H_2]^3[N_2]$. What if we don't know the concentrations? I write $\Delta G = -RT \ln K_{eq}$. That's fine and good, but how do you calculate ΔG? Um, $\Delta G = \Delta H - T \Delta S$. Yes, and what are ΔH and ΔS? At constant P, $\Delta H = mCp \Delta T$, and ΔS is, uh… I'm stuck at this point, so I write the Claperyon equation, which clearly only applies to phase changes, not formation. Prausnitz calls me out on this, but I can't really come up with anything better. He asks me the third law of thermodynamics (S = 0 at T = 0K), but I can't intuitively figure out how this lets you solve for ΔS. Prausnitz walks me through something about measuring S at very low temperatures and something to do with the standard state. I don't follow too well, which doesn't turn out to matter, because it's time for Maboudian's question. It's the Rankine cycle. I draw the T-S diagram and get it mostly right. She asks me to define an efficiency, and I educated-guess that it's the same as the Carnot efficiency (W out/Q in, or (Qh - Qc)/Qh), which seems to be correct based on their lack of corrections. She asks how to find those Q's, and I say you compare enthalpies at different points on the cycle. Prausnitz for some reason is immensely excited when I mention the word "enthalpy". Then Prausnitz asks what fluid we use in the heat exchanger in the condenser (water) and how we cool it once it's been run through the exchanger (took me a while to get to cooling towers). Now he starts getting back to design land: "why do we use cooling towers rather than just getting cold water from a river and pumping hot water back in?" I'm trying to think of a thermodynamic reason why, like something with pumping costs, and Prausnitz keeps shooting down my answers. Eventually he asks "have you heard of the EPA?" and I tell him, "sure, they probably don't want the fish in the river to die." Maboudian asks a) why we don't run several turbines, and b) why we don't keep superheating the steam after boiling. Again I'm stumbling through trying to justify that with thermodynamic arguments, but it turns out all they wanted were practical economic answers: a) turbines are expensive and b) if turbines get too hot, they break. We still have about ten minutes, so Prausnitz starts asking me random thermo filler questions, which is fine by

me. Do you know the Gibbs-Duhem relation (oh, do I ever; I write it to prove that I know it); why is it useful? If you know the fugacity coefficient or activity coefficient for one species in a binary mixture, you can use it to find the other; if you have the coefficients for both species, you can check their validity by comparing them to Gibbs-Duhem. I'd read this in an old write-up; I pretty much spat it back out verbatim, and Prausnitz was happy with it. He asked about relative volatility (P*a/P*b), and how it was an important parameter in distillation (the closer it is to 1, the more difficult distillation becomes). Then he asks if I know what it's called when the volatilities of two species become the same (an azeotrope), if I can name a common system with one (ethanol/water), and how to "break" it. I say add some benzene; he replies that they used to do it like that, but they've gone away from it—why? Benzene is carcinogenic, of course. He wants me to suggest an alternative, and I say hexane. He's pleased—the real answer is pentane, because it's easier to distill back out than hexane, but I'm only off by one methyl group. Finally, he asks what ethanol is used for—I say sterilization, which is a "drop in the bucket" compared to the "big use", which I then remember is fuel. He asks me how you get it, and I say the most common method in the US is corn fermentation. That was the end of the exam. Prausnitz tells me he's going to "write to Georgia Tech and tell them they're producing good people", which is more or less nonsensical, but I take it as a good sign—and actually quite an honor coming from this guy.
Thoughts: Prausnitz is obviously a heavyweight in the field, but don't let that intimidate you. He's a nice guy. Maboudian is tough to read and she was quieter than Prausnitz, but if anything, she's even nicer. Prausnitz asks the same questions year after year, so just be prepared for them (you might want to find some of his process design questions from 2009 or earlier). He doesn't expect you to know every little detail about every process he asks about. I thought this one could go either way (I was especially worried about completely missing the point of those practical questions), but I ended up doing the best on it.

Laura Quock
Prausnitz: Refrigeration Cycle. What is the temperature of the condenser? How do you separate O_2 and N_2 from an initial air mixture of those components? What are O_2 and N_2 used for? Talked about distillation columns. Talked about volatility, azeotropes, how to separate azeotropes, why benzene is not used anymore, what ethanol is used for, why ethanol is used, and where gasoline comes from. Basically, a process design test.
Tullman Ercek: What happens when you scuba dive? Talked about going from high to low pressure, how this affects your blood. Use of Raoult's Law.

Barry Shang
Prausnitz/Maboudian

This exam just consisted of a bunch of short questions. We started off with the Clausius-Clapyeron equation. I wrote it in kind of an unconventional way and that threw Prof. Prausnitz off. Lesson here is to just write down what it most conventional rather than trying to display knowledge of how a well-known equation can be written obscurely. Prof. Prausnitz then asked me what it was used for, and again, I made the problem too difficult and started talking about phase diagrams, and why the Antoine equation has

the functional form it does. All Prof. Prausnitz wanted to know, however, was that we can use this equation to find enthalpy of vaporization (doh!).

He then asked me about compressibility factor, corresponding states, and definition of acentric factor. I drew the Z vs. Pr plot with the Tr isotherms, talked about reduced properties, etc. Next, we discussed VLE, Raoult's Law, and non-ideality. I mentioned some molecular thermodynamic stuff about intermolecular forces, and how they are roughly balanced among species and within the same species for ideal solutions. Then, we discussed azeotropes and how to break them. One way is pressure swing distillation, but he seemed to favor extractive distillation. For example, you can add benzene to break the ethanol/water azeotrope, although this is not done anymore.

Next, Prof. Maboudian asked about the Carnot cycle. I drew it up and started talking about it, but again, started getting off track and into obscure theoretical issues involving thermodynamic temperature scales, ideal gas temperature, definition of the Kelvin scale, the difference between theta and Kelvin temperature, etc., and realized this was not going to end well, so I suddenly stopped and asked what exactly they wanted to know about it. These ten or so minutes were just weird because they didn't really give me any direction and whenever I asked if I should derive something, they quickly told me "Don't derive it".

Finally, we somehow got to the Rankine cycle, and compared it to Carnot. I mentioned the difference between an internally reversible cycle (Rankine) and a totally reversible cycle (Carnot), which they didn't seem to be interested in (or understand?) since I just got blank stares. I talked about how in practice, it was hard to achieve Carnot, due to isothermal heat transfer limitations, and two-phase flow in turbines and compressors. I also talked about different ways to improve Rankine efficiency (increase boiler pressure, use reheat, decrease condenser temperature). They seemed to like reheat the best. Prof. Maboudian also asked a simple first law calculation to find heat added in a Rankine boiler, which I messed up completely. Prof. Prausnitz also asked something about using a throttling valve right before the turbine increase the vapor velocity, and how to calculate mechanical efficiency of a turbine (actual work/ideal work), which I found out was usually around 90%, much higher than thermal efficiency.

Overall, this exam didn't really involve any long problems or a lot of math, just a bunch of short questions, for some of which I gave stupid answers. Then again, they were asking so many short questions that it was only a matter of time before I violated one of the three laws of thermo.

Regarding prelims in general, it's important to keep in mind it's not solely a test of knowledge, but also how well you can articulate it and give someone else the impression that you know the material. It's also very important to be a good listener during these exams, and absorb everything the professors say because most of the time, they are giving some sort of hint. It's also important to establish good communication early on and make sure you are on the same wavelength as them. Most

poor results on these exams seem to be more a result of poor communication and being unresponsive to professors' hints rather than a lack of knowledge/ability of the student.

Alan Yiu
Chu and Alexander
This was a tough problem for me, since I hadn't seen anything like it before. Chu wanted me to consider the drying of two hydrophobic plates submerged in water. Basically, if you bring the two plates close enough (within a critical distance, d_c), the space in between them is completely filled with air instead of with water. He wanted me to find d_c.

- I didn't even know where to start, except that I knew it had to do with the energetics of surface tension. I stared blankly at the board for awhile.
- He asked me to define my system first: I said the region between the two plates.
  - He asked what was in my system: I said water. He asked if there was anything else, so I said air, because I thought that there would be air there even when the two plates were far apart. He said no, there's no air. So I said it's just water.
  - He asked what kind of system I had: I eventually said an open system, which he liked.
- I wrote up the combined first and second law as dE = TdS - PdV, then he added that we were at constant 1 atm and 300 K. So given these conditions, I wrote dG = -SdT + VdP.
- He asked me to consider the surface tension I had mentioned, so I added a γdA term to my dG expression. He also had me add μdN. So now I had:
  - dG = γdA + μdN.
- He then asked me very ambiguously what G was and how I could find it, and I threw out all kinds of answers (Gibbs free energy of your system, you could find it from G = H – TS, find it from equilibrium constant, etc.). Turns out he just meant for me to say that if dG = γdA + μdN, then G = γA + μN. Took me forever to realize that's what he wanted.
- Then he had me look at state 1 just before drying, where there's G from surface tension of water at each plate surface and from the water inside. So you get:
  - $G_1 = 2\gamma_w A + \mu\rho_w A d_c$
- The he had me look at state 2 just after drying, where there's only G from surface tension of air and the chemical potential of air. He said that these were both negligible compared to before, so then you get:
  - $G_2 = 0$
- Then I said that energetically, the Gibbs free energy of the water inside had to equal that of the surface tension term. He said that this wasn't true, then somehow had me determine that since states 1 and 2 were at equilibrium, $G_1 = G_2$, so $2\gamma_w A = -\mu\rho_w A d_c$, which I told him is what I had initially said. He said he had wanted me to show it through equilibrium.
- Then you get an expression for d_c:

- $d_c = (2\gamma_w A)/(-\mu\rho_w A d_c)$
- This is weird because of the negative sign. Chu said it's because the μ in the expression is actually negative, given by $\mu_{water} - \mu_{air}$, where $\mu_{water} < \mu_{air}$. I had to justify this by saying that at 1 atm and 300 K, water would rather be liquid than vapor. Not sure how much I agree with (or understand) all that, but I didn't exactly want to press the issue.

Anyway, that was all, and then they let me go with 15 minutes left. Alexander didn't say a word the entire time. Chu was helpful—he walked me through how to do the entire problem—but looked frustrated sometimes.

Zheng Zhai
Cairns and Tullman
Fuel Cell. $2H2+O2\rightarrow2H2O$; what is the enthalpy in this reaction? (ΔH) If this reaction is coming from a fuel cell; what is the maximum electric work that this fuel cell can produced? (Electric work is $\Delta G=\Delta H-T\Delta S$). Can all the heat transfer to electric work? No, because of the second law.

How is the total electric work calculated? P=E(voltage)*I(current). There is a relationship between ΔG and E: $\Delta G=-zFE$. (I can not imagine I remembered these!) Show the electric work on the E-I plot. The curve is the irreversible working line. If worked on the irreversible line, the electric work is the area of OECD. The irreversible work (heat) is the area of AECB. The reversible work (heat) (which is $T\Delta S$) is the area of FABG.

Now you are creating H2 and O2 from H2O. At what voltage you should control to make sure there is no energy? In this situation, ΔG, ΔH and ΔS change their signs from positive to negative. The area of HIOF is the electric work ΔG and the area of JAOI is ΔH. The area of $T\Delta S$ in the left hand side should be the same as the area of $T\Delta S$ in the right hand side (area of JAFH= area of FABG). So we should operate at 1.48V (F point).
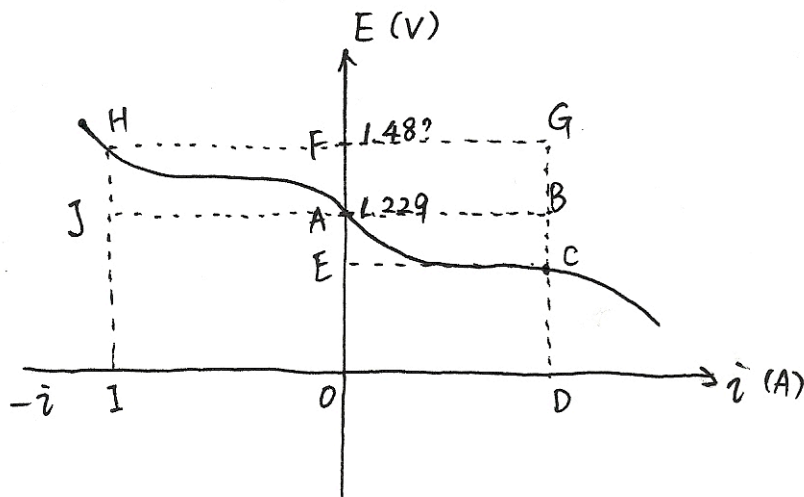
I am not sure whether these are correct or not….
Thermo is really difficult…..