Prelim Exam Transcripts (2015)

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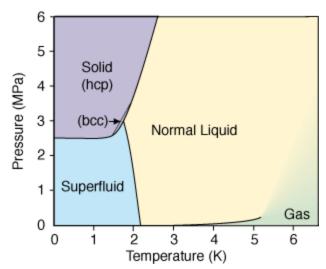
Balsara/Tullman-Ercek

KD

This was my first prelim and TE hadn't given thermo for a while so I wasn't sure what to expect, plus Balsara can really ask anything so it was very hard to know what I should know really well. I studied for it by reading Smith Van Ness and Abbott, as well as some of my undergrad book Elliott and Lira, as well as looking through old questions. I felt pretty good going in, but not good at all afterwards. They first had me sit and asked about my background, which was actually quite awkward because they just wanted me to talk without really asking me questions. Anyway, I told them about how my class was ok, fairly standard stuff but the first time the class had been taught by that professor. I also TA'd the class the next year, but it was not much better that year. They then told me they wanted to analyze a breathalyzer, come up with some way to get the fraction of alcohol in the blood. I started thinking about the problem and explained how we would want to look at the air composition at equilibrium in the lung with the blood. I then wrote $\mu_A^l = \mu_A^{\nu}$ and they said yes, but how can we get some relationship that we can use (as in PVT). So I started writing delta G but they didn't really want to go that direction so instead I wrote the fugacity of the alcohol is equal in both phases. They liked that and asked me how I could use it, so I tried to write up the relation from SVNA $y_i \varphi P = x_i \gamma_i f_i$ (there should be hats on some of these), but I had something wrong in the notation and they wanted me to explain. So I fumbled for what felt like an eternity trying to explain what each symbol was and where we would get each fugacity and what the poynting correction was. TE led me to the fact that the phi in the vapor is nearly one because atmospheric pressure is fairly low and there aren't many non-idealities about dilute

alcohol in air. Im not even sure that is right. Then the poynting correction is also about 1 because the liquid is not far from the saturation pressure or volume. This was all very confusing. Then they asked me to define volume fraction, how to get from mole fraction to volume fraction. I wrote something about the ideal gas law and they didn't say much, and I started to derive it there, but they didn't like that at all. After a lot of fumbling and back and forth with me saying I'm not really sure what you're after they led me to partial molar volume and $\sum n_a V'_a$, so I eventually had an equation for it. Balsara asked me to change it to mole fraction and then we finally moved on. I still have no idea what the final answer to this question is.

They then asked me about a P-T diagram, so I drew one up, but then Balsara showed me one for Helium at very low temps and Pressures. It has a couple extra phases, including a liquid at 0 MPa and 0 K, looks like this:



He then asked me how they would get the entropy of the superfluid. So I wrote the clapeyron relation dP/dT=deltaS/deltaV, which I said I could derive. They asked me to explain how I would derive it, so I explained the derivation, but they didn't ask me to do it. I kinda fumbled around with what Balsara was asking, he kept saying he wants a value for the entropy at like 0.5 K and 1 MPa. So I said something about doing a reversible process with the clapeyron relation between any points on the diagram so even not at a phase boundary it can be used. i wanted to do something with change in entropy equations but nothing seemed right. They pointed me towards the solid at higher pressures, and I said the entropy there at 0 K must be 0 because of the third law. Then I said something about dP/dT is 0 between those phases so the change in entropy is 0. so the entropy of the superfluid is just 0. Balsara then told me that the superfluid is actually 0 entropy at 0K, which is confusing and odd. I was thinking that might be the answer earlier, but ruled it out because it is weird. That was all they had, Balsara said I did well and then I left feeling pretty bad about the first half and ok about the second. Overall they were nice but a little confusing in their questioning. Make sure you have the fugacity relationship perfectly memorized because I did not and it made things much more confusing. I still got a B, the second half of my exam probably saved me there.

DG

I had a similar experience to the one described above. I too got the question about the Breathalyzer and the Liquid Helium at T~0K. I felt like this pair expected me to be confident in what I say and especially what I write on the board. Balsara pushed me, asking me whether I knew to derive the VLE expression or not, he seemed annoyed and that made things worse for me. There were a lot of awkward silences where I didn't know what was expected of me. The Liquid Helium question weant better, but there too they expected me to come to the -quite non trivial- conclusion that liquid helium had zero entropy without much aid. This was my

first prelim and my nerves certainly affected my performance in this one. Try to keep calm, know what you are doing and think twice before writing anything on the board. Also know tho derive the VLE relationship for ideal as well as non-ideal sytems... fugacity can be tricky.. Retrospectively, the questions they asked were not terribly hard but I ended up leaving the exam feeling stupid regardless...

SJ

Read KD's description for actual useful question information. This pair was less than thrilled with me. I got the breathalyzer question, got to writing that the chemical potentials in the liquid and vapor phases were equal ($\mu_A^l = \mu_A^v$). I then started to derive a general expression for the relationship between partial pressure in the gas phase and concentration in the liquid phase by writing: $\mu^0 + RT \ln(x_A \gamma_A) = \mu^0 + RT \ln(f_A)$. This is where we stayed for the next 35 minutes, because I had forgotten to write the standard state pressure in the gas phase fugacity (should have been: f_A/P_A , see the derivation of ideal gas phase chemical potential from Gibbs-Duhem). Balsara just kept saying something was missing, and eventually got to saying that my units were wrong. I could see this, but I was so flustered by how mean/frustrated he was that I couldn't fix it. I really don't know why they didn't just move on (I was the last of the day, so maybe they were hungry and grumpy), but they seemed so offended by this mistake that they decided it was worth harping on for half an hour and causing the exam to be a complete disaster.

This was my first exam, so getting to show absolutely no knowledge and being cut down by Balsara hurt my ego and self-confidence a lot. I had nightmares the whole night about the next two exams (we all had one exam on Thursday, two exams on Friday). My main piece of advice would be to try to not think about a bad exam after the fact, just move on. Even if one of your committees sucks, it is unlikely that all of them will. If one exam goes badly, eat some comfort food and just try to move on with your life. (And be careful with units:P)

NG

I was the first to go on Friday so I got the same questions as the above. The pair were very nice, I think partly because I was the first one to go that day, so I am quite thankful for that. I got the same as above breathalyzer VLE question. How does it work? I said it measures the fraction of EtOH in the breath and it somehow relates that to the fraction in your blood. That relationship can be obtained from equilibrium (must breath in long enough) which got us to talking exactly about that. Use the "Raoult's law for adults": $y_i^*P = x_i^*gamma_i^*P_i$ sat*poynting but it reduces to $y_i^*P = x_i^*P_i$ sat at low EtOH concentration. Then they said it measures a volume fraction, how do we relate that to the mole fractions in Raoult's law. Well in this case we cannot assume it's an ideal solution since volume changes upon mixing are definitely not zero (this was the first demonstration in my undergrad thermo class). Just use partial molar volumes assuming the blood is water: volume fraction= $x_EtOH^*V_pm_EtOH/(x_EtOH^*V_pm_EtOH+(1-x_EtOH)^*V_pm_H2O)$ where pm are the partial molar properties which depend on T,P but most importantly they depend on composition.

They were happy about this and asked me to draw a general solid-liquid coexistance line on the TP diagram (more or less a diagonal with a solid on top, liquid at bottom). They wanted me to get the entropy of phase transition. After some fumbling in which I tried to use the 1st and 2nd laws to get entropy (which I think you can, but it was definitely not what they were looking for), they basically had me derive the Clausius—Clapeyron, which I was thrilled about since I had studied it 100 times and did it well. After that I got the liquid He question which I was confused about and needed guidance but they told me to look at the slope and since dP/dT is zero (flat) you have not entropy change and we talked a bit about that.

I had Balsara and Tullman-Ercek for thermo on Friday morning, first thing. Having heard they did all but literally devour/breathe fire upon/demand the souls of the firstborn children of the poor first years who had them the day before, I was super nervous going into this exam. Figuring the subject might be non-ideal VLE, I studied fugacity until I realized I not only didn't understand fugacity, I didn't understand anything at all and should probably drop out and perhaps join a convent or be a ski bum or one of those people who dresses up as a robot and begs for change on the street (as an aside--I read quite a few books on the subject while studying. Smith/Van Ness/Abbott has a good section, but the clearest was Prausnitz' Molecular Thermodynamics of Fluid-Phase Equilibria in my opinion. If you're confused, you might try that one). As I showed up to the exam on crutches, unable to stand, Radke yells to my examiners "be nice to her! Don't injure her further!" Aww.

They started out by asking me about compressing a gas. I immediately thought about the Linde process, drew them a compressor with work going in, heat coming out, and flow in/out. Balsara stopped me to tell me it was not a flow system. Whoops! Perhaps I should've asked. He then said the gas followed the van der waals equation of state. I wrote it down. Balsara asks, "You have one hundred moles of gas. How much work does it take to compress it?" I ask if it is isothermal; it is. I write down dU = dQ + dW and stare blankly for a second. "Would I expect the gas to have a change in internal energy?" I wonder out loud. They stare back at me. I say, well, if it were an ideal gas, the change in internal energy would be zero, but despite never having thought about it I'm pretty sure this isn't the case for a vdW gas. They offer to let me do the case of an ideal gas first, which I jump on. dU = 0, dQ = -dW. I go through and actually solve for the heat. Balsara says, "that's nice, but I actually asked you for the work." I apologize profusely and point out that solving for dQ was equivalent, because dQ = -dW. Be humble! The rooms are small. There isn't space in them for both the professors' egos and yours. I solve for work, he asks for power, I say power is energy/time so I could just divide by the time of the process. He then asks me for the change of entropy. dQ = -dW = TdS. Sub in and solve—by decreasing the volume you decrease the entropy! Balsara asks me if that makes sense. I say it's an ideal gas and the Boltzmann definition of entropy is S = kln(omega); by decreasing the volume you are decreasing the number of possible places for the gas to be and thus decreasing the entropy (via a statistical argument). They love this.

Balsara then asks me to do the same thing for the van der Waals gas. We chat about why the internal energy of an ideal gas only depends on temperature, and I tell them how the van der Waals gas is different (you can see it from the equation—it takes into account molecular attraction, so you wouldn't necessarily expect it to be a function of just temperature, would you?) Balsara asks, what partial derivative of U would you really care about? I say, well, you're compressing it isothermally, so you care about (dU/dV) at constant T. Solve for it. I think for a second, write down dU = TdS + PdV, and divide by dV (divide, don't differentiate again!) dU/dV = TdS/dV + P. I look at dS/dV and tell them it looks like a Maxwell relation, which I can derive. Balsara says great. I derive it by thinking which potential function would have a -SdT -PdV and get that it's (dS/dV) at constant T = (dP/dT) at constant V. I accidentally mix up the sign, which Tullman-Ercek points out kindly. After a tiny amount of prodding from Balsara, I realize that the van der waals equation of state gives me P, which I can substitute in and differentiate. I mess up several times forgetting that the v in the van der waals is specific volume, not just volume, and I need to appropriately sub in for v = V/n to use it in my equations. In the end, dU/dV is not zero, and I've answered my question of if a van der Waals internal energy is just a function of temperature. Clearly, it depends on volume too! Balsara tells me "ok, we're not going to ask you to go through the math to solve for entropy, even though you could." I look down at the clusterf*** of symbols on the page. Uhh, okay, if you say so, I think to myself (although in retrospect you can use the same route I outlined above). Balsara asks me to jump to the end and tell him what the entropy change would be. Blink blink. He asks again and I realize he is asking me if the Boltzmann definition of entropy still applies, although I get confused by his wording for a solid thirty seconds. I say no, not in that form--not all the states have the same probability because of the intermolecular interactions. Balsara loves this.

Now it's Tullman-Ercek's turn. She says she has two enantiomers formed in equal ratios and she wants to know the minimum amount of energy to separate them. I think, energy of mixing! yay! and ask her how ideal I can assume they are behaving: if they are mixed ideally, there is no enthalpy of mixing. She says they are very similar chemically so that's a good assumption. I have a d'OH moment and explain this makes sense and I should've anticipated it based off the fact that they are enantiomers. If they were very different I could use those characteristics to separate them (I was thinking density differences, solubility, etc etc, all that good stuff—TE likes this and says we will get back to it) and say the reason the enthalpy of mixing is zero is because they are so similar chemically, because A interacts with B to the same degree A interacts with A and B interacts with B—the definition of ideal mixing. This was a little unnecessary, but she really liked that I knew why I could assume ideal mixing. I then write down entropy of mixing delta S = -Rsum(xi In xi), think out loud about how I'm checking the formula: xi is between zero to one, so In will be negative, so delta S will be positive, which I expect. Equal ratios, so xi = $\frac{1}{2}$, so I say delta S = +R(1/2 ln2 + $\frac{1}{2}$ ln2) = Rln2. Then, delta G = delta H – T*delta S. She stops me and says, "You're absolutely correct, but why are you writing that?" Seeing my suddenly concerned face, she says, "No you're right, I just want to hear your reasoning of why this is what you are calculating." Reassured, I tell her that Gibbs energy is what you care about at constant T and P and I expect the energy of un-mixing to be AT MINIMUM the opposite of the energy of mixing. She likes this. I write down the answer and note that it's clearly intensive because as I've written it there is no dependence on n. I scale it by n. She tells me since I brought it up they do use differences to separate them and generally do crystallization—the enantiomers don't co-crystallize. I smile and nod as if delighted beyond belief, which I have no doubt left me looking frantic and crazed. She doesn't seem to notice. They look at each other and tell me I can leave, I solved both their problems—it's about twenty minutes early. I ended up doing extremely well on this test despite not always knowing where to go and making some algebra mistakes—they really wanted to hear that I understood what was going on physically and not just using formulas. I studied the most for this exam and it definitely paid off--being able to just write down entropy of mixing rather than derive it is the sort of helpful thing you should do. Know where equations like that, Clapeyron, Van't Hoff, etc. come from, but also just be able to write them down. My strategy is always to talk out loud and explain what I expect to happen and how to get there before starting it, because then they know you are competent. This is key! I think I've forgotten a few of the other tricky little things they asked to see if I actually knew anything or if they could trip me up, but the best advice I can give is to just keep on. If you need to think, then think. If you are confused about something, start reasoning out loud rather than being silent and just saying, "oh, I think it is this...?" They want to know how you think.

Also, it probably helped that they were already in a good mood. Sometimes examiners aren't--it's not personal! They don't want to be there necessarily. It's not about you. Don't take it personally, don't let it get you down.

LC

Balsara and Tullman-Ercek are incredible! Probably the nicest prelim committee I had, and I still consider myself super lucky that I got them. I had a really poor background in thermo coming in, was delirious from an almost-all-nighter, and the entire 45 minutes was a prolonged brain fart...but they were still super patient with me. I had the same questions as KC: (1) calculate the power needed to compress a non-ideal gas to half the volume, and (2) find the minimum energy needed to separate a mixture of enantiomers.

For the first question I started with dU = dQ + dW and plugged in the pressure-explicit Van der Waals equation into -PdV (and spent some time explaining VdW since I needed to buy some time). At one point I was recalculating something so I could check my work, and when they asked me why, I smiled and said I didn't trust myself and my math (in retrospect maybe that wasn't the best idea). They smiled back and said they would tell me if I wrote something wrong. And that was where it all went downhill, because from then on I started relying on them correcting me.

The rest of my prelim pretty much consisted of me repeating the questions, thinking out loud, confusing myself, and phrasing everything in pseudo-question form ("hm...and I suppose now I would maybe perhaps possibly consider using Maxwell relations...perchance?"). It was kind of hilarious how bad it was, and for some reason they were both still pretty nice about it, saying things like "what if you considered it as an ideal gas instead..? How would you calculate ___? Are you sure there's a T in S = klnΩ?" [that seriously happened. I died of laughter/sad embarrassment afterwards.] Anyway, it was a mess but I somehow came out alive. I borderline passed, but honestly I didn't even deserve that. Whateva whatevaa~~ All I can say is smile, roll with the punches, and don't stress about it. It's just an exam, and what's the point of making fools of ourselves if we can't get a good laugh out of it? If you can demonstrate some knowledge about the topic, you'll be totally fine.

QQ

Same as LC and KC. However, I didn't know what to do at all. I pretty much wrote this first law equation and they stared at me. I vaguely mentioned about work being equal to heat for an ideal gas, but I wasn't that sure about this and they didn't say it was correct so I shut up because I thought I was wrong. They said "we're not going to give you any hits." Ok. I stared at the blackboard for thirty minutes of silence. Really though. It was good. I got some time to think about the latest episode of Downton Abbey and how silly the Crawley family is.

Tip for this one: actually learn thermo. I didn't, and, weirdly enough, understanding thermo is helpful on passing this one.

PG

Same two questions as KC/LC so I won't repeat much. Isothermal compression of a gas to half its original volume, determine work, heat, and entropy change. 1st for an ideal gas, then for a van der waals gas. For the ideal gas, I was asked to calculate entropy classically and using stat mech. When we got to entropy change for the van der waals gas, Nitash asked if it could be calculated with S = k In(omega) that I had used for the ideal gas. I got confused here - remember that because the different possible microstates of the van der waals gas will have different energies due to the attractive and volume terms in the EOS, the microstates will have different probabilities of occurence so you can't just use S = k In(omega). There would need to be some sort of weighting based on the different energies. Also, they like to test a lot of different concepts in one question - Maxwell relations, converting between molar volume and total volume to solve an integral - see KC's account for details.

Then I got Tullman-Ercek's questions about minimum energy required to separate two enantiomers. To "un-mix" the enantiomers, at a minimum you need to supply energy equivalent to the free energy of mixing. Nothing new to add here.

This pair is ok with silence - if you don't say anything, they won't really help you. Luckily I was also comfortable with silence in this prelim (surprising because I didn't feel that way in the other prelims) so there was a point where I got stuck on the van der waals gas thing before getting to Maxwell, and they didn't say anything. So just talk through it - propose ideas, explain what you approach you might take and especially why you would try that approach because they like to hear about the assumptions that you're making for a particular analysis.

Prausnitz/Schaffer J.Ro.

This prelim was a challenge because my undergraduate experience in thermo was a complete joke, and Smit's statistical thermo class was a bit disorganized (and not so useful either), so all of the undergraduate thermo I learned was in the two weeks preceding this exam. I walked in and Prausnitz and Schaffer were very nice, and proceeded to ask the usual "where did you go to school, what book did you use." We "used" Smith Van Ness and Abbot, although I don't think I opened it more than twice in undergrad. In preparation for this exam, I read the entire book cover to cover, which was debatably useful, and also practiced all of the guestions Schaffer and Prausnitz had asked in the past. The guestions I was asked were as follows:

- 1. Prausnitz: Do you know the definition of heat capacity? What is larger, Cv or Cp and why? (I wrote the equations on the board, and as soon as I mentioned that Cp is greater because of the work required to maintain constant pressure, he moved on.)
- 2. Prausnitz then asked if the heat capacity of Nitrogen or Argon would be greater. I struggled with this a bit, first suggesting that Argon would have a higher heat capacity because it was larger-that is wrong. Finally after some helpful hints, I reached the conclusion that Nitrogen does because it has more degrees of freedom (the triple bond can stretch/rotate/etc.)
- 3. After this, Schaffer asked his subcooled liquid problem. You have a tank of subcooled water and you put a dust speck in it which serves as a seed crystal for the freezing of the subcooled liquid. The question is: what is the final state of the system and what phase is it? He has asked this question in the past, so thankfully I had learned what some of the entropy contributions were. You need to add heat to make the system reach the freezing point of water (deltaS of temperature change), and there is an entropy change of the phase change, and then the heat from the phase change is released back into the environment. You need to consider the heat released to determine what the final state of the system will be. I neglected to mention that there is a contribution due to the fact that ice expands when it freezes, not sure exactly where this was supposed to come into play. But to help me out, Schaffer had me draw a phase diagram of water (PT) and explain the solid liquid line. I was expecting this to segue into a derivation of the Clausius-Clapeyron equation, but there was no mention of that.
- 4. Prausnitz then asked me if I knew the 3rd law of thermodynamics (S=0 at 0K for a pure crystalline substance) and what it's useful. I said "finding the reference states for entropic changes" but he wasn't quite satisfied until I related entropy change to G = H -TS and said that if you want to find an equilibrium constant for a reaction, you need a change in S to find change in G, to then use RTIn(Keq)=deltaG^o to find Keq. I called this equation the Arrhenius equation which Prausnitz was not happy with but we moved on once I wrote the relevant equations on the board.
- 5. Prausnitz then asked about how we would find the delta Hs for this reaction. I said use calorimetry. He asked me to describe this process. I derped and forgot that it's an enthalpy of formation and so two things would have to react to find the temperature change of the reaction. I think the example he used was making butane. They gave me the reaction after I stupidly started to write CO2 +.... Schaffer joked that if I knew how to make butane out of CO2 I should patent that. Derp.
- 6. Schaffer and Prausnitz then looked at the clock and said they had time for another question, so Schaffer gave me his "how much work can I get out of a hot block" question. You can look on previous testimonials for more details. But I got the problem more or less. He just wanted me to explain things and didn't make me do much math at all. In fact this whole prelim there were no derivations and not much math at all.
- 7. Prausnitz then asked me if I'd ever been to europe, and proceeded to say that Boltzman's gravestone says S=kln(omega). He asked me why. I mentioned that that is Boltzman's definition of entropy and that omega is the number of microstates. This developed into an interesting conversation about canonical ensembles and statistical mechanics and what the assumption is called when you can say that the average of time points is the same as the canonical ensemble average.

This was not a normal Prausnitz/Schaffer topic but I rolled with it, since they said they wanted to "give me my money's worth."

All in all, I felt okay about this prelim, since it was my first one, and I survived. Both were nice, and I passed. I will note though, I studied the hell out of the Linde process and the joule thompson coefficient and it wasn't brought up at all... kinda disappointed, but still some classic Prausnitz was involved in this prelim.

EΜ

I was asked about the significance of Gibbs-Duhem, how to find ternary component LLE data from binary LLE data (See previous transcripts for these). Why cp of diatomic gases is greater than that of monoatomic gases (see JR's write up). Standard Prausnitz trivia.

For Schaffer, I had the same problem as JR. Make sure to practice previously asked problems; hot topics: carnot heat engines, heat pumps, refrigerators, subcooled liquid with ice crystal seeds and all tangents associated with these topics.

One thing to note with this pair is that they will not guide you along every step of the solution and correct you as you are making mistakes. So, do not expect to be helped with every step of the solution.

ΕZ

First prelim slot of the year - both profs seemed to be in a good mood. I felt pretty comfortable. We made a little chit chat about the holidays and Schaffer told me he was recovering from the flu, and he had up to a 104 degree fever over the break. Good thing we're hanging out in a tiny office together for 45 minutes!

Prausnitz started off with a question about heat capacity. Is it higher for argon or for nitrogen gas? The answer is nitrogen (I got this wrong but they gave me some hints). Key word was degrees of freedom. Nitrogen is a diatomic molecule and so it has more degrees of freedom than argon (rotation and vibration). I concluded that it takes more heat to excite the molecules, aka more heat to raise nitrogen 1 degree, which they seemed satisfied with. Then Prausnitz asked me what kind of information I would need to predict the pressure-dependence of the heat capacity. I struggled with this one for a while - started with the first law, took the derivative of the expression with respect to T at constant volume (using Cv) and used the Maxwell relation from helmholtz free energy. Not sure exactly how to do this part, but eventually they said I'd gotten most of the way and the rest was just math so we moved on.

Then Schaffer gave me his ice crystal question - you have subcooled water, perturb the system by seeding an ice crystal. What happens? Is it reversible? The system, being perturbed, will have an ice crystal grow in size. The heat released by the growing crystal's heat of fusion will be absorbed by the water, causing the water to heat up to it's freezing point. It is irreversible (non-equilibrium, can't move spontaneously backwards, and heat transfer between bodies with non-differential temperature differences). Is there any case where the system will not end at the freezing point? Yes, if there is just a little water, or it is very subcooled, it will all freeze before reaching the freezing point (compare the thermal mass of the subcooled water to the heat of fusion). What is the entropy change of the system? Just like always, construct a fictitious reversible path between the initial and final states along which you know how to calculate the entropy. Entropy is a state variable, so the change in entropy along this path will be the same as for the irreversible path. Using the second law, and $\Delta G = \Delta H - T \Delta S = 0$ for a phase change, I wrote $\Delta S_{heat} = \frac{C_P dT}{T}$ and $\Delta S_{freeze} = \frac{\Delta H_{fiscion}}{T_{freeze}}$. In the end, Schaffer asked if there was any other entropic term - I figured out that it was caused by the PV work done by the expansion of water as it froze, but not sure the exact form it would take.

Calculate the lost work? Lost work is just (W_reversible - W_actual). Recognize that $dU_{rev} = dQ_{rev} + dW_{rev}$; $dU_{irrev} = dQ_{irrev} + dW_{irrev}$. Since U is a state variable, we can equate the two. Incorporating the second law: $dQ_{rev} = TdS$, identifying $dQ_{rev} = 0$ since the system is insulated, and rearranging gives us $W_{lost} = T\Delta S$. We already calculated ΔS so we get the lost work.

Prausnitz stepped in with some standard trivia - how do we produce pure oxygen (Linde process followed by cryogenic distillation), talk about inversion temperature, how do we produce liquid hydrogen (cool to below inversion temp with liquid nitrogen, then throttle), liquid helium (use the liquid hydrogen to cool, then throttle). How do we get to below 1 K? MAGNETS. Make sure you know what units are used in the Linde process. He didn't ask anything here he hadn't asked before, so look at old write ups too.

We had 10 minutes left so Schaffer gave me his classic finite hot reservoir problem. EY had a great writeup in the 2011 questions, so I won't repeat it here, but I found it very helpful and breezed through this problem. They told me that was fast, and let me leave early.

Overall, they were really nice and didn't let me flounder for too long before nudging me in the right direction. If you get these two, be happy, because they are really predictable. I did best in this exam. Schaffer's questions can be a bit abstract and physically confusing, but I think as long as you find an approach that makes sense to you and demonstrates you understand the 1st and 2nd law and Carnot cycle, and you speak it confidently, he'll accept a range of answers.

Schaffer/Maboudian

MN

Q1: (Schaffer) You have subcooled liquid in a closed and insulated vessel. A tiny grain of sand is dropped into it. What do you expect to happen? Is this reversible? Can you calculate the change in entropy? I talked about how energy and entropy were state functions. (to be continued)

Q2: (Maboudian) Describe the Linde process. What is the goal? How would you determine whether temperature increases or decreases during an isenthalpic throttling process? I talked about the JT coefficient and showed how I could derive it by writing dH as a function of T and P, rearranging, writing as a function of heat capacity, etc. They stopped me here and asked how I could use the virial equation of state to determine this.

PD

Started off with the usual chit chat. They smiled when I told them I had taken thermo from a former Berkeley PhD student. Schaffer started off by asking how much work can be extracted from a block of cold material. It's a classic Schaffer question and I had studied the carnot cycle pretty thoroughly, so I "burned through that one quickly." The next question they asked was about the Linde process. I drew it out and they asked me how I would determine the liquid/vapor fraction in the V/L separator. What they were looking for was the an enthalpy balance, but I hopped directly to the Joule Thomson coefficient. I had memorized it just because I had derived it out a couple times in preparation, which they said they were impressed at, but they kind of gave me a funny look like I had prepared too specifically. I kind of shot myself in the foot because I struggled to eloquently explain the molecular mechanism. It took me awhile to arrive at a succinct description using a Lennard-Jones potential. In the course of this they also asked me about equations of state. The VdW EOS was one I had studied, and the truncated virial was one I had not. So of course they drill me on the truncated virial. They let me go pretty early and I left feeling bad about it because I was literally guessing about the

virial coefficient sign and different behavior of that equation. I don't know how, but it turns out I got an A so either they're nice, or my lack of knowledge on the virial wasn't so important. This pair was pretty predictable. For Schaffer, know your carnot cycles and irreversibilities in different processes. Maboudian asked the Linde process question, but was a bit quieter and Schaffer was more vocal. She will tend to ask questions that are more characteristic of her co-committee member so keep that in mind.

Balsara/Maboudian

JL

Balsara starts by asking a very similar question to the one he asked KC. You have an ideal gas in a cylinder at some V1, P1. You compress it isothermally to some V2, P2. What's the power requirement? For some reason I start by writing basically every thermodynamic equation other than the simple, useful W = -JPdV, and for this period of time they are both totally silent. Gr8. After a bit I drew a P-V diagram, put down two points for V1,P1 and V2,P2, talked about how pressure has to rise, drew an isotherm, and then shaded the area under the curve and said that that integral is equal to the total work. I think they liked this explanation and from that point on they were more helpful (meaning, not totally silent). So then we use the ideal gas law to substitute in for P, do the integral and then you have an expression for total work for going from V1 to V2. To get the average power, just divide this by the time needed for the compression. Next Balsara asks how you get the heat requirement for this. Because it's an ideal gas, energy is only a function of temperature. Because the process is isothermal, dU then = 0 so using the expression of the first law I had written down early on (because I wrote a bunch, whoops) we get Q = -W. I also get the same entropy question KC had from Maboudian, and they seemed pleased with the stat mech description (fewer possible conformations at lower volume, so entropy decreases).

Now Balsara says we're doing the same thing with a VdW gas. So I write up the VdW equation, and he says "so you know everything, then." In my head I say "no, I'm trying to pass this exam, so to that end I am trying to demonstrate what I do know when you ask me questions that I can answer." They ask about the meanings of a and b. Anyways, solve for P, make sure you change molar volume to V/n for the integral, and integrate basically the same way as for the ideal gas to get the total work. Now he asks about the heat requirement. I say that because we're no longer assuming it's an ideal gas, we can't say that the internal energy does not change even though the process is still isothermal. So first we should calculate the change in internal energy, and then using this and the expression for work we can use the first law ($\Delta U = W + Q$) to get Q. This part took me a little while and I don't remember all of the (wrong) things that I said, so here's just how it works: I do remember I started by saying we need some expression for $\left(\frac{\partial U}{\partial V}\right)_T$. They liked that. After tossing out a couple (wrong) ways I thought we could get that, eventually I say that by taking dU = TdS -PdV and dividing through by dV we can get an expression. At this point they're more helpful, so Maboudian nods in approval, and I write $\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T$ - P. They like that I immediately included the subscripts for holding temperature constant. We can get a more helpful expression by using a Maxwell relation to swap out entropy change. I start by writing down the equation for dG, realize that's not helpful, and then write the one for Helmholtz. I think they were fine with that mistake because it was at least the right direction (whereas before there was a lot of sort of exasperated head-shaking.) So our expression is now = $T(\frac{\partial P}{\partial T})_V$ - P. You substitute in the VdW equation for both terms, and it simplifies so you just have your expression = an^2/V^2 . Integrate as before, and you end up with $Q = -RTnln[(V_1-bn)/(V_2-bn)]$.

Now Maboudian takes the lead. "Talk to me about liquefying gases." I pause, look around the room to make sure that Maboudian hasn't somehow turned into Prausnitz, and have to refrain from saying "...magnets?" I didn't study this at all, so I wing it based on what I'd heard everybody who did have Prausnitz for thermo

talking about. Sort of. Start by saying "...refrigeration cycle? Reverse Rankine?" To which they respond "Didn't you cover the Linde process in grad thermo last semester?" and, instead of laughing, which is probably what I should have done, I just say no. But after a little I remember it uses Joule-Thomson expansion, so I draw up a lil picture with a valve, gas going in at P1,T1 coming out at P2,T2, talk about how it's isenthalpic. Write up the expression for the Joule-Thomson coefficient, and get another "well since you know everything, talk about how we know what the sign of the JT coefficient is." A silence follows. Totally lost. Try to spout off some stuff I had thought I'd heard people say about some like critical temperature where some gases start acting weird, but none of it is working. Cursing at myself for not being like "hmmm let me see if I can remember how to derive the expression" instead of just writing it down and using most of the rest of the exam for that instead, which I had practiced. Maboudian, eventually, having lost all hope in me, asks me to write a virial expression for a gas and then wants me to think about the sign of b. Still lost. So she asks me to draw a diagram of potential energy vs. distance between particles. Goes up to infinity at zero (no overlapping allowed), drops to a little below zero at a minimum, then rises up slowly to approach zero at infinite distance. So she has me think about that. The particles want to sit at that energy minimum. As you decrease pressure, they're farther apart, so their potential energy increases. Because of conservation of energy, that means the kinetic energy must decrease, so the temperature has to decrease. And we're done, with a few minutes to spare.

This was a little frustrating. I kind of felt like I had done the best in this one, because I was proud for getting the math for the first part in a fairly timely manner (thermo is weird), and the second part came down to less of having an understanding of how to manipulate the fundamental equations, and more of a "did you study this random process." But that's prelims. Still passed I think because the first question went reasonably well and after I'd gotten many, many hints I was able to get some things right for the second one. Again for these two (and maybe others as well), they might not say much at all until you demonstrate that you can at least get something right. If you're not getting a response, just stay calm, write down some basics of what you know, see what sticks. They won't start with a question that's going to be so outlandish that you really won't have studied it/won't have any way to approach it.

Kinetics

Reimer/Zhang

KD

I had a pretty good undergrad kinetics class and did alright in Iglesia's grad class, so I thought this one would go ok. I had skimmed through all of Fogler the week before prelims, but I should have spent more time on understanding things during the week of prelims. Reimer went first and asked me about a semibatch process, where you have a solvent with some solute and a catalyst in it. You add a gas, say hydrogen to the reactor. He asked me what I expected that flowrate to look like. I said constant because I didn't really see any reason to have anything else. He had me write that on the board and then we continued. He asked how i would analyze the problem and I said a mass balance. I started writing it on the board but ended up writing a mole balance so he asked me to clarify. I really hurt myself by continuously messing up my notation on the board, choose something and stick with it but I kept subconsciously switching in my head and getting confused. He told me that the hydrogen is fed such that there is an equilibrium constant amount of hydrogen in the reactor. So then the mass/mole balance can be solved to show there is an exponential decay of the solute with time (which I stupidly said originally was linear, because I can't read differential equations). He then asked me what the hydrogen flowrate would look like, and since he had said the concentration is constant, I could see that the hydrogen is also an exponential decay. He then asked me about the rate constant, tell me what I know about it. So I went into the arrhenius equation then transition state theory and

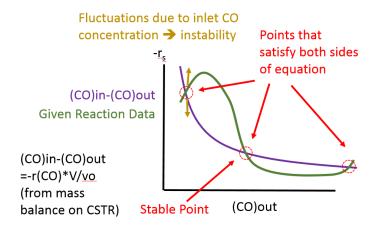
the fact that A is entropic with the vibrational partition function as well. He said he would have liked to ask me why planck's constant was in it but we didn't have time.

Zhang then told me that in the bio industry people always use CSTR's, and in the petroleum industry it is usually PFR's, and asked why I thought that was. I know nothing about the bio industry so I said it might have something to do with enzyme's needing to be more free in the solution than catalysts? She had me write the mikalis equation on the board and said that things are usually run at very high substrate concentration, so the rate is just a constant Vmax. I was drawing a levenspiel and saying how I thought the PFR would require more volume or something. I think I was drawing the levenspiel curve backwards or something, but no matter what I said here she was not happy at all. Kept sighing, we were just not on the same page. We went back and forth for what felt like an eternity where she would ask me so do I think PFR or CSTR, what is the common rate order for petroleum processes, ok so PFR or CSTR. I was talking myself into a giant hole and she wasn't pushing me in any particular direction, I felt like she had some answer in mind with a specific explanation but I didn't know what it was. She did not give useful hints that led me in the right direction. She then moved on and said if I had A->B->C and we know the rate constant what parameters should we tune to maximize the selectivity of B. So I wrote selectivity and started talking about the rate law and about maximizing [A]/[B]. Then she asked CSTR or PFR, and again we kept going around in circles. I don't know what was going on but it was bad. Finally I said something like "I'm just confused. I don't understand the question", and we ended up moving on somehow. So she said what if we have a particle with enzyme inside, draw the rate as a function of substrate concentration. At high concentration is it rate limited or diffusion limited. I of course was so confused by this point that I think I got the two mixed up and wrong. This just was bad overall, we were not on the same page at all, like I could understand what she asked me but we were listening to different questions. Somehow I still swung a B on this prelim, I feel like they should have failed me though.

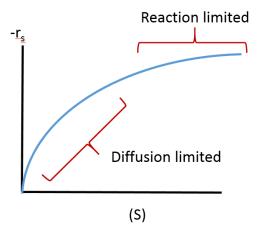
J.Ro.

This was my last prelim, and I was exhausted but Reimer and Zhang were (for the most part) pretty nice.

Reimer started by asking why we use a PFR in a catalytic converter in our cars instead of a CSTR. He set up the problem for me by having me draw a CSTR with CO coming in and CO coming out. I derived a design equation for a CSTR, he was satisfied with that. Then he had me draw a graph of -r(CO) versus (CO)outlet. He had me draw what this would look like for 0th order, 1st order, and 2nd order reactions too. He had me do a bunch of other graphs too, and was a little indecisive about what exactly to ask me. The problem developed into asking me to graph -r(CO) versus (CO)outlet and also plotting (CO)in-(CO)out versus (CO)out. This gives you a graph with 3 intersections. He asked me which ones are stable (the middle one) and why (varying flow of CO in makes the first point unstable). The part of this question I derped on was the very end, when he said, "so why does this mean we don't want a CSTR?" I think I said the answer but he just said of course we don't want it because the CO concentration out is not lower than the CO concentration in. Not sure if I see it still, but I got the graphs right and so he moved on. Here's what it looked like to the best of my ability (don't count on it though!):



Zhang started by asking me to draw a porous catalyst sphere with enzyme embedded in it. She then asked what would happen if a substrate were reacting with the enzyme. I was asked to draw a graph of reaction rate versus substrate concentration, and explain what was going on on the catalyst surface and why the graph levels off. I had to label which part was reaction limited and which was diffusion limited. I said it right and proceeded to write it wrong. This was me derping again, and Reimer said "are you sure?" and I said of course I switched them.



Oops. Zhang then asked what we could use to analyze diffusion and reaction. I said thiele modulus, and wrote the definition. She was satisfied, and asked what else I could use. I said the effectiveness factor, and defined that too. She had me draw a graph of thiele modulus versus effectiveness factor, and that was fine. Things got confusing when she said "what if you have data for rA and (S), how do you get the Vmax. I wrote the Mikaelis Menten kinetics equation and showed Vmax on the graph, and that its equal to Kcat*(Etotal) but she didn't seem satisfied, so I went into some rant about experimentally determining it, but then I pointed to the graph again and she was like, "yeah that would be easier." I must have not been clear the first time I said it because this was a bit of a waste of time.

We were running out of time, so Reimer asked me a new question. What is a rate constant? I said its a constant we use to find the rate of reaction, and the units depend on the order. He was looking for the Arrhenius equation. (He gave me some vague hint- "his first name is Svante", I didn't know who the hell that was, and he said "what part of the country does that sound like" and I said "I don't know, Russia? I don't know history... I mean geography" that was embarrassing) but at any rate I wrote down the equation, explained the significance of the pre-exponential factor (molecular vibrations/interactions). The big thing he

wanted here was that the rate constant is dependent on temperature. Then asked me what two theories we use to describe this (collision theory and transition state theory). And that was the end of the prelim.

With the exception of a sigh from Zhang at some point (or maybe it was a yawn?) they were pretty nice and helpful when I got stuck. I felt horrible after this prelim, but I passed.

LC

Reimer and Zhang are a good pair and really try to help you out. They give pretty good visual cues if you're totally off base, so that's super helpful.

I had very similar questions to KD. Zhang started off asking why CSTRs are more commonly used in biotech, while PFRs are used more in petrochem. I honestly had no idea, but I started with CSTRs/biotech, saying that bioreactors are CSTRs because they provide homogeneous mixing, which is beneficial for cell growth. Zhang nodded so I said PFRs are used in petrochem because petrochem reactions are often highly exothermic; PFRs can be tailored to better control temperature runaways. I wasn't sure how true this was but Zhang didn't look too displeased about it so I left it at that.

She then asked what reaction order we would expect in each of these cases. I mentioned Michaelis Menten growth (I had prepped this knowing Zhang's past trends and wanted to bring it into the conversation) and said something in terms of enzyme or substrate concentration, but she gave me a confused face and asked me what I meant from that. I wrote the rate equation on the board and explained the terms, and we ended up concluding that it was 0 order in terms of the cell concentration. They kind of nudged me toward this answer by introducing some assumptions about substrate/total enzyme concentration. In any case, then they wanted me to plot what 0 order meant so I plotted a flat line for rate vs. [C] but reimer made me correct the abscissa to conversion instead (he's very particular about his graphs). I brought up Levenspiel plots and compared the 0 order to 1st order and said CSTR vs. PFR size wouldn't matter in 0 order, and again CSTRs = homogeneous so that would be better. In petrochem, which I guessed would be typically 1st/2nd order, s

Reimer/Ciston

MN

These two were a good pair. I felt that both were encouraging overall. I took Ciston's professional preparation in teaching last semester, so I think I was used to being around her and a bit comforted by seeing a familiar face during my exam.

Q1: (Ciston) You have parallel reactions. $A \rightarrow Desired Product and A \rightarrow Undesired product, with different rate constants and different reaction orders. How would you maximize production of your desired product. This is straight out of Fogler, but I took some time to make sure I was explaining everything well. I talked about how the concentration would be important depending on the relative order of the reactions. I also talked about how temperature would be important depending on the activation energies of the reactions. Know your basics in Fogler very well for this. They then asked me how I would execute this. For example, if I want to keep the concentration of the reactant high, I could use a semi-batch or membrane reaction. Think of as many things as you can while you are studying.$

Q2: (Ciston) You have a spherical particle with catalyst sites within. Describe/draw the steps of the reaction. This is in Fogler as well. Reactant diffuses from bulk through the boundary layer to the surface of the particle. Then it diffuses into the particle, where it adsorbs to the active sites. Then it reacts on the surface, the product desorbs, and diffuses back out. See Fogler for diagram. Now write the rates laws for the steps occurring inside the catalyst particle. I was really comfortable with this from taking Professor Iglesia's class,

but the notation in Fogler is different, so I tried to make sure I explained the differences as I went along. Now if the surface rxn is rate limiting, how would you write the overall rate in terms of known quantities? I assumed that the adsorption and desorption steps were quasi-equilibrated and then solved for the concentration of the adsorbed species (which you can't measure)

Q3: (Ciston) Tell me about the thiele modulus. Draw the concentration profile inside a spherical catalyst particle for low and high thiele modulus.

Q4: (Reimer) This question was a little tricky for me. In catalytic converters, CO is reacted inside a PFR. I didn't get too many details about the reaction. The goal of the guestion was to figure out why catalytic converters are PFRs instead of CSTRs. First he had me set up a graph of rate vs concentration of CO for a simple 1st order and 2nd order reaction. Because he had previously told me that the reaction took place on a catalyst, I kept messing this up because I let the rate plateau at high [CO], which is what would happen if you were limited by the number of catalyst sites available for a reaction. I finally got it in my head that he wanted me to forget about the catalyst for now, so the rate just keeps increasing with increasing [CO]. Then he asked me about the case in which the reaction happens on a catalyst, so told him my reasoning about why the rate would plateau, and he agreed with me. Then he said that in this particular reaction, another species must also adsorb onto a site for the reaction to occur. In this case, the rate does not plateau, but rather decreases at high [CO] because you are outcompeting a necessary reactant for catalyst sites. He drew this on the graph for me. Then he asked how I would answer his question about why CSTRs are bad for this. I didn't know exactly where to go, so I did a mole balance on a CSTR. I ended up with (Fa o-Fa e)/V=Rate. You can solve this graphically if you plot the LHS over the graph of the RHS, which he has drawn for me. I did this, and the intersection points were the solutions. We did similar things in Professor Iglesia's glass for energy balances. With the graph, do a stability analysis to see which solutions were stable and unstable. I found that the solution with low [CO] was unstable. This was the reason he was looking for. In a CSTR, you operate at outlet conditions, so CO on the x-axis is the exit concentration of CO. You want a low exit [CO], but this can't be achieved in a CSTR because that solution is unstable.

Q5: (Reimer) Series reactions in a batch reactor. $A \rightarrow B \rightarrow C$. Plot concentrations vs time assuming your reactor is initially charged with A only. How would you solve for these concentrations? How would you find the optimal operating time? (Solve for [B] and find it's maximum)

Q6: (Reimer) Tell me everything you know about the rate constant. I talked about the activation energy and the frequency factor. I could tell he was walking me into the death trap of transition state theory, so I avoided mentioning it for as long as possible. Then finally I could find no better way to address his follow up questions, so I said, "I'm not sure if I want to go down this road, but I can explain it in terms of transition state theory." He didn't ask me to derive anything, but I just mentioned the assumptions and talked about how the frequency factor has entropic considerations in transition state theory. I also mentioned some of the differences between transition state theory and collision theory.

Overall, this exam was not too bad of an experience, and I was happy with how Prof. Reimer and Dr. Ciston executed the exam.

JL

Reimer starts by describing a semi-batch reactor. There is some flow rate of a gas A going in, and inside the reactor there is a liquid B. A dissolves into the liquid and then there is some reaction to produce a product C. He also said we maintain a slight overpressure of A. He said I could imagine this was a hydrogenation process, so A = hydrogen, B = some unsaturated hydrocarbon, C = saturated product. Question 1: would

you expect the flow rate of A to change over time/why? This threw me off a little bit because it felt like there was still very little info. I think the way Reimer asks questions (or at least how he wanted this one to work) was that I wasn't really expected to show that much solving of equations, just name the processes/equations that would dominate in the problem and then use those to go straight to the answer. That is not how this went, because whoops. I started by just doing a general mole balance on A: flow rate in + rate generation = dNa/dt. Then after looking at that for a minute, probably mouth breathing, I said that this wouldn't really be toooo useful because really we only want to look at the A that dissolves into the liquid. So I say we need Raoult's law and write up the ideal case, because fuck if I'm going to try anything with fugacity in kinetics, and Reimer says "I'm glad you wrote that." Weird. But don't let that throw you off. I also write up generic rate laws, because for some reason I wasn't adapting the hydrogenation mindset. So using aA + bB -> C I had exponents for the stoichiometric coefficients. Reimer asks what they'd be for the hydrogenation process, both are 1, so he asks me how we'd describe the reaction order. First order with respect to both reactant, second order overall. Back to the main question, at this point I was thinking that because the dissolution of A into B is probably going to be very limited, we could do a Michaelis-Menten type assumption that the concentration of B is always going to be way bigger than the concentration of A in the liquid phase (like saying the concentration of water is constant), so we could basically assume that Cb is constant and everything is simpler. Reimer says "that's an interesting assumption." Also weird. Means you said something wrong. I can't blame you if that throws you off a bit. So I do a mole balance on B and say no, that won't be constant. Eventually I get that because there's an overpressure of A, we say instead that there's a constant amount of A dissolved in the liquid, but with B being consumed the rate of consumption of A has to decrease with time. So the flow rate decreases with time. Poof!

Then Reimer points at my rate laws and starts asking about k. So I write up the Arrhenius equation, but since I'm thinking ahead toward a question about Eyring, instead of writing E_a in the exponential I write ΔG_a and Reimer has a field day. "Do we really say ΔG for this? Isn't that something else?" I say no, this is activation energy but it is in units of Gibbs energy. He's not letting up, so I draw a transition state plot (always. label. your. axes. and. domain/range. immediately. for every prelim or they'll go into some kind of melodrama) and talked about where we find the activation energy and then the reaction energy (the ~true~ ΔG) and Reimer seems satisfied but says that if I must insist on writing activation energy as a kind of ΔG I should use the special transition state subscript (idk how to type it, soz). So again back to main question, talk about temperature dependence of k. Then break it down into the eyring equation, talk about how the pre-exponential factor also varies with T, but the T dependence is much weaker than that of the exponential term so we can usually ignore it. Then he has me draw and explain an Arrhenius plot, asks for an Eyring plot, I say $\sqrt{(v)}$

so he just tells me the answer and now it's Ciston's turn.

Ciston proceeds to ask basically the exact same questions she has asked every year. Parallel reactions: what reactor for each type, temperature dependence, etc. She then asks me to list how, beyond just reactor type, you could maximize your selectivity. So I talk about adding inerts to keep concentration low if the concentration dependence is higher for the undesired reaction, doing a semi-batch reactor or "semi-batch PFR" by continually adding reactant to keep concentration high for the opposite case, and fumble through some more. If Ciston is on your committee, dream up a baker's dozen before your exam and prepare to rattle them off.

At some point in my fumbling I talked about adding a mass transfer limitation to keep concentration low, so this leads into a little question about heterogenous catalysis. Very basic just conceptual stuff. Where can we have mass transfer limitations (outside fluid BL, inside diffusion limitations), how do we describe them etc. Drew some plots. Just rattled stuff off.

I think these two work well as a pair. Reimer annoyed me at points, Ciston was very kind and helpful when I was clearly flustered/just messing up saying something that I clearly knew/had said correctly a few minutes before. Stay calm, breathe deep, always write E_a . Anywho, after this one (my first one, btw), because I also finished like 10 minutes early, I started off being like "I definitely passed!" then later that day I was like "they probs could fail me if they reaaaaally wanted to" then that evening/night I was like "I totes failed." Ended up doing really well so basically lesson learned don't think about that too much and just relax and then study for your other exams.

Katz/Ciston

DG

This was, for the most part, a pleasant experience. Both Ciston and Katz were extremely helpful. This was a morning prelim and we started out with the discussion of a very dense (non-porous) catalyst particle coated with an enzyme carrying out the non-elementary reaction A>B where the system is diffusion limited.. I was tasked to analyze the reaction rate -which was some unknown function of A. Katz led me to the discussion of what happens in the boundary layer and asked me why boundary layers occurred in the first place. I fumbled and gave a few stupid answers so we took of tangent discussing heat transfer in order to come to the conclusion that boundary layers were in fact a product of the no-slip condition on velocity - transport and kinetics go hand in hand apparently... Having figured that out, we went back to discussing the problem to - Katz told me the system was diffusion limited - overall it came down to a mass balance equating the amount of A diffusing in to amount of A reacting. He asked whether we can come up with an expression for the rate of reaction if I knew the concentration profile - I just wrote Fick's Law and told him amount reacted would be equal to the amount diffused, that seemed to satisfy him

After this, Ciston asked me her about selectivity in parallel reactions and how using different types of reactors affect the selectivity. This question was elaborated in detail, previous years but know that besides being able to do the maths, Ciston expects you to come up with creative and realistic improvements you can do in reactor design (change temperature, dilute feed, use PFR vs CSTR vs Batch and why) It would be useful to especially think about how temperature affects parallel reactions before going in.

Finally we had about 15 minutes left and Ciston started a discussion of the Langmuir Hinshelwood mechanism with some modifications. I didn't have time to derive it but I conceptually explained you can solve the question with making a bunch of PSS assumptions and a balance over the number of sites.

Overall, I had to be pushed/pulled around a lot to come at the right answers, both Katz and Cistion did a lot to push me in the right direction but I eventually got there which seemed to please this pair.

EΜ

Lovely pair, with clear questions and helpful feedback.

Katz: You are given a reactor with known thermodynamics and inlet conditions and unknown kinetics; a flow reactor but you don't know which one. How would you find the conversion of this reactor, if it is adiabatic. I start off asking him if we were using a differential reactor, but that comes with the assumption of operating at low conversion, so that is not a great start. I wrote out the mole balance and realized we need the conversion and the outlet flow rate. Then wrote down a generic energy balance and canceled terms until we had the feed heating term and the reaction heat generation term. From which we can solve for x, because we know the thermodynamics of the reaction fully (ie del Hrxn is known). That was done.

Then, the next question he asked was about a dye in a CSTR with a flow rate of 0 dye flowing in. I performed a mole balance on the dye but mistakenly set the accumulation or rather depletion term equal to

zero and realized my mistake where the concentration of A was not at steady state after Katz pointed it out. Then I found the concentration of A decreasing with respect to time.

Ciston: Describe how you would try to maximize the selectivity of the desired product in all scenarios (compare all cases of rate constant and activation energy inequallities). Classic fogler problem.

Katz: Finally, to explain qualitatively as we had run out of time: what type of reactor would be better for a series reaction? PFR or CSTR, in terms of maximizing the production of the product in the middle.

PG

This was my least favorite prelim, I think because I fumbled through some of Katz's fundamental questions at the beginning of the exam and then he was not in a great mood. But we talked about a lot of different topics and I think that helped. If you can demonstrate some knowledge on each of the questions, you should be ok. With Katz, be very precise about what you say and write, otherwise he'll keep questioning you about it. And like others have mentioned, I felt like Katz was always disappointed in me. Just ignore it, I don't think he means to come off that way.

Q1 (Katz): Katz asked how to describe the rate of a reaction, so then we got into a discussion about the rate constant k and the Arrhenius equation, and this discussion went entirely too long. He said imagine that he had never heard of the Arrhenius equation and knew nothing about it, how would I describe it and why it takes that functional form. Explain the significance/physical meaning of each term. I fumbled through this so we went on and on, talking about the units of each term and he made an analogy about buying lottery tickets. Oh what fun. KC's description below has more detail.

Q2 (Katz): EM's first question above, about an unknown type of flow reactor. It took me some time to understand the question and I didn't do well on it, but I think EM's description shows what he was looking for.

Q3 (Ciston): Shannon's fav question about parallel reactions, A -> D (desired product) and A -> U (undesired product). Like others have mentioned, think of a bunch of ways that you can maximize D vs U. The more ways you can tell her, the better.

Q4 (Ciston): Question about reaction on a catalyst pellet. I drew the Fogler picture showing external diffusion, internal diffusion, and reaction on the surface. She says let's forget the diffusion steps for now. She basically wants me to write the rate equations for adsorption, reaction, desorption, but doesn't really say that, so it takes longer than it should have.

Q5 (Katz): With 5 minutes left, Katz asks about Thiele modulus. This makes me happy because I had studied it a lot because it seemed like he asked about it every year. See previous years' descriptions for details.

Katz/Iglesia

KC

This was my last exam and their last exam. I hadn't taken advil and my broken foot (torn ligament, several broken bones, y'all) was absolutely killing me, so I limped in on crutches feeling like death. Katz seems concerned and asks if I'm in pain. I am. Little did I know I was about to feel way, way worse! We chat about my background, which is basically two weeks during physical chemistry and 244 with Iglesia. He shoots me a look and says something along the lines of, we shall see if you are even remotely competent despite your lack of preparation! This was foreshadowing. Katz starts out with A --> B, elementary. He wants to physically understand the rate constant I wrote down, k. I write down the Arrhenius equation. We talk about the exponential term. I write down an energy/reaction coordinate diagram and show where Ea is. He says, yes,

but what IS IT? After twenty seconds of prodding, I tell him it looks like a probability a la Boltzmann. He likes this. We then proceed to turn to the pre exponential term, and five minutes of philosophical torture commence. He asks me what it means. We chat about how the reaction is elementary and so I know that it can't be a Lindemann mechanism, or else the rate law would be proportional to concentration of A squared—thus collision theory tells me nothing. Nothing is colliding. I tell him the units of the prefactor (s^-1) and he tries to get me to give him a significance of this. He keeps saying, look at the units! You were right! They tell you a lot! Then he goes into an extended metaphor about how it's like the lottery and the exponential term is like the probability of any one ticket winning but what if you also bought more tickets. Apparently the prefactor is like buying more tickets. I say maybe A needs to be in the right configuration of something and it's entropic, it's a frequency of being in the right position to react. They aren't thaaaat satisfied with that. Honestly, I never got a super satisfactory explanation of how it's the lottery. I don't gamble. Apparently I don't know kinetics either. Iglesia jumps in with, "so the prefactor is just kT/h, which has nothing to do with the molecular identity. Doesn't that just keep you up at night? Do you toss and turn? Are you having trouble sleeping?" What a personal question! Yes, I have had a lot on my mind, but perhaps now isn't the right time for you and I to have a heart-to-heart? He asks me if I remember where that came from. I briefly go through TST and say the rate was proportional to the weak vibration along the reaction coordinate, and when we write down the partition functions you pull that mode out of the vibrational partition function of the transition state by assuming it is small and approximating it with a taylor expansion. This is what you pull out; this frequency cancels, and you are left with kT/h. I could write down the form of the vibrational partition functions. Being able to clearly explain this is the only thing I felt went well.

Katz then said, this is taking place in an adiabatic flow reactor. You have a temperature at the inlet and outlet, and you know your initial flow. Determine conversion. I struggled so hard trying to write a good energy balance—the total flow rate is the same, but I don't know the conversion and I don't know the heat capacities of either A or B. I point out in words that it is adiabatic and all the heat of reaction is going into the enthalpy of the flow, but fail hardcore in writing a coherent balance because they start getting really picky on what flow rate to use where and how to know and what it would mean to average a heat capacity—along temperature or along flow and how would I possibly know how to do that. I am now so flustered I am probably bright red and am considering just curling into a little ball. Katz points out that enthalpy is a state function. Hm. That's a good point. He points out I can use any path I like to calculate it and suggests a path in which I first raise the feed to the final temperature and then do the reaction at that elevated temperature. I probably should've thought of this, but I was just not in a thermo mindset. With that hint, I could write it down. Iglesia asks me how to get the adiabatic flame temperature from this. I stare blankly at him and say, uhh, it's the same thing isn't it? Adiabatic, so all the heat of reaction goes into a temperature change of the reactant. He says, is that the only factor? Katz keeps giving these sad sighs, as if bemoaning that anyone could be this bad at kinetics. I look down and realize, ohhh, of course, the max temperature is at full conversion. We move on and I am deeply shaken.

Iglesia then gives me a reaction at a surface and gives two forward processes and a QE step. He asks for the rate at which a reactant is being consumed. I look down and write the rate involving the consumption of that reactant. He then proceeds to give me a few minutes of hell as to why I used that step to write it and not another, and why I would think that the rates were the same. Katz is giving these sighs over and over again as if I had just terribly let him down and he might have to go home and buy some ice cream and watch a movie just to try to cheer himself up. His terribly long exhalations make me think I am somehow a symbol of the eventual doom of the planet due to the incompetency of the younger generation. I point out that each has to happen once, but that's wrong because that doesn't mean one isn't slower than the other. Honestly, I was never that satisfied with exactly why they were happening, he didn't write all the steps out—I'd look at someone else's testimony, because maybe they understood it better than I did. It was like Iglesia wanted me to know that I didn't understand reaction kinetics as well as he did. Oh boy, I was well aware of this fact and I wanted to go home. Also, it involved two sites and I originally forgot to write the

second site as */L, since I had to take into account the probability of two sites being next to each other. Do not forget this. I was just super shaken by this point. I write down enough to solve it and Iglesia says, ok, I trust you can do algebra—just write down the final answer. Seriously? Well, I knew it would have L^2 in the denominator and he gave me MARI. He leads me through writing down the final answer and we talk about when something might be rate limiting and what this would do to the equation. I limped out of it thinking there was no way in hell I passed that and that I should have to go back to high school to relearn conservation of energy. Turns out I got an A despite my idiocy, so try to stay calm even if you think something's going poorly. Katz is definitely really helpful. Iglesia can be harsh but he's not mean. And if someone keeps sighing as if you are the biggest disappointment they've ever seen, don't take it personally! Maybe he was thinking about the death of his dog during childhood or something, I don't know.

QQ

Q: talk about internal concentration and temperature profile in catalyst particle if it is severely mass transfer limited?

A: Standard profile stuff. Profile has zero flux at center because that would mean there's an infinite sink. How would you calculate temp profile if have reaction profile in adiabatic pellet? Relate using heat of reaction and conductivity.

Q: What would the temp profile of adiabatic reactor look like for exothermic reaction? What would it look like if heat was removed?

Q: see KC

Overview: I liked this pair. Nice and pushed me to discover new stuff. But I might be alone on this. Iglesia does give off the air of disappointment if you don't remember stuff from his class. Also, protip: don't make small talk by asking him what his thoughts are on how the adult film industry in Havana would fare if the blockade were lifted. Some details you just don't forget.

PD

This was my last Prelim, and also my most entertaining. They ask me about my background, undergrad kinetics and some enzyme kinetics during a biomolecular engineering class, along with 244 with Iglesia. I'm not sure if I appear like an abstract thinker, or if they were bored, or something else I'm missing, but Katz asks me an "abstract" question which goes as follows: You are walking through a field of strawberries with uniform concentration and picking strawberries at a rate which is inversely proportional to the amount of strawberries in your pack. I want to know at a distance L, how full is your pack of strawberries? I described the behavior of rate as a function of distance and then said you just integrate the rate over the length you want to determine how many strawberries you have. Katz made me go back and do a mole balance over a differential length and then take the limit to arrive at the design equation for the strawberry field. I left out a negative sign so then he wanted the definition of a derivative and showed where I forgot my sign. We moved on to an adiabatic reactor and talked about the temperature profile and how adding in cooling will change this profile. Iglesia wanted an energy balance which I hadn't studied so closely so I struggled a bit, to his visible disapprovement. After I arrived at the final energy equation and talked about what we can change to avoid a runaway reactor, we moved on to a catalyst pellet. They asked me about the concentration profiles in reaction vs diffusion limited regimes then asked if I didn't know the rate law how could I determine the rate in a diffusion limited system. It's at steady state so the rate is equal to the flux into the particle. So finally we had a couple minutes left and Iglesia wrote down the catalytic reaction listed above and asked me to explain verbally what I would need to solve it. The way he worded this was weird and I thought I was missing some piece of information. I ran out of time but all he was looking for was 3 assumptions: QE, PSSH, and MASI. So this one didn't end on the best note. While I thought I did the best on this one, I ended up in the middle

with a B+. If you have Iglesia for 244, expect visible disappointment when you fail to answer a question on material from his class. Overall though they were both pretty laid back and a good committee to have.

Iglesia/Zhang

SJ

Zhang started off with a question about Michaelis-Menten reactions happening inside porous catalysts with enzyme embedded inside them. It took a while to understand what was happening - the catalyst was uniformly distributed throughout the enzyme, there was no external boundary layer. Zhang drew a graph and said that I had actual reaction rate data versus bulk substrate concentration, and then asked me to determine the lumped rate constants kcat and Km for the Michaelis-Menten rate law from this graph. This graph looked like the standard Michaelis-Menten graph - first order at low substrate concentration, zeroth order at high substrate concentration. I was told that I know enzyme concentration inside the catalyst pellets. diameter of the pellets and effective diffusivity of substrate inside the pellets. We can split this problem into two parts - when the reaction rate is first order (low reacting substrate concentration) and when the reaction rate is zeroth order (high reacting substrate concentration). Let us think about the zeroth order case first rate = kcat*(E0). After a bit of prodding from Iglesia after I failed at understanding Zhang, I realized that you could never have a zeroth order reaction that is mass transfer limited because the reaction rate inside would always have a first-order dependence on the bulk concentration outside (see diffusion equation in a sphere results). Ok - because of this, we can directly relate the rate in the observed zeroth order regime to the Michaelis-Menten rate law, and solve for kcat. Now, we need to solve for Km, which shows up in the first order case - rate = kcat/Km*(E0)*(S0). I waffled about with Thiele modulus for a while, then we talked about how I could get to effectiveness factor from the Thiele modulus. If I have the effectiveness factor, I can relate the actual observed rate (which I have) to the rate that would occur at surface conditions. In this case. because there is no external boundary layer, the rate that would occur at surface conditions is the same that would occur at bulk conditions (I have bulk substrate concentration measurements). Since I can find what rate I would have at bulk concentrations, I can use the first-order observed rate data to find bulk condition rate data, and then use that with the first order rate law (along with the kcat I have already determined) to find Km.

Iglesia then asked me about adiabatic PFRs. I drew a sketch of adiabatic temperature rise along the flow axis of a PFR. He then said the I have a very long PFR that I am cooling constantly - what happens? I was confused about whether or not all the reactant was converted, but eventually I got to a sketch of a smaller temperature rise when reaching maximum conversion, and the the reactor is cooled to the coolant temperature. Back to the adiabatic PFR - solve for adiabatic temperature rise. I waffled a bit, but it is a very easy energy balance when I realized that all the reactant was being converted (no integration necessary - just do a total balance over the reactor).

I derped a little but did okay on both parts of this exam, so I passed.

NG

I was the most confident in kinetics going in but actually my strength was in the mathematical derivations and I ended up getting a bunch of conceptual questions, which threw me off a bit and I had to do a bit too much thinking on my feet. I can't exactly recall all the questions but we started off with if you have M-M kinetics 0th order why use PFR vs CSTR. I think I drew a Levenspiel plot and ended up concluding it's the same, but that in the biochemical industry it's easier to control a CSTR, where as in petrochemical it's better to use a PFR (don't trust me 100% on this...) Then at some point I also got the question of the adiabatic vs. constantly cooled PFR just like above, and drew the profiles (one goes to the adiabatic temperature, the

other goes up and drops). Then the enregy balance: Fa0*delta_H_rxn = (Fa0 +

Fa_inerts)*deltaT*heat_capacity. El asked me how I would use inerts to control tempratures etc which was straightforward.

Finally I got a surface reaction mechanism question in which I basically just derived a L-H mechanism just like we did 100 times in Kinetics with EI the semester before. I did it well since we had gotten practice on that a bunch, and after a few conceptual questions on the mechanism I was done.

ΕZ

First off, I'll just say that Zhang asked me a lot of open-ended and vague questions. The worst thing you can do is not say anything, or sound confused. Take a guess about what she's asking and be confident - if you're going in the wrong direction, she'll step in.

Zhang started off with an open-ended question about why PFRs are used more frequently in the chemical/petroleum industries, and CSTRs more frequently in biological applications. I have no clue, so I just start talking about the differences in PFRs and CSTRs, what assumptions are involved in the theory behind them, and why one might be more successful than another. I use the words 'reaction order' and operation at exit conditions for CSTRs. Zhang wants to talk about reaction order, and so I draw a Levenspiel plot. When pressed, I come to the conclusion that bio-applications often have Michaelis-Menten kinetics, which occurs as a 0th order reaction at high substrate concentrations. Chem/Petroleum usually uses reactions of 1st order or higher. The Levenspiel plots I drew helped me out here.

Then was a question about selectivity of an A->B->C reaction. B is desired and C is undesired. I wrote the selectivity equation $S = \frac{k_1[A]}{k_2[B]}$. They asked how I would maximize selectivity. I subbed in the Arrhenius equation for each rate constant and math-ed to get $S = \frac{A_1}{A_2} exp(\frac{-E_1+E_2}{T})\frac{[A]}{[B]}$. I was told k2>>k1, so I assumed E2<<E1, and said that the exponential argument would be negative. Thus, to maximize selectivity, we want to operate at high temperatures. Zhang asked what else we could control. I told her we could pick our reactor. Selectivity is high at high concentrations of A, low concentrations of B. Assuming we're putting pure A into the reactor, we want to operate as close to inlet conditions as possible, so let's use a CSTR. Zhang seemed happy with this and turned the floor over to Iglesia.

This is where the exam turned bad. Iglesia asked me two questions, one on nonisothermal reactors, and one on surface kinetics (MASI type problem very similar to those he teaches in 244). Both questions were as described by others. I did poorly here and needed a lot of help through every part, so I won't try to write out the dialogue. What did help me here was, through Iglesia's class, I could do the mechanics of the MASI problems in my sleep.

Overall, I was worried because I felt good about the first half and very poorly about the second. Turns out I did well enough, so don't stress if you feel like you bomb a portion of the exam.

Transport

Muller/Mesbah

KD

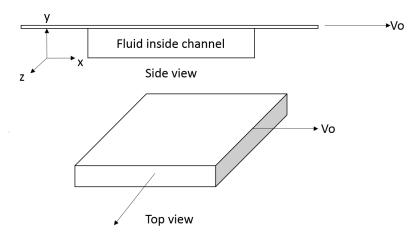
I didn't have a very good background in fluids and mentioned that most of what I knew was from Radke's class, though I had pretty good mass and heat transfer. I hadn't studied for this one very much, just reviewed my notes and some stuff from undergrad. I should have done more though. Muller went first, she

drew up the problem from a previous year with the sliding plate on top of a channel, and asked me to go about solving the problem. So I described the velocity profile, though I drew it kinda poorly since I was a bit nervous. Then wrote out NS for the single rectangular dimension and started simplifying. I tried to simplify some in my head, but that confused Muller a bit. I initially canceled out the pressure term and she let me head that direction for a bit, but after solving the diff eq I clearly couldnt satisfy the mass balance I knew had to be there. So I put the pressure back in and she asked where to get that term. So I said I needed a mass balance and wrote up the equation for the average velocity and mass balance, she said did I need all that and eventually I realized the average velocity over the whole distance must be 0, and that gives condition for dP/dx, which they were satisfied with.

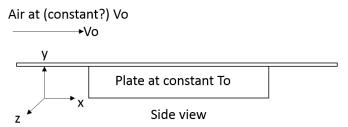
Mesbah then asked his question, which was boundary layer over a hot plate, where do we get the correlations. So I started talking about the thermal and momentum boundary layers and that they scale with Re and Pr. I got confused here because I talked myself in a circle as to whether it should be Pr^-\(^1\)3 or Pr^\(^1\)3. Eventually I just moved on and talked about the local vs average nusselt numbers and that the correlation on a flat plate has the Re¹/₂ Pr¹/₃ form, but I said I didn't remember how to get from the scaling arguments from the boundary layer thickness to the Nusselt correlation. So Muller asked me what would happen if it was a curved plate, does this still work. I said no because the boundary layer is much more complex, explaining the stagnation point separation point stuff. She then started talking about the analogies between mass heat and momentum and whether we could use the correlations for that. I explained that mass and heat can be used in the chilton colburn analogy either way, but that the Cf/2 is only applicable if there is no form drag from the normal force, which isn't true in the curved cases. Overall Mesbah and Muller were very nice, they let me say wrong things a lot without correcting me, but were nice about letting me figure it out. Mesbah was very straightforward and nice, though I was confused initially if we were dealing with a boundary layer problem or just an infinite plate. I ended up with a B, which was fair. I said a lot of things that were wrong, but enough to pass. I wish I had studied more for transport because I felt like I should have done better based on the class we took. But no complaints really.

J.Ro.

Muller: You have a closed channel that is infinite in the z direction, and the top plate is moving with a velocity Vo. Find the velocity profile. Use Navier-Stokes in the y direction (I memorized this), and remember that you have a pressure drop. There are three boundary conditions (I struggled to remember that you have mass conservation as a boundary condition, because as the fluid hits the side of the channel, it needs to go back in the other direction. Draw velocity profiles. She had me solve the whole thing, and set up the integrals for the mass conservation equation. I made it through this problem alright but I derped pretty hard core on flow rate. I got nervous and spent like 5 minutes writing out F=A*V because I was having a hard time relating my velocity profile to my mass conservation equation.



Mesbah: This problem was confusing, we had a plate at constant To so I guess there was an internal energy source inside maintaining it at that temperature. Air is blown past, so this is a forced convection problem. I was confused because Mesbah wanted a fluid velocity profile (but I thought it was constant Vo), and a temperature profile (even though the plate is constant temperature). I derped on this problem, ended up writing an energy balance, which Mesbah didn't seem content with. Then they asked me about dimensionless numbers for this problem. I named a few (Raleigh, Peclet) but they weren't too happy and we ran out of time anyway.



Overall this was my worst prelim, Mesbah and Muller were nice but very quiet, and they are picky about partial derivatives versus total derivatives. I probably would have done better if I hadn't derped so hard core on the mass conservation equation (which involves integrating from y=0 to a point y=delta where the flow switches direction, and from delta to y=H (height) and velocity profile (which goes backwards and forwards), other than that I got the first problem. And the second problem was so vague that the fact that I didn't know my dimensionless numbers for convective mass transfer was apparent. I would say for these two, make sure you practice setting tons of these problems up and be careful with the little details.

SJ

Mesbah went first, asked the same heated plate problem described by KD and JR above. I was the first student that Muller/Mesbah had, so they were not totally in sync. I was pretty unclear about what Mesbah was asking, so I sort of just talked about boundary layers. At times, Muller did not seem to know what Mesbah was asking. In retrospect now knowing Mesbah's style, I think I would have written more analysis on the board. I was always waiting for him to actually ask me to solve for something, but he just kept asking specifics. I would suggest just going through some analysis to show that you know how transport works - for example, when he says "define shear stress", just go ahead and write an expression in terms of areas, tau's. Write everything you know!

Muller asked me her sliding plate problem, which I had seen (that was very helpful). KD and JR has the same problem, but to describe it again: you have fluid inside a rectangular reservoir that is being dragged by some plate in one direction at the top, but the fluid cannot leave the reservoir. The reservoir is a lot longer than it is tall (fluid is being dragged in the lengthwise direction). Muller wanted to know how to describe the velocity profile somewhere in the middle of the reservoir. I explained what would happen in the reservoir using continuity - close to the (lengthwise) end of the reservoir, velocity would have to change because it could not leave the reservoir or continue into a solid wall. By continuity, another directional velocity would be created, and fluid would essentially circulate in the reservoir. In the middle of the reservoir, there are no end effects (only one-directional velocity) but the circulation is still taking place. As a result, there is drag flow near the top of the reservoir, and there is pressure-driven flow (from the buildup of mass) near the bottom of the reservoir. I drew this profile. Muller then wanted me to solve for the profile. I wrote out Navier-Stokes, explained which terms I did not have. I then solved for my velocity in terms of constants. I wrote out a no-slip boundary condition at the bottom of the reservoir and a drag flow boundary condition at the top of the reservoir. I then needed to solve for the pressure gradient - to do this, I set up an integral mass balance over the cross-sectional area in the middle of the reservoir. Muller then asked a few conceptual questions - why do I not have density in my final answer? Because I have no inertial terms - i.e. momentum is not being

convected into my control volume by a different velocity field. What is the significance of the viscosity term? If I have a more viscous fluid, I will need a higher pressure gradient to drive flow.

These two let me out 10 minutes early and I left feeling like I had nailed the exam. I didn't do as well as I thought (still fine though), and I think this is because Mesbah was not satisfied. I think he wanted me to do more analysis, but I didn't know what he wanted. So, the key point with him is to just show what you know, he is not very good yet at giving clear directions.

Graves/Mesbah

KC

This was my first exam and the first exam Mesbah ever gave. We chatted about my background, Graves asked how I could possibly know anything about engineering since Dartmouth doesn't have a full chemical engineering department—that's a good start—and he let Mesbah go first. The whole exam was mostly me trying to figure out what the heck it was that Mesbah wanted and having Graves derail it with questions about molecular transport, not continuum transport. Mesbah says, you have a plate that is heated. There is air with constant velocity blowing past it. He then just blinks at me for ten seconds and I realize that this is all he is going to say, and he isn't going to ask a question. This is a trend throughout this entire prelim. I point out there's going to be a thermal and a momentum boundary layer and I say it's dictated by the Prandtl number. I point out for a gas the Prandtl number is actually less than one and so the thermal boundary layer isn't inside the momentum boundary layer like it is for a fluid. Mesbah says, let's not get into that yet. We talk about the heat transfer at the edge of the hot plate. Graves proceeds to severely confuse me by asking about conduction versus convection and why I chose to write convection. I was like, errh, well you have forced convection. He doesn't really like this. He also tries to get me to use a few correlations that I didn't think applied since the thermal boundary layer wasn't contained in the momentum boundary layer due to Pr. I don't think Graves was paying attention to the fact that it was a gas and not a liquid. Know your correlations, Nu, Pr, Re. Mesbah says, "turbulent flow" and nothing else. Apparently I'm supposed to infer what the question is from his inflection and/or by mind-reading. I said the boundary layer gets thinner. Graves hijacks again, and asks how this will affect the heat transfer coefficient. I talk about the temperature drop and they are horrified, because of course the temperature difference remains the same. By temperature drop I meant difference—I was using electrical engineering terms (voltage drop = voltage difference). Do not do this—I tried to clarify that this was exactly what I meant and the gradient changed so the heat transfer coefficient must have changed. It was just a miscommunication--most of my exam got derailed by explaining miscommunications and/or trying to read Mesbah's mind--and Graves trying to get me to talk about how thermal/momentum diffusivity would be different between a gas and a liquid by imagining the atoms bouncing around. Super frustrating, because I would say something and Graves would be like, "no, [same thing but phrased slightly differently]". Mesbah says, "drag force." Seriously, where are your full sentences? And do you mean on the plate or on the air? He meant on the air. Uhh, ok... he doesn't really like my answer, but I talk about how there is a laminar section next to the wall. I didn't let it get me down, we moved on to Graves' silicon dioxide question. I didn't really make any progress on it by the time I had to leave. It was a bit frustrating, but I passed, I had to keep reclarifying my wording. Oh he also kept asking about things like temperature dependance of gas diffusion through a solid. It's an activated process--proportional to exp(-energy/RT). Spend a little time looking over temperature dependences of physical properties if you have Graves.

QQ

Q (Mesbah): Describe heat transfer away from a plate with fluid flow

A: After writing out the NS and the heat equations, they told me they didn't want to go that fundamental. I asked if they just wanted newton's law of cool. Mesbah tilted his head to the side. I took that as an indication

that is what they wanted. I wrote that and discussed the how I would get the heat transfer coefficient from correlations (Nu#). I'm not sure exactly what he wanted with this.

Q (Graves): You have a layer of SiO2 on Si and O2 is diffusing to the surface of Si and reacting (Deals-Gove problem). Can you assume time scale of diffusion is much faster than film growth rate? What is the time scale of diffusion? Can you assume pseudo SS? How would you calculate film growth rate? A: As he was asking the question I told him I had already briefly looked at it since he asks it so frequently. I set up diffusion through a film to a reacting surface. At SS flux equals the reaction rate at the surface of Si. I talked about PSS and how you could assume that if L^2/D was much smaller than the characteristic time for film growth (measured experimentally). I I talked about how I would use density and rate of reaction to get film growth. He told me I didn't need to bother finishing it since I had already looked at the problem Overview: It was fine. Mesbah is a little vague and it's tough to know what he wants. It's good to talk to him a lot. I felt pretty good coming out of this final, but ended up just doing OK. I must have said something that was wrong. Maybe I confused Pr with Sc number or something. Or maybe they didn't like that I went off on a tangent about cannibalism and how I thought society was clearly didn't have our priorities straight when we buried perfectly good sources or food.

PD

I was pretty nervous because this was my first Prelim and Mesbah was a wild card. I walk in and Graves asked me about my undergrad, what classes I took and such. I mentioned my one class had Deen as a recommended text and he seemed shocked at the idea, but made a comment about throwing everything at me if I had used that book. It was recommended, so I hadn't used it, but that didn't seem to register. I was hoping for his Deal-Groves problem or a simultaneous thermal/momentum system, but he deferred to Mesbah.. Mesbah asks, "You have pure water and you bring it into contact with air. What happens?" I think the combination of nerves and vagueness on Mesbah's part threw me off and I didn't know exactly where to start. I think what they wanted was for me to talk about the different processes at different time scales. Early on you'll have simultaneous mass transfer of O2 dissolving and H2O evaporating. Eventually O2 will reach a solubility limit and then you'll just have H2O evaporation. This is what I should have said, but I fumbled around just talking about O2 solvating in water with a PSS assumption. We talked about mass and momentum boundary layers and I eventually fumbled through to talk about boundary layer thickness and scaling with Re and Sc numbers. This should have been fairly easy because it's somewhat analogous to thermal/momentum BL over a flat plate, but I was pretty nervous and didn't realize this till the exam was over. The last part of the problem was Graves asking about using Mass transfer coefficients versus diffusivity and Fick's Law. I again fumbled around before arriving at the point that Fick's Law is for a point in space and to know the specific diffusivity and concentration gradient at that point is hard. Back in the day is was easier to use approximate mass transfer coefficients that were for the system and not for a point, because PDE solvers weren't available for turbulent flow/complex systems. There was a couple minutes left when they asked me about if the system wasn't isothermal, how would you treat the interface now? I only got "Wet-bulb problem" out of my mouth before Graves said, "Done!" and they let me go. Both were pretty nice throughout the exam. I think the key with Mesbah is, because he is quiet, definitely try to ask him for clarification or for him to be more specific if you don't know what he wants. Graves was pretty predictable and followed his past behavior. I wasn't sure if I passed or failed walking out of the exam because I barely got through basically one problem. Turns out I got a B, which I was alright with.

Graves/McCloskey

MN

This was the most comfortable prelim for me. Both professors were very nice, and McCloskey was especially wonderful and easy to work with. My favorite thing about having him as an exam proctor is that he

tells you when you are right so you can move on. For some reason, some professors like to be mysterious and stare at you after you say your answer. Instead, Prof. McCloskey says, "Right, that exactly right. Now think about this..." I felt like things were always moving along and I was constantly getting feedback, whether it was positive or negative. Be very happy if you have this pair.

Q1: You have a flat infinite plate with a layer of water on top, and then air above that. The plate is parallel to the x direction. The water is height y=H. At t=0, the plate is stationary. At some time just after t=0, you pull the plate with velocity U. Draw the velocity profile in the fluid at t=0, t just after 0, t=infinity, and a few times in between. Just be calm through this. Start by saying what you know and qualitatively describe what you expect to happen. They encouraged me to write the equation of continuity, write NSE, and set up a graph of y vs v_x. Talk through simplifications of the equations you wrote for your system and write the initial conditions and boundary conditions, and use this to fill out your graph.

I solved for the velocity profile at t=infinity and used this as an upper bound for graphing the velocity within the fluid at various times.

Follow up questions:

- 1. What is the work required to pull the plate? Will this be different at early times vs at t=infinity? Force=stress*area. I found that the stress would be 0 at t=infinity, so the work required at long times is 0, but the work at shorter times is >0.
- 2. What is the characteristic time for reaching steady state (SS)? First I thought H/U, but realized that this did not incorporate the properties of the fluid at all. So they told me to think about my non-SS equation. I non-dimensionalized this to find a characteristic time that incorporated momentum diffusivity and the height of the fluid. They helped me through this, and asked questions about whether the time to SS would be shorter for a high viscosity fluid or for a low viscosity fluid.
- 3. Now say the viscosity of the air is not negligible. Now draw the SS velocity profile of the liquid and the air above it. Through continuity of stress, realize that the slopes of the velocity in the air and liquid must be different because their viscosities are different.
- Q2. Now you have the same plate with a volatile fluid on top of it, and its being pulled out of a tunnel. Derive the height of the fluid outside of the tunnel as a function of x. I did a mass balance on a differential delta x element of fluid, accounting for flux leaving the surface due to evaporation. How would you find the flux? How could you find the concentration of the volatile component just above the fluid layer? How would you find the mass transfer coefficient?

If the place is held at T=Tair, and the ambient air is at Tair, draw the temperature profile in the liquid and in the air above the liquid. You should realize that there must be a flux of heat to the interface to supply the energy required for vaporization.

Overall, I made some errors through this, but they helped me to catch myself and correct it. Don't get flustered if you do something wrong. These two were great for keeping me on track. Note that Professor Graves didn't look thrilled at some points, but I think he was in a hurry to leave after that.

Cerretani/Muller

DG

These two were a very cordial pair. This was my last prelim and I was pretty anxious to get this one over with. Thankfully, it all went better than I expected. Muller asked one of the questions she asked in

previous years about a closed rectangular cavity with the top of lid moving with a constant speed of V. The solution reduced to the Navier-Stokes equation where the dP term can be calculated from an overall mass balance on the system. I asked her permission while making the assumptions of newtonian fluid with constant density, she seemed to like that :). After I came up with the appropriate form of the mass balance (hint: it's an integral over the cross sectional area) we moved on to Cerritani's question.

Cerritani asked about a droplet of liquid metal, spherical in shape, that is dropping through air from a height of H as it solidifies and cools down. I had to divide the question into to and make to different energy balances for the case where the droplet temperature is changing and for the case where fusion is happening. After a discussion of the Biot number to maintain the temperature of the metal sphere is constant compared to the change in temperature in the boundary layer, the solution reduced to two overall energy balances to get the amount of time needed to cool the sphere. The discussion then became about the velocity of falling, air drag and the calculation of the terminal velocity (Hint: Drag coefficient is a function the Reynold's number) After this they seemed satisfied. In the last few minutes Muller asked me how I would calculate the convective heat transfer coefficient to which I gave the classical answer about the Nusset number and its corrolation to Re and Pr numbers, defining all these on the board.

I felt exhilarated after this prelim ended, and turns out I didn't do bad either. Especially if you have Muller, it is important that you be precise, respectful and confident in what you say.

NG

My perlim was exactly like the one above. The pair were helpful, and if they saw you were going in the right direction but did an algebra mistake, they would help you out and correct you. An interesting thing I would add to the above is that despite viscosity appearing in the integrated N-S equations, it actually does not affect the velocity profile, which depends only on the velocity of the top plate!

Radke/McCloskey

LC

This prelim (my first) was probably the most hilariously terrible experience ever, and I almost didn't take my second/third prelims because it was so traumatic.

To preface, I didn't take grad transport with Radke last semester and was in for a treat. I had heard about his antics and specific "style" from multiple people, but I quickly found out that it's really not the same until you experience it in person. I'm pretty much the least confident person in the first place, but by the end of this I was frazzled beyond belief. I had a pretty simple flat plate film problem that others have mentioned (see the other McCloskey transcripts) but was dumb and got psyched out by Radke's incessant interruptions. I guess he has a very specific way of solving problems, which didn't really help my cause. Oh, I should also mention that apparently he's not the biggest fan of Professor Deen (gross understatement), so if you've ever taken a class with Deen (bless his soul), sweep that shit under a rug and avoid bringing it up if at all possible. Just sayin.

In any case, I would like to say that McCloskey is the most wonderful man in the world and was so incredibly nice to me while witnessing the beating I was getting from Radke. At one point I was moving on to a new equation and I just let out a heavy sigh because I was so tired of it. At another point I forgot what the whole point of similarity solutions was. Toward the end I wrote out an equation that Radke determined was utterly useless. By some miracle I passed this and I have no idea why. But know that if you get Bryan McCloskey, you have been given a gift and should profusely thank the heavens for your good fortune.

I think the takeaway from this is to have faith in yourself and don't let anything get to you! We're all completely capable of solving these problems, but the key is to keep your composure and just do what you came to do.

JL

Also the same flat plate with a film problem. Starting just by getting steady state velocity profile, writing down and describing/explaining boundary and initial conditions, NS equation and explaining what terms we can ignore, continuity, characteristic time, all that jazz, describing how we would solve the whole thing (splitting into a transient plus a steady-state solution, essentially homogenizing the boundary conditions so we can use separation of variables. Do not for your life say the words "Sturm Liouville" tho)

Then we say it's a volatile liquid evaporating coming from a tunnel and then evaporating off the plate, so we're using the steady state velocity profile (plug flow), set up a differential mass balance, talk about the concentration profile. Go into energy balance/temperature profiles, because these affect mass transfer rates. Nusselt number will be related to Grashof number since this is a case of natural convection (air on top of fluid is not moving).

And now, some moments of comedy: 1. I said something incredibly stupid/messed up algebra whatever, Radke says "You're too young to have senior moments like that," I correct myself, we all laugh. 2. After drawing the temperature profiles, Radke asks me to compare the temperature at the surface of evaporating liquid to a wet bulb experiment/temperature. I'm lost for a bit, then eke out "well this liquid is methanol, so we can assume there's no methanol in the air, so there's no "relative humidity" to measure." Radke loses it, says I made his day. Technically correct, but also just like. Not intelligent. Whoops. Eventually I get it and say that it's because in this problem we hold the temperature of the plate over which the fluid is moving constant. In a wet bulb experiment there's no internal heat source for the liquid. I am hopefully forgiven. 3. At the end of the exam, we're exchanging pleasantries, Radke says "Thanks for coming in," I say "Any time" then correct myself and say "Actually wait nevermind. Never again. Please" and everybody laughs once more.

Radke will hound you and make jokes. It's tough, but if you can you should just flow with it, laugh a little with him, stay calm, and refocus yourself. He and McCloskey are both generally very helpful.

PG

This was my favorite prelim. I knew what to expect from Radke because of grad transport. I think the prelim was all about attitude. I went in with a good mood, ready to joke around and laugh with Radke while he laughed at me. So it was a fun experience and I did well. Radke likes to have fun, so have fun with him. And McCloskey is super nice, be happy if you get him. I got the same questions as JL, although when we got to the dimensionless number part, I didn't know what they wanted. Eventually Radke was like, have you ever heard of the Grashoff number?? I was like, I've heard of it....doesn't it have something about buoyancy in it? Oh well. They didn't really care. Just know the basics, be able to set up a problem, and have a positive attitude.

Overall Advice

J.Ro.

Studying for prelims is rough, but put in the work and it will show. I started studying 2 weeks before the exams. For the first week, I read all of Smith Vann-Ness and Abbot for thermo, and most of Fogler's elements of reaction engineering. I made a summary of notes and equations for these two subjects which

was pretty useful but also pretty painful to make. I did several practice prelims and had several sessions practicing doing problems with friends. These were very useful as sometimes you think you understand something, but then you get up to the board and you know nothing. While it's useful to have a general understanding of all of the topics, it's also good to look at all the past questions your examiners have asked. It's not quite fair, but examiners tend to ask the same sorts of questions. Keep calm, and don't get flustered. Don't look at your examiner's expressions, this will stress you out. I felt a nervous pounding in my chest for weeks/days before the exam, especially upon walking in, but once you're in there, you're just solving a problem, and it can be comforting, and even fun when you're actually getting it. When I was stuck, I just explained my thoughts to them, and went through the ideas. Sometimes I wasn't sure if something was this or that, so I let them know that I knew it was one of the two and would proceed with that in mind. I made a TON of silly mistakes, and said some dumb things under pressure, but if you do make a mistake and then you realize what it is, explain why you realize you were wrong and own up to it. Some professors offer more help than others. Listen to their hints and focus on what they're saying. Although you only need to pass 2 of the 3, I would not recommend focusing on only 2 because its a bit of a crap-shoot how it goes in the exam room, so you should be prepared for all 3. After the exams, I felt pretty awful and thought it could have gone either way, but I passed. I believe in you <3 put the work in, practice by yourself and with others, ask us for help. It sucks but you learn a LOT and it's pretty cool how the subjects start to come together.

KC:

I read all of Smith/Van Ness/Abbott, Fogler, BSL, and a number of other books. Only you know if this is a good way for you to learn. I didn't practice that much, but it is absolutely essential to start practicing. You will never feel prepared to start practicing. Do it anyway. It helps you learn how to think on the fly. It feels impossible, but you will get through it! Get enough sleep--you will never know everything, so it is better to be able to think on your feet than to waste four hours trying to memorize things that are statistically unlikely to be on the test. Look through the last few years of testimonies at least, and if you see a topic on several years, make sure you know at least vaguely something about it. I didn't have a bunch of the classes I should've had in undergrad because my background was more chemistry, but two weeks was still enough for me... if you study too early (I tried to start during break), you can get a bit burned out.

DG:

Practice makes perfect. It was a lot of help to work with the older students but nothing really prepares you for the pressure of standing in front of the committee. Be aware of this and try to stay calm. Statistically, you first prelim is more likelier to be worse simply because your nerves may get the better of you. Don't fret, power through and trust in your knowledge. Don't be afraid to discuss what you are writing on the board with your committee. Don't admit to not knowing something essential if you can avoid it. Keep cool, stastistically you are very likely to pass:)

EM:

I would suggest trying and going back to the curriculum used by Berkeley Professors (email TAs/Professors) for undergrad Transport, Kinetics and Thermodynamics course curricula. Hold yourself accountable to the list of benchmark fundamentals every ChemE is expected to know during their undergrad careers. Check off topics you cover here to make sure you are able to verbalize them, know what each equation represents and apply them to important sample problems. I also used CU Boulder's Learn ChemE videos (http://www.learncheme.com/screencasts) as they helped me imagine how I would verbalize my thoughts on specific concepts which I had not seen before. Lastly, take at least 2 practice prelims for each subject with upperclassmen, if not more, whether you know the material well enough or not. Make sure to verbalize everything you study as you go through your study plan, to save time. Also, in case you are on a severe time

crunch for any of the three, turn to the binders on the GSAC website for the very bare essentials you need to know.

KD

I think I studied too early for this exam, and didn't trust myself in knowing that I burn out quickly. I never studied for exams more than a day or two in advance during undergrad so studying for two weeks straight is just really rough, not something I had ever done. I started January 2nd for real, reading books for 6-7 hours a day, but by the end of the first week I was just not interested in doing anything. I felt prepared for the exam on that weekend, figuring that practice would help me during the week. I think that practice prelims are useful, maybe I should have done more, but realize that older grad students are not the same as professors no matter how good they are. I had even had a practice prelim given by Radke in front of the transport class, but that was a different experience too. I had read SVNA, Fogler, my thermo book, BSL during the previous semester, and a bit of Welty Rorrer Foster. Its important to have some key equations memorized, but just being able to talk about anything is important. I hurt my grades in all of the exams by not being sure of what I was saying and talking in a circle. In my practices, including in front of Radke during the transport class, everyone would be more direct about saying 'correct', but none of the professors I had confirmed my answers. So I tried to interpret their faces whether I was right or not and just went in circles. If you know yourself and can be confident in your answers you'll do much better. I do have to say though, there is a lot of luck involved, no matter how much you study, if you get the wrong question things can be really weird. This happened to me in both kinetics and thermo and I got very lost, it was lucky that I was able to say enough right to still pass. They don't even have to be hard questions to confuse you, so just don't get worried if you're messing up. Transport I just didn't study enough because the question was something I had seen before, should have aced it.

LC

My approach to prelims was kind of a mess and I wouldn't recommend it to anyone. But learn from my mistakes! Have fun and don't stress out about prelims, but do have a plan so you don't have to cram too intensely.

Like others, I arrived back on campus almost right after New Years (Jan. 1). I guess I had high expectations for my future self when I booked the tickets in September. In reality, I ended up hanging around and just relaxing for a good period of time. I probably ended up studying for a max cumulative period of maybe 0-3 hours/day for the first week. By some strange coincidence, my music library and photos got really organized, my room was super clean, Napa became a dry valley, and lots of cookies were made in that period of time.

My study plan involved going through my old undergrad cheat sheets and trying to reinternalize all the topics again. (I didn't take transport/thermo last semester). I spent a few days redoing all my undergrad fluids/heat+mass transfer problems to relearn it all, but I think this was a waste of time and I would have been better off just setting up a bunch of problems. I used Deen when I took grad transport (and therefore studied it cover to cover), but Radke isn't a fan of it, and I think it shows. If you have him on your committee, I would recommend at least skimming through BSL to know how they set up problems, because in some cases the methodology is slightly different, and that can bite you in the ass if you have Radke.

For thermo, I skimmed through Smith/Van Ness/Abbott (which I've never used before) to get a gist. In the end, it wasn't really that helpful since I didn't absorb anything towards the end by going through it so quickly.

I did two mock prelims, but if I was smart I would have done them earlier and more frequently. I didn't do mine until Wednesday (literally the day before prelims), and they were held by two panels of older grad

students. These were probably more helpful than most of my studying combined, since it finally gives you a chance to be at a board and forces you to explain yourself clearly/succinctly. The older students also gave super helpful tips that I otherwise wouldn't have known. Also, reading these testimonials is incredibly helpful, especially when you have older professors who might show patterns in what they ask.

The worst thing I did was stay up on Thursday night to cram more material before Friday's exams. I ended up sleeping 1.5 hours and was completely non-functional for the entire day. I used to do this in undergrad all the time...but it's **really** not worth it. Sleep >> learning a tiny bit more material.

In the end I ended up doing fine, but my method of madness was definitely not ideal. I'm pretty good at handling stress so it worked for me, but the last few days were seriously crazy. It reminded me why classes are taught over a span of 1 (or more) semesters and not 1 day. Oops.

The more important takeaway though, I think, is that prelims are meant to test what you know. The professors aren't out to stump you, and I am 100% certain that we all know (or can figure out) how to solve the problems that we're posed. The key is to keep calm and don't let minor hiccups get to you. It's all mental--just believe in yourself and work through things like you would any homework assignment. These questions are often much simpler than you think.

tl;dr sleep, pace yourself, and relax! The department wants you to do well and if you've done some preparation, you'll be fine :)

MN

I also returned to Berkeley on Jan 2nd, about 2 weeks before the exams. I did not study during the Christmas break, and I'm glad I didn't because I was definitely burnt out by the second week. To study, I read almost all of Fogler and my undergrad thermo book by Koretsky. I didn't study too extensively for transport because I took Radke's class and I thought he did a great job of teaching the material. For transport, I focused on undergrad material by reading Denn and reviewing my dimensionless numbers, and then I did a lot of key problems from BSL to get me accustomed to thinking about the assumptions that go into setting up a problem. I highly recommend reading through all the problems that have been asked by your committee members in the past. I would do this after a few days of studying so that you understand the questions, but don't wait too long because this will help you focus your studying. If you can, for the most recent years, read some questions by other professors besides yours. This can give you an idea of the general things that the Berkeley faculty expect you to know, and it might help you out in the event that your schedule is changed. I think that this is unlikely to happen overall, but it never hurts to be prepared. I took at least 2 practice exams for every subject. This is very, very important. Be sure to reach out to older students, especially ones you do not know. Not a single person said "no" to me. We all care about you guys and are more than willing to pay it forward to help you out! As KD said, you might not feel ready for a practice pre-lim, but you should do it anyway. I took my first one 6 days before the real exam, and it was very helpful.

Before the exam, make sure to sleep and eat. Take a deep breath and be confident. There is no way you can possibly learn all the material to completion, but focus on the core and be confident. It is scary, but you can definitely all pass. With that being said, DO NOT underestimate the exams. Put in the time and you will do great!

JL

I started studying Monday the week before prelims. I would get to my office on campus around 9-10 am and most days would stay until about 7 pm. I think for me working in the office was helpful because it minimized

the time that I would spend dicking around. Then when I'd finished for the day I'd leave everything on campus and just take the nights off. The brain needs a break, and I think I definitely was a lot more energized during the day/able to get more done because I wasn't working that late. Wednesday and Thursday night of prelims week I stopped earlier around 5.

The first couple days were spent mostly just solo reading through textbooks and taking notes. I went through Fogler, Sandler, and parts of SVNA. I didn't reread BSL, but I picked out sections on common topics to read through (like Stokes flow, BL theory etc) that can be approached a little more from a discussion standpoint (as opposed to derivation) in the exams. Pretty early on I started working at a whiteboard in the office talking to myself, just to get used to working through problems vocally. I also started basically writing and rewriting some key equations (NS, reactor design equations, basic thermo stuff etc) for a couple minutes each day starting maybe a week before the exams, just to have those down super solid. I think that was very, very helpful, both for just getting used to working and talking at the board, and also because it helped me recognize when I didn't reaaally understand what was going on if I couldn't get it to make sense. I had one sort of formalized practice prelim, but most of my group practice was just with other first years. I think this--not having that many formal practice prelims--worked out fine for me because I spent a lot of time just talking through things on my own early on. Definitely any group practice you can get is important though, at least after you've had enough solo time to have some level of familiarity with the material. You need to break out of your head and have other people challenge what you say.

Roughly two weeks of studying seems to work for most everybody. I ended up taking both mornings the weekend before off and just worked from maybe 2 pm - 8 pm because I was getting burnt out. Don't overexert yourself prepping for these. Certainly take it seriously, and if you really do feel like you're behind you should put in more work, but the most important thing is to keep yourself healthy and relaxed so you can demonstrate what you know come test time.