

# Prelim Exam Transcripts (2014)

Created: Jan 21, 2014

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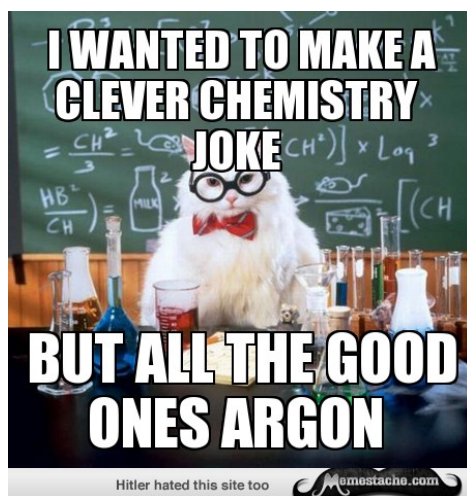
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## Preparation Advice

## Google Docs Usage Notes

ctrl-alt-m	inserts a comment
ctrl-enter	inserts a pagebreak
ctrl-(0 to 6)	formats the text as a heading that will show up in the Table of Contents
insert (in toolbar)	inserts symbols, horizontal lines, etc
drag-and-drop	images from the Web directly into the document



# Thermo

## Balsara / Maboudian

JB

I want to condense a gas to store it. What process would I use? Liquefaction/throttling. I drew a stream in and out of a throttle valve with  $P_1$ ,  $T_1$  and  $P_2$ ,  $T_2$ . What is the relevant parameter which correlates the temperature change to the pressure drop?  $(dT/dP)_h$  or the Joule-Thompson coefficient. What does constant enthalpy mean? Adiabatic, work done by gas expansion is converted into internal energy of the gas. What sign do we want the JT coefficient to have for this process? Positive. Relate the JT coefficient to measurable quantities. Start with  $H(T,P)$  and set the total differential to zero, rearrange and then use a Maxwell relationship. What is the JT coefficient for an ideal gas? They just wanted me to show that if you plug in the EOS  $PV=RT$  into the equation I just derived, the JT coefficient becomes zero. Before that, I explained the molecular mechanism of JT expansion, see "Physical Mechanism" section of

[http://en.wikipedia.org/wiki/Joule%E2%80%93Thomson\\_effect](http://en.wikipedia.org/wiki/Joule%E2%80%93Thomson_effect)

If there is no attractive potential, there is no way a decrease in pressure can affect the average kinetic energy. I think this explanation is what won them over. What happens if we use a virial EOS? The  $(dV/dT)_P$  in the expression for the JT coefficient doesn't just drop out a  $T$  because the virial coefficients are a function of  $T$ , so the JT coefficient is nonzero. After this, they had me propose a couple other unit ops in the liquefaction process and then do an enthalpy balance but before I finished they said we were done with this problem. After that, they asked me what restrictions there would be in determining an equation of state as  $f(P,T,V)$ . It took me a minute to figure out what they were asking, and then I figured out that they just wanted me to say you can't manipulate two conjugate variables independently, e.g. you can't have  $T(P,V)$ . This was only 20 minutes into the exam, and they told me that we were done.

This pair is pretty cohesive, and the things they expect you to know are pretty standard. I got lucky with the JT expansion question in that I knew the mechanism and I had memorized the equation so that the derivation was easier.

MT

I got the same questions JB got. But because I'm stupid it took me a while and I kept thinking that they were asking me more profound things and I kept getting stuck and blanking out. But I did the derivation confidently but I don't think I explained it well. So to understand the answers to the questions look at JB's testimony.

Overall, they were pretty nice, they kept encouraging me and telling me that I was doing well. I think they could sense that I was nervous. I tried not to seem stressed and I tried to write things out and show my thought process. I scribbled some stuff on the board to help me remember but when I did it ended in questions like 'what are you drawing?', 'what do you have there?' It wasn't bad. I was able to explain what I was doing but if you don't want to be scribbling on the board I suggest memorizing more concepts. I don't know how I passed this exam. I thought I failed it. I even made a mistake on when the ideal gas is applied. They were really nice. Maboudian was too nice. Sometimes she helped me a bit too much and it was hard to show that I knew the concept because she would say the answer before I did. I tried to stay excited even

though I felt like it was going pretty bad. At the end Balsara discussed the answers with me. And I tried to not break down when he was going over what I did wrong. Anyway, I ended up getting a B. Horray! Prelims, they are kind of unpredictable that way.

## **Smit / Prausnitz**

ML

Asked me to tell them about myself, so I told them where I went to undergrad and who my thermo professor was. Prausnitz said he knew my professor well, and then proceeded to ask me ...

(1) Do you know Gibbs Duhem, can you write for a bi-component system ( $0 = -SdT + VdP - NAd\mu_A - NBd\mu_B$ ). Smit then says, write for a single component system. How do you get Gibbs-Duhem? I say you derive from combined first and second law (write  $dU = TdS...$ ) and do some Legendre transformations. What is the second law? How do you get that from the second law? What they wanted to hear was that entropy of the world is always increasing and some elaboration on that.

(2) Now to VLE: Back to a bi-component system. Prausnitz asks: at const T and P what does Gibbs-Duhem tell you? (You can use it to derive the Lewis-Randall rule? This was not what P was looking for) After much prompting, I say that if you have the chemical potential of one component, Gibbs-Duhem will tell you the chemical potential of the other component via integration, and we are done with this question.

(3) Smit: How would you make a model of VLE of components A and B? (I am very confused so Smit helps me out) For example, model the gas as an ideal gas, and you then want to know the rate of molecules moving from V to L phase (equal to the rate from L to V). What does that depend on? Me: Temp? Pressure? Smit: Assume those are fixed. I am still confused, so he helps me more: Rate of A going from V to L is proportional to number of moles of A. I finally come up with the rate of  $V \rightarrow L$  being proportional to the partial pressure of A. Now Prausnitz joins in - How about the liquid? I struggle some more, and Prausnitz prompts me to think about volatility - what does that depend on? I say partial pressure (ding ding ding) and then it dawns on me that they want me to write  $y_i^*P = x_i^*P_{\text{sat}}$  (basically Raoult's law). This is for an ideal gas and mixture, so they then ask me to add in "arbitrary constants" for a non-ideal VLE. I write  $\phi$  and  $\gamma$  and tell them I just picked random letters of the Greek alphabet. They laugh. We move on.

(4) Prausnitz: How do you make ammonia? I write  $N_2 + 3H_2 \rightarrow 2NH_3$ . Where do you get each of the components? (Nitrogen – Linde liquefaction of air to get liquid nitrogen. Hydrogen – electrolysis or steam reforming of methane. Classic Prausnitz) P: If you increase the pressure, what happens to the reaction? (Pushed forward due to Le Chatelier's Principle) P: How do you measure the equilibrium constant ( $\Delta G_{\text{rxn}} = -RT \ln K_{\text{eq}}$ ). P: Why is  $\Delta G_{\text{rxn}}$  non-zero when  $\Delta G$  is equal to zero for equilibrium? ( $\Delta G_{\text{rxn}}$  is measured at standard T and P, not necessarily at equilibrium) P: How would you measure  $\Delta G$ ? (Get H from heats of formation - 0 for pure components, calorimetry for the reaction. Get S from 3<sup>rd</sup> law of thermodynamics and  $S = \int C_p dT + \Delta H_{\text{melt}}/T + \int C_p^* dT + \dots$ )

(5) Smit: Draw the phase diagram for CO<sub>2</sub>, now superimpose phase diagram for N<sub>2</sub>. They ask me the standard phase diagram checks (where is critical point, stuff about the slope of the solid-liquid line). Then Smit asks me to draw the two-component phase diagram for N<sub>2</sub> and CO<sub>2</sub> at a given T. I draw a Pxy diagram. Then Smit points out that the T he indicated (he went up to the board to mark a temperature) goes through the region where CO<sub>2</sub> is supercritical. How would I modify my phase diagram? I hem and haw for what seems like a long time but keep guessing wrong. I talk through everything I'm thinking though and that

seems to help me. Eventually Smit just tells me the answer (it looks like [this](#)) and they let me go, not seeming to mind that I had no idea how to answer this.

Overall: Some of this was standard Prausnitz, but Smit was pretty unpredictable. I felt that they both helped me out a lot though because I tried to stay calm and positive, and I did not get frustrated when I didn't know what they wanted from me.

AH

Prausnitz started this one off and it mainly went him for 25 minutes, then Smit for another 20 (mine went closer to an hour than forty minutes, I think because I was last for the day). First, he wanted me to talk about Henry's Law. I wrote it on the board. We discussed when the equation is valid (dilute systems) and talked about the Henry's constant (Is it a function of temperature? Yes. Is it a function of pressure? Yes). He then asked me what the opposite case would be. I responded with Raoult's Law and wrote that on the board. They wanted to know what Raoult's law was assuming (higher concentrations, ideal solution, ideal gas) and how I could change it to account for non idealities (fugacities, activity coefficient). What is a fugacity? How can you calculate it (residuals)? In the residuals equation I wrote on the board, there's  $\ln(\text{fugacity}) = \frac{RT}{P} \int_0^P \frac{Z-1}{P} dP$ . What is that Z? Where do I get it? I wrote down the virial equation. Where does it hold (non-ideal gases, less-valid for solutions). What EOS would be good for liquids? I knew this was coming... VDW equation. Write it on the board (Prausnitz said "you better get this notation right") as I was writing it. What do a/b stand for? What happens when you increase each one and why? Well for b, if you have molecules taking up space then there is less overall space for other molecules and pressure goes up. For a, if you have intermolecular attractions the molecules will be attracted to each other and less likely to hit the side of the container, thus the pressure goes down. Why is there a  $V^2$  term in the denominator of the second term? One is for frequency, I wasn't positive for the other volume term. I think Smit said it was for the amount of molecules you have left (like the density), but don't quote me on that.

They then wanted to talk about the Haber process to make Ammonia. Look at (4) from ML's testimonial... I was asked the exact questions. Keep in mind that the 3rd law is important to provide a standard so you can calculate  $\Delta G = \Delta H - T \Delta S$ , because  $\Delta G = -RT \ln(K_{eq})$ . You can't calculate  $K_{eq}$  without the 3rd law. Prausnitz loves this question, definitely know that if you have him. We also talked about how you make  $H_2$  (water splitting or flowing methane over coal). I didn't study that so that guessing game took me a while and killed some time. Linde process, of course. Why don't we use turbines instead of throttles (throttles are cheaper).

We then talked about phase diagrams. Look at (5) in ML's testimonial for those questions. They realized we went over on time partway through that, so I didn't get through all of her questions.

Overall: Prausnitz is a process exam. I studied a lot of derivations, but it was none of that. I didn't even write the Legendre transforms on the board. Less board time, more talk time. It's like as soon as you hit a key word, they move onto the next subject. No math, they didn't want to waste time on that. Read over his old stuff and you'll definitely be fine. He was very tired during the entire test, and his eyes were kind of fluttering. He sighed a lot. He didn't seem to be in the best of moods. When I left Prausnitz yelled out "Make sure you LEARN, not MEMORIZE" which kind of freaked me out but I ended up getting a B+ and I'm more than okay with that. I thought Smit was going to make me nervous, but he was actually one of the nicest of my prelim professors. He was smiling and laughing. Just go along with him. He's always going to ask VDW EOS, after that I think it's a little bit of a guessing game. He's very friendly, just confusing sometimes. Asking for

confirmation or re-stating a question is always okay, and he isn't upset when you get stuff wrong. Be happy if you get this combo.

**Balsara / Katz**

**Balsara / Smit**

**Head-Gordon / Schaffer**

CH

Head-Gordon: Gold nanoparticle attached to a piece of DNA. I pull the nanoparticle adiabatically. What is the equation that describes this process  $\Rightarrow dU = -Fdx$ . What about an isothermal process?  $\Rightarrow TdS = -Fdx$ . What drives this process? Entropy, but more specifically, the DNA in the unstretched state has more configurations (a.k.a. microstates) than the stretched-out DNA. How can you describe this with statmech? It's a simple question, but for some reason my brain freezes and I begin to draw pictures of random DNA configurations everywhere. H-G attempts to walk me through it and I eventually get it by discretizing 1-D space and getting that for  $M$  amino acids, the number of configurations with length  $L$  is " $L$  choose  $M$ ."

Then, I was asked to use the results I had just derived to figure out the  $\Delta S$  of compressing a gas cylinder isothermally. I knew how to derive it normally with statmech, but I couldn't figure out how to tie in my previous results. In the end, I just said something about a gas cylinder being a 3-D version of the previous problem and started to perform the textbook statmech derivation to get  $\Delta S$ . So for the next 10 minutes, I decided to entertain H-G and Schaffer with my dismal algebra skills. I had natural logs and exclamation points flying everywhere. H-G finally tells me to just write the answer if I know it, and I derived  $\Delta S$  using classical thermo in 30 secs. Meh.

It's Shaffer's turn now. You have solid methanol in a tub of water. What's the  $\Delta S$  of the process? Is it reversible? How much work can you extract from this process? I recognized that this was a combination of his sub-cooled liquid problem and finite cold reservoir problem, but I was still too rattled from the previous question and made a mess of the problem. Essentially, you just have to recognize that there's 3 terms that contribute to  $\Delta S$ : heating the methanol, melting the methanol, and mixing the methanol in water. It isn't a reversible process since heat is being transferred inside of your system. I began to solve for the amount of work you could extract from this process, but time was up so I just quickly described in words how I would do it.

I felt like I completely failed this prelim, but somehow I still managed to get a good grade. I think the trick was that I never stopped talking, even if I was saying the most trivial and obvious things.

KS

My questions were the same as above, though Head-Gordon did ask me about statmech probabilities and linking that to the Boltzmann distribution. I started with the definition of entropy in two ways:  $S = k\ln(\omega)$  and  $S = -k\ln(P)$  where  $\omega$  is the number of microstates,  $P$  is the probability  $P = 1/Z[\exp(-E/kT)]$ , and  $Z$  = Partition function =  $\sum_s e^{-E(s)/kT}$ . I didn't actually get to finish my analysis, but she seemed happy that I was using these two definitions to start with. I think she wanted me to discuss why higher energy states don't necessarily mean higher multiplicities by connecting  $\omega$  and energy through the two entropy definitions.

Final notes: these two were slightly intimidating to stand in front of as they don't offer a ton of support. If you ask for a clarification, Schaffer is okay at rephrasing a question to guide you to what he wants you to say. Head-Gordon doesn't exactly have this ability. Try not to get upset because that will just distract you further.

## Schaffer / Smit

NC

I had a really poor thermo background as I only had one poorly taught semester of it (I have a bio focus so I was excused from taking separations.) So my understanding of what they wanted might be off. I also only prepared for this final by reviewing what questions Schaffer typically asked and then praying that Smit would be merciful. Schaffer doesn't really throw too many curveballs, but sometimes Smit will like to "put you in a corner during a fencing match" (quoted from after prelims).

Schaffer set up a problem where an ice cube of methanol is within a tank full of room temperature water. He asked me whether or not the reaction was irreversible or reversible. I said irreversible because at room temperature and pressure the state of methanol and water are both liquids. He then asked me what a reversible process would entail and I struggled on this for way too long (the answer is that each microstep of the entire process be reversible or something like that. I don't know.) I started getting flustered, but I just kept going. This sounded pretty much like one of his previous questions of a Carnot Engine with a finite cold reservoir, which I had practiced. He then asked me to find the  $\Delta S$  of the "irreversible reaction". I totally struggled with this and Schaffer held my hand the entire time. (Ask someone else how to do this one because I have no idea how this is supposed to be done. Like see CH in the previous section) We finally get to the Carnot cycle when he asks what is the maximum work that we could have gotten out of this system. I explain the Carnot cycle gets the most amount of work from the system since each step is reversible. Smit then interrupts and asks how this Carnot cycle could ever be theoretically done and where work would come from? (I said the difference in the  $\Delta S$  would create the work? He didn't seem too satisfied with this) Finally, I got to the end of explaining how to get the work and it was Smit's turn.

Smit asked me to draw a T-x diagram of nicotine and water. I was gonna put the traditional curve where the temperatures at the end were their boiling points...but Smit cuts me off and looks at me going "Do you know the phase diagram?" and it seemed like he expected me to know it already. I said I didn't and he said "of course you don't I'm going to draw it for you." and he drew a long oval in the middle where inside the oval the nicotine and water are immiscible and is a homogeneous mixture elsewhere. (*This is just Smit's style. He'll try to say things as statements that are false where you have to contradict him and sometimes he'll make you feel like you're supposed to know things even if you don't. Just roll with it.*) I got some questions about what would happen at certain temperatures and what the composition of the nicotine-rich or water-rich parts would be. (Lever rule & basic reading of T-x diagrams). He also asked me which is the more interesting critical temperature. I said the higher temperature is less interesting since that is where the entropic mixing exceeds the  $\Delta h$  of mixing. We ran out of time. He left me with "I guess we'll never find out why the other temperature was so interesting"

I felt like I totally train wrecked Schaffer's part but managed okay with Smit. I think the trick with Schaffer is to really know your classical, explain each step & your assumptions, and do his old questions with knowledgeable friends. Just do not lose your cool with Smit. If anything helped me, I didn't seem too flustered throughout the thing and I kept telling them things I knew even when I was completely lost which was 90% of the time. Overall, passed with decent grade.

This was my last exam of the three. Thinking I had failed the other two exams, I went into this exam strongly believing I had nothing to lose. It starts off great, with me arriving about 10 minutes late to the exam since I could not find the room (obviously, its in Smit's office for some reason I thought it was somewhere else). Smit and Schaffer briefly ask about my background in thermodynamic, seeminging somewhat surprised when I tell that I only had training classical thermo. I tell them about my undergraduate courses, and we begin the exam.

Schaffer tells me he has some solid methanol and he places it inside a water bath. The container has no head space. From this information, he wants me to calculate the change in entropy of the methanol. The first thing you should realize is that the melting point of methanol is  $-30^{\circ}\text{C}$  (making this number up), so naturally methanol will melt when placed in a bath of liquid water (which should be above  $0^{\circ}\text{C}$ ). Since entropy is a state function, I divided the change in enthalpy into three components:

- Total change in entropy = Change entropy (melting) + Change entropy (temperature change) + Change entropy (mixing)

I then proceeded to talk about each component, why they make sense, and why they should be exhaustive in considering the types of entropy change in our system. I had forgotten the forms these entropy changes took, so I had to derive them from first and second law. When talking about entropy of mixing, I got into a philosophical discussion with Smit about Gibbs Paradox. This discussion consumed a good 15 minutes of the exam, and was rather enjoyable and did not require any formulas or calculations.

Overall, this prelim felt short and I ended up doing best on it. Even tho I lost some points for not remembering how entropy of mixing should look like for a solution, it saved me that I was able to justify general forms of equations, and what contributions needed to be considered.

### **Prausnitz / Head-Gordon (*changed from Tullman-Ercek/Head-Gordon the day before the exam!*)**

EB

Head-Gordon started by asking a question she had asked before. If you have a piston compressing a gas adiabatically, what's the thermodynamic state function that's the driving force? Answer: since  $dU = dQ + dW$ , and  $dQ$  is 0, internal energy is the driving force. Next question: what about if you're doing it isothermally? This time,  $dU$  is 0, and since  $dQ = TdS$ , entropy is the driving force.

Next, she asked a few stat mech questions. She started by asking me to calculate the entropy of an ideal gas. I first put up  $S = k_B \ln(\Omega)$ . I then put up a grid with  $M$  bins and  $N$  gas molecules.  $\Omega = M^N / N!$  for an ideal gas with indistinguishable gas molecules. Do further simplifications.

Question: if a system is exchanging energy with its surroundings, what is the partition function, and what's the probability of being in a particular state? Answer: canonical.  $Q = \sum(e^{-\beta E_i})$ .  $P_i = e^{-\beta E_i} / Q$ .

Question: What's the Boltzmann Distribution? Answer: draw  $P_i$  as a function of  $E$  (just an exponential, as you get from the canonical ensemble).

Question: At higher energy, there are more possible states of the system, but the probability of being in that state is going down. How do you reconcile this? Answer: well, the system is exchanging energy with its surroundings, and the energy of the surroundings and the possible states of the surroundings is going up. I drew  $P_i$  vs.  $E$  for the surroundings, which is a positive exponential. Head-Gordon said that if you add together the two distributions, you get a Gaussian distribution. What's the standard deviation of it? Answer: specific heat.

Prausnitz asked standard Prausnitz trivia. Nothing I hadn't heard before and memorized, and that you could look up elsewhere. It felt like I was acting in a play, in which all I had to do was recognize my cues and say my lines. Do a dance of joy if you get him as your prelim examiner. I was actually originally assigned Head-Gordon and Tullman-Ercek for this one, but Tullman-Ercek pulled out the day before due to an emergency, so another first-year who had been studying Prausnitz questions helped me learn his trivia in the 4 hours before his exam.

KT

Prausnitz: Refrigeration! and the standard 3rd Law question.

Head-Gordon: Boltzmann definition of entropy. Probabilistic definition of entropy. Boltzmann distribution.

Minimization of entropy in the canonical ensemble under the conditions  $\sum(P_i)=1$  and

$P_i = e^{-B^*E_i} / \sum(e^{-B^*E_i})$  and solving for the Lagrange multipliers.

## Kinetics

### Reimer / Zhang

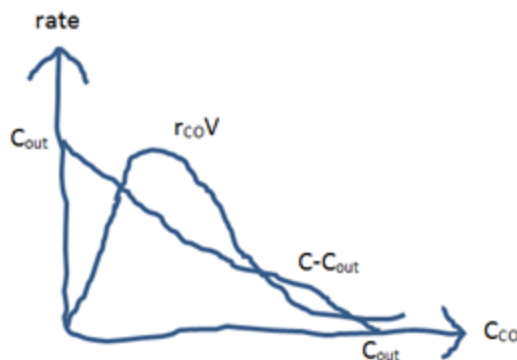
CH

Usual chitchat about undergraduate coursework and profs. Reimer then sets up a timer on how his iPad while Zhang looks over her notes and reviews the ten fundamental concepts of how to ask confusing questions to grad students.

Reimer: "As someone who has taken kinetics with Iglesia, I'm sure you know all about catalytic converters."

Me: "Uh..."

Reimer has asked this question in previous years, and thankfully I had studied this problem before. He has me set up the problem with  $\text{CO} + \frac{1}{2}\text{O}_2 \rightarrow \text{CO}_2$  and  $\text{CO} + \text{NO} \rightarrow \text{CO}_2 + \frac{1}{2}\text{N}_2$  both occurring on a platinum catalyst. I was asked to describe how CO consumption rate would vary with CO con'c, first with words and then on a graph. Then, Reimer asks if I only had the second reaction, how would this reaction would proceed in a CSTR? So I write down the CSTR design equation and plot  $C - C_{\text{out}}$  vs.  $r_{\text{CO}}V$  and get something like this:

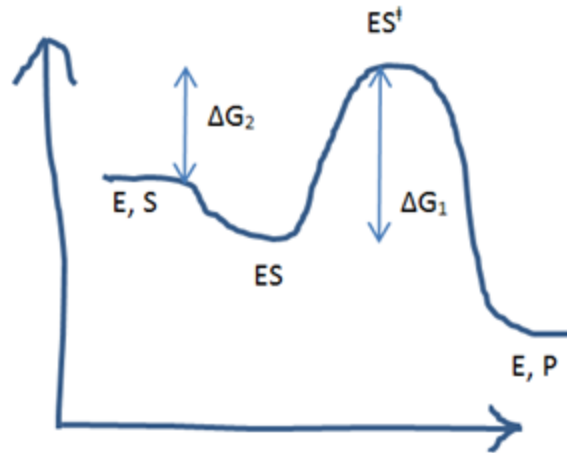


After talking about how the intersections of the two curves give the steady-state and that the top and bottom ones are stable, Reimer snidely remarks how I must have studied this in some notes somewhere (which I had) and asks me about the constant volumetric flowrate assumption I had made earlier in my CSTR equation. I tell him the approximation is good for dilute CO con'c but that I would need to incorporate a



molar expansion factor at higher con'c. Reimer then asks what would happen if I had an additional reaction  $\text{NO} + \frac{1}{2}\text{O}_2 \rightleftharpoons \text{NO}_2$ . I didn't know what he was getting at, but I remarked that the NO con'c in the CSTR would be lower and I drew a lower  $r_{\text{CO}}V$  on my plot. Reimer didn't seem to know where he wanted to go with this problem, so he stopped and let Zhang take over. In the end, I think Reimer was just attempting to throw me off my game by asking something new.

Zhang: Transition state theory with an enzymatic reaction \*cough Michaelis-Menten cough\*. She has me write the M-M equation and describe  $v_{\text{max}}$  and  $K_m$ . She has me write the Eyring equation and draw the reaction co-ordinate diagram for the reaction. After telling me that the ES complex has a lower energy than the reactants, I end up with something like this:



We switch gears a little bit and talk about what would happen if we immobilize the enzyme inside a particle (effectiveness factors, thiele modulus, qualitative and mathematical definitions, relationship between the two for severe mass limitations). Finally, Zhang comes back and asks given  $K_m$  and  $v_{\text{max}}$ , how would I calculate  $\Delta G_1$  and  $\Delta G_2$  in my plot? Umm...magic? So after some hints, I realize that at high substrate con'c, rate looks like  $r = v_{\text{max}} = k_{\text{cat}} \cdot E_0$  and plugging  $k_{\text{cat}}$  into the Eyring equation gives  $\Delta G_1$  while at low substrate con'c, rate looks like  $r = k_{\text{cat}}/K_m \cdot E_0 \cdot S$ , so plugging in  $k_{\text{cat}}/K_m$  into the Eyring equation gives  $\Delta G_2$ . I was done after that, and they let me out 10 minutes early.

Overall, I felt Reimer and Zhang were a decent pair and they provided hints whenever I needed them. The hardest part is figuring out what Zhang is trying to ask you. If you don't understand, be sure to ask for clarification.

NC

Who was your teacher, what books, your experience blah blah. For this prelim, I just reviewed Fogler (elements not essentials)...and certain key parts of grad class with iglesia (Collision Theory, Transition State Theory, Thiele Modulus, Heat balance)

*Reimer*: First makes me do a diagram of concentrations of A, B, C in a series reaction ( $A \rightarrow B \rightarrow C$ ) done in a batch reactor. Asked me to make "mathematical deductions" about the relationship between  $k_1$  and  $k_2$  ( $dB/dt = 0$ ) Midway, he told me to erase the problem because I knew it too well...

Then, he asked me to have a cooling jacket around a batch reactor. This threw me off because I was used to CSTRs. Started with the basic formula ( $dE_{\text{sys}}/dt = Q + W_s + \sum(F_{\text{in}}E_{\text{in}}) - \sum(F_{\text{out}}E_{\text{out}})$ ). There's no F's so you just have a difference in Q where one part is the cooling from the jacket ( $Q_{\text{jacket}} = -UA(T - T_{\text{cool}})$ )

and  $Q_{rxn} = H_{rxn} \cdot dN/dt$  you get  $dN/dt$  from the design equation ( $dN/dt = -r_a \cdot V$ ). Since I got a 0th order reaction,  $-r_a = k$ . Since  $k$  has a temperature dependence, you would also have  $k = A \exp(-E_a/RT)$ . The whole point of this was to find runaway conditions. I said that you could find a ss condition where  $dE/dt = 0$  and I couldn't figure out where runaway was. Something about the second derivative (we ran out of time). He also told me that batch reactors are super sensitive to the cooling water temperature and that's why if the reaction is exothermic and has potential runaway, people don't use batch reactors. He looked really excited to tell me this so I acted really interested even though I was nervous.

*Zhang*: Good old M-M (called it enzymatic reaction). No derivations though. It's good to know the assumptions, final form, and the definitions of  $K_m$  and  $v_{max}$  just in case. She had these enzymes in weird catalytic particles because she wanted to add in the thiele modulus. I wasn't asked to derive it, but was asked for both qualitative and the formula for it. She had also given me a list of "knowns" and asked if I would be able to figure out the thiele modulus. I also was asked to relate it to the effectiveness factor and what the effectiveness factor meant. They asked me some qualitative questions about these two things. Then she gave me a plot of a rate observed vs. concentration of substrate. She asked me how to get  $v_{max}$  (go to large  $[s]$  and assume that the large bulk  $[s]$  reduces mass transfer limitation.  $v_{max} =$  the max observed  $= k_{cat}[E_0]$ ) and how to get  $K_m$ .  $K_m$  was confusing because originally the definition of  $K_m$  is the  $[S]$  that gives you half of  $V_{max}$ , but she wanted me to use the effectiveness factor. Since effectiveness factor = rate obs/theoretical rate where  $[S] = [S_{bulk}]$ , you have to say since you know the effectiveness factor, the observed rate, and the MM equation (knowing  $v_{max}$ ), you can solve for  $K_m$ .

*Notes*: Reimer is easy to understand and helps you along the way with some hints. He once cut me off before I finished what I was saying because he said I was doing it wrong...then he took it back later? Just try to be friendly and indulge him. Zhang was REALLY hard to understand mainly because of her accent and the way she phrases things. She also cuts you off all the time saying you're wrong but sometimes it's because she hasn't understood where you're going with it. Sometimes I was saying the right thing but then she'd cut me off saying I was wrong so I tried other approaches which were wrong. It would take me a while to realize that my original was right. Reimer helped by actually getting up and circling some terms on the board because I think he understood that Zhang can be hard to understand.

*Verdict*: Passed. Decent grade. Keep your cool with Zhang and ask what she is asking for like 30 times if you have to. She's sometimes looking for exact phrases that might seem equivalent to what you said. Reimer isn't too bad and he can be decently easy going, but he doesn't hold your hand through the problem. Overall, I think that going over their old questions helped a lot to know the realm in which they would ask. Stating what you know/assumptions all the time helped too. Lastly, keep calm and prelim on.

## **Bell / Katz**

KT

Bell: You have a gas phase reaction to produce hydrogen chloride. What is the reaction?  $H_2 + Cl_2 \rightarrow 2HCl$ . How do you think this happens? I say hydrogen molecule hits chlorine molecule and reacts. Is that likely? Probably not. So, this is not an elementary reaction. What do you think is the mechanism?  $H_2$  decomposition and  $Cl_2$  decomposition  $H_2 \rightarrow 2H$ ,  $Cl_2 \rightarrow 2Cl$ , then reaction. How does hydrogen decomposition happen (it's not elementary)? I say one hydrogen molecule collides with another hydrogen molecule to create one activated, higher energy molecule:  $H_2 + H_2 \rightleftharpoons H_2^* + H_2$  with the decomp reaction now being  $H_2^*$ . Ok, now you have three reactions that govern hydrogen, what is the rate of hydrogen decomposition?  $d[H_2]/dt = k_1[H_2]^2 - k_2[H_2][H_2^*] - k_3[H_2^*]$ , and you need to substitute for  $[H_2^*]$  which I say can be done by assuming quasi-equilibrium on the activated  $H_2^*$  step assuming the forward rate is approximately the same as the reverse rate. Bell says that may not be the best assumption so I say that it would be better to assume

PSSH on the  $H_2^*$  activated species. Bell says good and I derive the complete rate expression by setting  $d[H_2^*]/dt$  equal to zero. They don't even make me do all the math.

Bell: What is the rate constant? I say a function of temperature and write the Arrhenius expression. How do you determine the activation energy of a reaction? Experimentally. Bell says what if you don't have experimental data? Theoretically with transition state theory or collision theory. Bell says ok, but you cannot determine the activation energy from collision theory. Ok, using transition state theory then. Bell briefly describes TST instead of asking me to outline it, up until Eyring–Polanyi equation. I chime in. He says what now? I say the Gibbs free energy is a function of the entropy and enthalpy. Right but we want an approximation of activation energy, what governs the energy barrier between the reactants and transition state? The free energy difference. How do you approximate it? You can approximate that difference in energy using partition functions. Right, so which partition function governs the energy barrier? I say vibrational. Bell says no, which is even larger? I say translational. He says yes that is larger but not the largest. I say rotational is larger than vibrational but smaller than translational. Clearly I don't know the answer and this has turned into multiple choice at this point. Bell says what do you need to know to calculate rotational? Moment of inertia. Ok. I say the only other one that could be relevant is electronic, but I frankly tell him that we didn't cover it in any detail in 244 so I am not sure whether it is larger or smaller. Bell says the electronic is the one that governs the activation energy barrier. I say cool. Bell fell asleep for Katz's part.

Katz: You have a porous spherical catalyst pellet, what does the concentration profile look like in the pellet? I assume a first order reaction  $A \rightarrow B$  and say I am looking at the concentration of reactant A. Katz says yes. I say the concentration profile depends on the Thiele Modulus or relative rate of reaction to diffusion. Katz says ok what if I have a very small Thiele Modulus, what does the concentration profile look like? I draw a graph. Great, now what if you have a Thiele Modulus around 5 or 10. I draw another line, approximately linear. It looks linear, is it linear? I say mostly, except for at the boundary and at  $r=0$ , where it is continuous. Ok, so what exactly is happening at  $r=0$ ? It is continuous with the other side of the pellet and  $dC/dr=0$ . So what is that boundary condition? Symmetry. Right, now say you want to determine the order of your reaction, but all you know is the concentration profile and temperature profile inside the pellet, what do you do? I scramble around a bit and say that if you know the concentration profile and it's at steady state then you can just solve for  $N$  in  $C^n$  part of the rate expression in the concentration profile. Katz says let me rephrase the question, what is the boundary condition at the interface? The fluxes are equal  $D_{\text{pellet}} * dC/dr = D_{\text{bulk}} * dC/dr$ . Now since you know the concentration profile, you know the total flux into the pellet. How does this relate to the total reaction rate? The total flux in is equal to the total reaction rate and now you can find the order by finding  $C^n$  proportional to the flux in.

Katz: You have a PFR that is leaky on the sides with flow rates blah blah blah. I draw the reactor with stuff coming out of the sides and whatever Katz told me, I labeled. You have a reaction  $A \rightarrow B$ , what does the concentration profile look like? Is the concentration profile in this leaky reactor different from if it was not leaky out the sides? No.

If you read this transcript you can see that I didn't know everything and I didn't necessarily get the right answer right away, but I got an A so don't worry if you don't immediately answer every question correctly. Just keep moving on with the question and saying/writing everything that you know, this will help the professors lead you to the right answer.

## Iglesia / Zhang

EB

Zhang started off by asking me how to plot the reaction velocity (Iglesia clarified that this meant rate of reaction) vs. substrate concentration for an enzyme-catalyzed reaction (Michaelis-Menten). I put up the standard plot. She then told me that if I got this data from an experiment, how would I figure out whether it

was rate limited or diffusion limited if I knew the catalyst radius and the diffusivity coefficient? I said to calculate the Thiele Modulus. From here on out, the question went over my head, so I can't really write down an accurate description of it. Apparently the Thiele Modulus could be changing as a function of the substrate concentration, and I wasn't allowed to run more experiments to get the effectiveness factor and make a correlation between it and the Thiele Modulus. After about half an hour of struggling to get down a basic equation that I pretended to understand (while having Zhang shoot lots of "Is this guy an idiot?" looks at Iglesia), Zhang ceded the floor. I still don't know what she was asking. The only reason I trust that she knew what she was talking about was because Iglesia seemed to think she did, and that man knows his kinetics.

In the final 10 minutes, Iglesia asked me a very straightforward question. You have a CSTR in which there's a first order irreversible gas phase reaction  $A \rightarrow 2B$ . How do you get the concentration of A as a function of conversion? I derived the CSTR equation from Fogler chapter 2,  $V = F_{A0}X/(kC_A)$ , and then got to the equation from chapter 3,  $C_A = C_{A0}(1-X)/(1+\epsilon X)P/P_0T_0/T$ . Iglesia told me no pressure drop and isothermal, so I got rid of the P and T terms. He then stopped me short, and asked me how I got that epsilon term, so I re-derived the equation using the stoichiometric table.

I was a little worried by this one because even though I aced half of it and bombed half, I thought that since the part I bombed took up 3/4 of the time, I might get judged harshly. They awarded me a B+, so I guess that as long as you're able to get part of a prelim right, they'll allow you to pass. If you get Zhang as your prelim examiner, cry a little bit, and then learn Michaelis-Menten backwards, forwards, and upside-down.

## JM

Enter the classroom and begin with some small talk about which book I had used for kinetics in undergrad. I made it very clear to Iglesia that I had only used ESSENTIALS of chemical reaction engineering, not ELEMENTS. He did not seem to care, since the first question was about thiele modulus and effectiveness factor.

That said, I came into this prelim with a strong background in classical kinetics (you know, what you learn in undergrad), and only a rough idea of how to calculate thiele modulus and use effectiveness factor. Zhang asks about an enzyme tethered to a particle (same question as above). They had to walk me thru how to calculate the thiele modulus for this system. Then things get confusing when they ask me to find the reaction rate in the system given some data. 30 minutes passed and I did not get far in this problem, so we switched to Iglesias questions.

Iglesias first question was very straight forward. We have a CSTR with a gas phase reaction  $A \rightarrow 2B$ . What is the conversion as a function of residence time ( $\tau$  = Volume of reactor/ inlet volumetric flow rate). You run thru similar calculations that are done with a gas phase PFR reactor, realizing that the outlet volumetric flow rate must be greater than the inlet volumetric flowrate. After getting thru the derivation and finding his answer, he asks a second question.

Iglesias second question asks to find the difference in conversion if we had a gas phase CSTR system (same as above) but with a membrane that instantaneously and selectively removes B as soon as it forms. If you do a Initial Conversion Final (ICE) table, you realize that you just eliminate the B portion of it. The reactor now functions as a first order decay, with A just disappearing as a function of residence time.

Being able to answer Iglesias question like a robot is what saved me in this prelim. Luckily, I did not fail even tho I spent 30 minutes getting absolutely no where in Zhang's question. KNOW YOUR BASICS!

## Bell / Ciston

JB

Aside from a couple of things on TST, everything they asked was straight out of Fogler. Bell started:  $\text{Cl}_2 + \text{H}_2 \rightarrow 2\text{HCl}$  in the gas phase, propose a mechanism. I said  $\text{Cl}_2$  decomposes to give 2 Cl radicals and then one of them attacks the  $\text{H}_2$ . What is the rate law? I said it would be first order in  $\text{Cl}_2$  concentration. Bell said I was close, but it's not always first order. This made me realize that he was getting at a Lindemann mechanism, then I told him verbally what that meant and he was satisfied. He then asked how to determine the rate constant of a reaction theoretically. Collision theory or TST. What goes into collision theory? Mass and size of reactants and the temperature. What is TST? I went through:  $\text{A} + \text{B} \rightleftharpoons \text{AB} \rightarrow \text{C}$ ,  $r = k^*[\text{AB}]$  where  $k^*$  is the weak vibrational frequency.  $[\text{AB}] = K_{\text{ts}} * [\text{A}][\text{B}]$  and then explained how to get  $K_{\text{ts}}$  using partition functions. Which partition function dictates the activation barrier? Electronic. I said some stuff about how I don't know what goes into the electronic partition function, but that I'd guess it had to do with the number and types of orbitals in the reactants and transition states. He then agreed with me by saying something about a symmetry condition, and I nodded like I understood which won me some major points. Bell was pretty much done and then Ciston went. She asked the same question as previous years about parallel reactions, so I went through the analysis of which orders and activation energies led to high/low T, high/low P, and PFR/CSTR. Then she asked about reactions on a surface, and instead of drawing out the external/internal/adsorption/reaction/desorption/internal/external diagram that I was so tired of by this point, I just explained it. If the surface reaction is rate limiting, what is the rate expression? I wrote the equilibrium adsorption equation and the site balance, then jumped to the answer of a Langmuir isotherm. She was done so Bell asked a few more questions on heterogeneous catalysis. Basically the answer was Thiele modulus and effectiveness factor. He then asked how to derive effectiveness factor, so I wrote the equation for flux at the surface and said this would be the actual rate. He then wanted to know about the diffusivity, so I explained how the effective diffusivity is  $\sim \text{porosity/tortuosity} * \text{molecular diffusivity}$ , then we talked about the physical meaning of porosity and tortuosity, and how they would affect the flux. We finished with  $\sim 10$  minutes left.

ML

Got almost the same questions as JB above, except I also was asked:

Bell: if your rate expression looks like  $r = k/C$  (-1 order) how would you design your reactor? I'm super confused and start talking about making catalyst particle packing more dense. He then gives me some choices (at this point I'm like oh no, you just had to turn your question in a multiple-choice question... this means I'm doing poorly): You can put more catalyst on the inside of the pellet or on the outside. I say okay, if you have a rate inverse in concentration then you want lower concentration where there is more catalyst, so put catalyst on inside of pellet. Bell says this is called an "egg yolk catalyst" (as opposed to egg shell) and I act like I find this fascinating.

Overall: Bell and Ciston are both really supportive and definitely helped me out whenever I tried to think out loud.

## Reimer / Ciston

KS

Ciston: Describe qualitatively what happens during a reaction that occurs on the surface of a catalyst (reactant approaches catalyst pellet from bulk solution to surface. Reaction occurs. Products leave surface).

I would study the concept of Langmuir-Hinshelwood and Eley-Rideal mechanisms to be familiar with the terminology they might use. Then we discussed selectivity for two parallel reactions  $A \rightarrow D$  and  $A \rightarrow U$ . There is a section in Fogler that goes over the different cases for different orders of reaction/different activation energies which is what they are looking for. Know which reactors to use and why. Also I was asked about selectivity in gas phase reactions briefly and how changing the pressure would affect that. Reimer: Asked me what questions of his I'd previously studied, so he could avoid asking me those. I told him the  $A \rightarrow B \rightarrow C$  one and the  $SiH_2$  one as I could really only remember those and I didn't want to get the Si one. He then asked me about the problem CH describes in the Reimer/Zhang section about a catalytic converter with the graph that shows the stable/unstable equilibrium points. He also asked if I would want to use a PFR or a CSTR for this (PFR, because you want high conversion so you don't have a bunch of carbon monoxide running around).

## Iglesia / Katz

AH

Of course they first asked me what textbook I had used. I used Fogler. They asked which version - I said the fat one. Katz responded with "since you've seen all of Fogler (my undergrad actually only went up to Ch 10/14 but I had read that book cover to cover) let's start with stuff from the later chapter. First, explain the Thiele Modulus in words. Next, they wanted me to write it on the board. I wrote the super generalized form (which is derived in Fogler) and takes into account any reaction order or geometry. The form is:  $Thiele = [k''p_c s_c Cas^n R] / [Da(Cas-0)/R]$  where  $k''$  is the rate constant in terms of surface area and  $p_c$ ,  $s_c$  convert between rate/volume to rate/surface area. Katz then asked me why at first order terms there is no  $Cas$  in the equation. In my mind I was thinking "because they cancel in the equation..." but I thought I needed a deeper answer. I think about this for a while. I'm bad at vocalizing my thoughts so Katz makes the comment "let me know what you're thinking. If you just need more time, take it, but I can also help if you tell me what you're saying". Like I said, Katz is awesome. Well I fumble around for a while and then he said "look at the equation" and I finally say...  $Cas$  cancel out... that's what he was looking for. So if you're thinking it, just say it. Doesn't matter if you think it's wrong - it's probably at least sort of (or totally) right. He then wanted me to draw thiele modulus versus concentration at high and low thiele modulus. After that, he wanted to know how temperature affects diffusion. He then asked me to draw the temperature profile of a low thiele modulus, exothermic, steady state particle under mass diffusion. I struggled because there were so many different things to take into account, but eventually got where he wanted me to. I was then asked to draw the corresponding concentration profile.

Next, he asked me about how he would find the rate for a non-isothermal reaction where you knew it was mass-limited or something. I got super confused, but eventually realized he wanted to talk about the flux \* surface area @  $r=R$ . That's the actual rate occurring. Sorry I don't remember this one very well.

Iglesia then asked me his question about  $A \rightarrow 2B$ , in a CSTR, isothermal/isobaric, gas change. how do you find conversion? Straight out of Fogler, although he didn't like how I got to the answer (I didn't memorize the formula, I had to derive it out). He then asked me how changing it to equimolar would affect conversion. How would a semipermeable membrane on the outside that pulled B out a little bit at a time would change conversion. And how would a semipermeable membrane that pulled all of B out change the conversion? Each time I went back to my conversion table and plugged in the values to see how that would change the overall conversion. Take your time, don't rush. As somebody told me in one of my mock prelims - let the math tell you the answer.

Overall: I was petrified for Inglesia, but he seemed to be in a good mood. Katz is always calm, helpful and patient (be happy if you get Katz). I passed.

MT

First, the usual, what books, how many semesters of kinetics, etc questions. And then Katz started.

Questions: You have a gaseous batch reactor,  $A \rightarrow 3B$ . Quickly solve the conversion vs time for me? I tried to be quick and started using pressure instead of concentration. They asked why? I asked why I chose that I said that since it's a gaseous reaction you can measure pressure instead of concentration. They asked me to keep using concentration. The key to solving this equation quickly actually is to use total mole so they asked me to use total moles instead. So I did using  $N = \text{Conc} \times \text{Volume}$ . As I was going through the math they asked me how the volume would change and I showed how it would change 3 times as much. And I showed them how this relates to conversion. And then Katz stopped me and said 'okay you got this. It's all math after this.' Then he asked me what would change if it was a PFR. I said that it would be the same except instead of time volume would be the differential. He then asked what would happen if it had a leak in the first question, how would it affect certain conversion, would it take shorter time or longer time. I said shorter time because the system was now like a semi batch reactor but check my answer. Then Iglesia took over. He said if you were given rate vs substrate data for a porous spherical catalyst reaction, and you were not allowed to do any more reaction, what would you do to find reaction rate. I drew the spherical catalyst. He also gave me the diameter and Diffusion. I also drew a Langmuir or MM rate vs. Substrate graph because he told me that was what it looked like. Well I should have jumped to Theile modulus knowing Iglesia but I first said fitting data and stuff but then he told me that I can't do anymore. Then I said I would use effectiveness factor. And then he said what else, I said Theile modulus. He asked me for the definitions, and I wrote up the general form of equations for theile modulus. Then he asked me questions about the limits at low concentration and at high concentration. At low concentration reaction acts like first order. At low concentration, theile modulus is not concentration dependant, i.e. diffusion limited. He asked me to draw the effectiveness factor vs theile modulus graph and explain the limits. He asked me what I would do to find k. I said I would use the theile modulus definition we just wrote, and since I know that at theile modulus is  $1/\text{effectiveness factor}$  when diffusion limited. We can solve for actual rate using maximum concentration to be ideal rate. And we can do this because at high concentration, it's not diffusion limited. Therefore, whatever reaction rate we are given is the maximum rate. Anyway, he kept asking series of questions like these, but it was kinda clear where he was going so it wasn't a whole lot difficult. I showed the math for solving for k, and actual rate. He also asked what I if I were allowed to do one more experiment, what would that be? First I said I would use non porous catalyst, thinking that would eliminate my issue of diffusion through porous catalyst. But then they pointed that would be totally different, which is true. Then Iglesia asked me what the theile modulus was most sensitive to and ...I got it! ... It was the radius. So if you use different radius catalyst you can verify the theile modulus behavior you're assuming. He asked me if I would use low or high concentration. I said low because that would give us information of mass transfer and actual rate. He asked me why not high concentration. I said that wouldn't tell us anything new because effectiveness factor would be 1. And that was it!

Overall: I think I got lucky. They both seemed pleased with my answers. They were nice. And I thought it was going to be really hard. But it wasn't too bad since I made sure to understand theile modulus really well. I got an A-. I tried to show that I was excited to try their questions. I used the whole board and wrote down my process clearly. I told them to give me time when I needed to think a bit. Their leading questions were really helpful. Iglesia told me not to overcomplicate and said that it wasn't a trick question when I started

talking about activation energy and stuff. I totally made mistakes but it worked out well. This was my favorite prelim and my last too so I was really happy!

## Transport

### Graves / McCloskey

KS

McCloskey asked the main question first: You have a fluid in between two plates. Top plate has a velocity of  $U$  (say in the  $x$  direction), bottom plate is stationary. Top plate also has a temperature  $T_1$ , bottom plate has temperature  $T_0$ . I asked if  $T_1$  was greater than  $T_0$  and they said sure. This is a standard Couette flow problem. If we are assuming constant density and viscosity and thermal conductivity ( $k$ ), the temperature differences of the plates doesn't affect the velocity profile (because the viscosity or density doesn't depend on temperature with our assumptions). So you can figure out the velocity profile  $[V_x(y)]$  and temperature profile  $[T(y)]$  independently with the Navier-Stokes equations and the energy equation for pure Newtonian fluids found in BSL's appendix B. I wrote out the whole equation and then went through each term and explained if I could ignore it or not and why. When I got to the viscous loss term in the energy equation, I was going to ignore it, but they said leave it in as a constant for now. They also asked me what the viscous loss term actually was (something like  $[\boldsymbol{\tau} \cdot \mathbf{v}]$ , make sure you distinguish  $\tau$  as a tensor and  $v$  a vector)). I then went through the boundary conditions for each problem (temperature ones for the energy equation and velocities for the momentum equation) and went through and solved for the profiles, but without wasting time with the algebra to get the constants. I also described the shear profile ( $\tau$  ends up being constant).

Graves then asked about starting this problem with Newton's law of cooling:  $q = h(T_1 - T_0)$  and solving it from a heat transfer perspective (Fourier's law of conduction). This led to a discussion about how to find heat transfer coefficients (from Nusselt correlations) and their dependence on Reynolds number. He then asked about the effect of changing the Reynolds number of our flow system and how that would affect the heat transfer coefficient. I'm not sure exactly what Graves was trying to get at here, but the conclusion was that Nusselt correlations don't apply to this Couette flow situation because there isn't a characteristic length associated with the heat transfer... thus, starting with Newton's law of cooling is bad. For completeness, they also asked about the definition of  $Nu$  and what each term was, etc.

We had about 10 minutes left at this point (I was working/explaining everything pretty slowly) and Graves then tried to sneak in his famous silicon dioxide problem. It took him about 5 minutes to talk about the problem and so when I start to set up the problem, we obviously had no time to really go through this. He mentions this and then asks me to skip to the end and just describe how the concentration varies with time. Alright, Graves. Well because we are dealing with pure diffusion flow (no convection) I knew it had to curve around, I didn't really know how it varied with time, but he was understanding because I didn't actually go through the math. I think he just likes that problem and wanted to tell me about it. Before I was officially done he told me it varied with  $(\text{time})^{1/2}$  which I then remembered: standard diffusivity time scales. All the units of the momentum/thermal/mass diffusivities are  $\text{length}^2/\text{time}$ . If you are calculating the characteristic length of the boundary layer, it goes as  $\sqrt{\text{diffusivity} \cdot \text{time}}$ . Not that I remembered that in time for the question, but it's useful to remember the units for boundary layer problems.

Notes: McCloskey and Graves were both encouraging. They were not trying to trick you with anything. They were looking for you to demonstrate your approach to problem solving.

JM



This was my first prelim, I was more nervous than I should be, partly because I do not know these professors very well. I enter the room and enjoy some small talk about my background in transport phenomena (BSL, 1 year). Almost immediately, we begin:

Question 1: The same question as above (from KS) and same set up. We have two parallel plates. The top plate is kept at a constant temperature  $T_1$  and bottom plate is kept at a constant temperature  $T_0$ . The top plate is sliding at a velocity  $U$ . Find the velocity profile. State all your assumptions.

I began answering this question by stating my assumptions. Assumed constant density, steady state, 1 dimensional flow, and ... this is where I made my first mistake. I had said I wanted to assume viscosity is temperature independent, but there must have been some inflection in my voice because Graves probed deeper into this. Why? I honestly had no idea. I mistakenly attributed the temperature independence to the fact that we had a Newtonian Fluid. Of course, then they asked me to define a Newtonian fluid. I talked about the viscosity being independent of shear stress. Then they asked me again: does Newtonian fluid imply temperature independence? I ended up saying no and we moved on. I wrote out the Navier Stokes equation, crossed out terms, and justified why each term could be neglected. I also had to write out the equation of continuity (as a total differential and then expanded version), to show why it would be 1 dimensional problem. I ended up finding a linear velocity profile and a constant shear stress profile.

Awesome, that's exactly what they wanted apparently.

We then moved on to talk about the heat transfer portion of the problem. They wanted me to include a viscous dissipation term within the heat generation. I happen to know what viscous dissipation looked like and then they said to just treat it as a constant (I think they were expecting people to struggle with writing this term). I ended up solving the differential equation but not solving for the constants (They asked we just skip that to save time). They then wanted a profile for the temperature. With a generation term, you expect to see a parabolic profile, with a maximum somewhere within the slab. The boundary conditions are fixed at  $T_1$  and  $T_0$ , so they are the respective local minima. They then asked about how much heat needed to be removed in order to maintain the boundaries at this temperature. Finally, they asked about the  $Nu$  in a slab. I defined the  $Nu$  and how you could find the heat transfer coefficient using correlations. They then wanted to know why or why not it would apply to this case. The answer they wanted was that  $Nu$  correlation is only valid for boundary layers, and is irrelevant in this problem. We ended here.

I thought I had failed this prelim exam because of how nervous I got towards the beginning. I was not confident in any of my answers, but I ended up answering what they wanted so I ended up doing really well. This is a case where 0 confidence and only correct answers gave a nice passing grade.

## **Muller / Cerretani**

EB

Muller started by saying that you need to flow a viscous fluid through a pipe, and your calculations show that the pressure drop would be very large, so you'll need a big pump. To reduce the pressure drop, it's been suggested that you flow the viscous fluid (viscosity  $\mu_a$ ) in the inner part of the pipe (a radius of  $BR$ , where  $B$  is some constant less than 1), surrounded by a less viscous fluid (viscosity  $\mu_b$ ) in the outer part (total radius of  $R$ ).

First, draw the velocity profile. How would you determine the velocity profile in the pipe?

Answer: Put up the N-S equation in cylindrical coordinates for velocity in the  $z$  direction. For both the inner and outer portions, it comes out to  $dP/dz = \mu_i \cdot 1/r \cdot d/dz(r \cdot dP/dr)$ . Since the left hand side is a function only of  $z$  and the right hand side is a function only of  $r$ , set them each equal to a constant. You need 4 boundary conditions, 2 for each fluid. For the inner, you have  $dv_z/dr = 0$  in the center and  $v_{z,a} = v_{z,b}$  at the

interface. For the outer, you have  $v_z = 0$  at the outer pipe and  $\mu_a \frac{dv_z}{dr} = \mu_b \frac{dv_z}{dr}$  at the interface. I wasn't asked to solve this.

Second, how do you solve for the total flow rate of the inner fluid?

Answer: I said you integrate over the area of the inner film, dividing by the cross-sectional area.

Third, how would you solve for the optimal value of B to minimize pressure drop?

Answer: I said that you have Q (total flow rate) as a function of B from the second part, and you can relate  $dP/dz$  to this from the first part. So set  $d(dP/dz)/d(B) = 0$  to find the minimum of  $dP/dz$ . I wasn't asked to solve this.

Colin then asked me to figure out how fast water diffuses from the thin film surrounding your eye in the time it takes to blink.

I recognized it as a mass balance, so I wrote  $dm/dt = J''A$ . They asked me how to determine  $J''$ . After my getting confused about whether it was diffusion or convection, they told me that air was flowing past the eye, so I said convection, and  $J'' = h_m A (C_{inf} - C_s)$ . You get  $C_s$  from  $C(\text{water in the thin film}) \times \text{Henry's coefficient}$ . (retrospectively, I think it should have been Raoult's Law, but they accepted my answer since I spoke it confidently). I wrote Henry's Law as  $C_{liquid} = H C_{vapor}$ , and they said I had it backwards, but I said that I was in Smit's group, and in the adsorption literature they plot  $C_{liquid}$  vs.  $P_{vapor}$  and call the initial slope H, to which Muller joked, "Being in Smit's lab won't help you here."

Next, they asked me how to get  $h_m$ . I said from a correlation of the Sherwood number in analogy to a correlation of the Nusselt Number. They asked me for the form of this, and I said a constant plus a constant  $Re^a Sc^b$ . They wanted a more specific form for this particular type of flow, which I said I didn't know, so they told me it would be constant  $Re^a Sc^b$ . I don't think they really cared that I didn't know the exact form...why would I have bothered to have memorized all the correlations? They then asked me what the change would be if there were no air flow, and there were just natural convection. I said you'd replace Re with Gr. I admitted I did not understand free convection beyond knowing that the Gr number is the Re number of free convection, and they left it at that.

They then asked me what else would be changing with respect to time? I looked at all the terms, and it didn't seem to me that anything would be changing. They asked if Henry's coefficient was dependent on temperature, to which I said yes, but that the temperature wouldn't change in the blink of an eye. They asked me about whether there were energy terms I wasn't considering. After I thought about it, I realized that there would be temperature change from the evaporation of the water. They asked me to write the equation for this. I asked whether I could assume that the Biot number was low, and I was told that I could, so I wrote  $d(\rho V C_p T)/dt = h A (T - T_{inf})$ . They asked me how I'd solve this problem, to which I replied that it was a set of coupled ODEs, so you'd need to feed it into MATLAB.

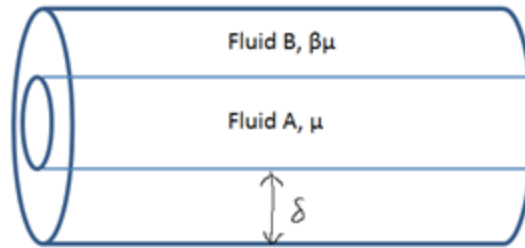
They ended me by asking me not to tell anyone these questions until prelims were over, to which I jokingly remarked, "You assume that I remember your question." Dr. Muller, ever the wit, quipped, "No, I don't believe that, as it's apparent you didn't remember anything from transport this past semester." At this point my face must have dropped, because she quickly and seriously remarked, "I'm kidding, I'm kidding." Muller is the best. Her prelim questions seem to be rather straightforward questions in which you just setup the constitutive equations, cross off what you can, and give her the necessary boundary conditions.

## **Muller / Radke**

CH

Muller starts off with a question about two fluids in a concentric geometric flowing in a pipe. The inner fluid (A) is highly viscous, and the purpose of the less viscous outer fluid (B) is to act as lubrication. For a given

volumetric flowrate of the viscous fluid A, what should the thickness of the lubrication layer be to minimize pressure drop? She begins to draw a diagram on the whiteboard to explain her question:



Radke: (to Muller while drawing the diagram) “mu A.”

Muller: “what?”

Radke: “Label it as  $\mu_A$  and  $\mu_B$ .”

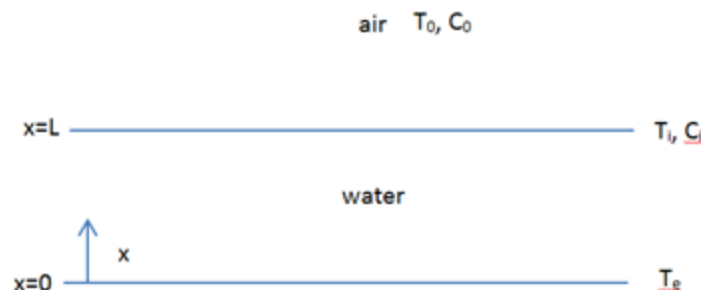
Muller: “It’s fine as it is.”

Radke: “It’s confusing. Label it as  $\mu_A$  and  $\mu_B$ .”

Muller: “Just...just work with here” (gives Radke the death stare)

The Muller-Radke tirade gave me enough time to process all the info in my head, so by the time they were done, I knew what to do. They had me guess what the velocity profile would look like (almost constant across fluid A because of high viscosity) before showing it with math. Basically, set up the N-S eqns for both fluids in cylindrical coordinates so you end up with 2 eqns and 4 B.C’s. Along the way, I subconsciously switched from Muller’s notation of viscosity to Radke’s, which made Radke’s eyes beam with superiority. Muller didn’t say anything. Anyways, I didn’t have to go through all the algebra, but needed to explain that once I solved these eqns, I would set  $d\Delta P/d\delta=0$  to find the optimal thickness of the lubrication layer.

Next up was Radke’s question about an eye with a water film on top that slowly evaporates to the air. How does the height of the film change with time? Basically do mass and energy balances. Radius of eye  $\gg$  radius of film so ignore curvature effects. Energy balance on water air interface gives  $-A \cdot k_t \cdot dT/dx = \Delta H_{vap} \cdot dm/dt + h \cdot A \cdot (T_i - T_o)$ . Mass balance on interface gives  $dm/dt = \rho \cdot A \cdot dL/dt = k_m(C_i - C_o)$ . Get  $C_i$  from Antoine’s eqn. Get mass/heat transfer coefficients from dimensionless correlations. Characteristic time of heat conduction in water  $\ll$  time of evaporation so assume pseudo steady-state in the water film and  $dT/dx$  becomes  $(T_i - T_e)/L$ . End up with two coupled eqns to solve for your two unknowns. Draw what the temperature and con’c profiles look like. Radke asks if this is like the wet bulb problem. Kinda, but the wet bulb problem neglects conduction of heat in the water which you can’t do for this problem.



After I finish, Radke tells me that in actuality,  $T_e$  changes with time and the real problem is much harder to model. Oh ok, thanks for letting me know Radke. After that, I was finished and free to go. On my way out, Radke and Muller pull out their boxing gloves and began to duke it out for the title of transport god.

This was probably my most enjoyable (and hilarious) prelim experience. Surprisingly, Muller and Radke only interrupted me if I made a math error or a faulty assumption, and after correcting myself, they never pushed the subject further. I know Radke especially likes to jump around everywhere and ask a gazillion questions, so maybe I just caught him in a sleepy state. Also, I think it helped that at the start of each problem, I briefly explained the “big picture” and how I would approach the problem (mass/energy/momentum balances on these control volumes) before throwing down any equations.

AH

I got the EXACT same questions as CH described above and others have described (I think Muller used the same question for everybody she had). I wrote out the simplified cylindrical NS, 4 boundary conditions and described how to solve it, why  $dP/dz$  was a constant and  $dP/dr$  was zero. How to find the volumetric flow. How to find the optimal value of beta.

I was then asked the eye question that Radke gave. Again, this has already been explained above. I also butchered it, so I'm not going to try and write what I think the correct answer is...

Overall: Radke was sighing a lot. He seemed upset in general and was upset when I didn't get the right answers. I definitely don't think he was in a good mood. Muller is a sweetheart. If Radke said something harshly or confusing, she re-said it. She was calm and pleasing and would interrupt me, but was always so nice about it. I think she could tell I was super nervous. At the end of my session, I kind of wanted to give her a hug but I was also ashamed at my performance that I didn't want to look her in the eye. They passed me (probably only because I got Muller's tube problem, definitely not because of the eye problem).

KT

Same exact questions as above. I was slow on the uptake throughout the exam and Muller and Radke were nitpicky about everything that I drew and wrote. They were both not in a good mood it seemed. The first concentric flow in a pipe problem I got through in a decent amount of time, stumbling a little along the way to get the final differential equation solution and the boundary conditions that they wanted. For the eye problem, I got down the governing equations for the heat transfer and the diagram of the concentration profile reasonably easily, but we spent a very very long time drawing the temperature profile until it finally looked the way they wanted it. They were both clearly frustrated with how long it took and Radke gave an exasperated sigh at the end of the prelim. I got a solid B though, so it seems that if you can get to the correct form of the governing equations and boundary conditions you are ok.

## **McCloskey / Cerretani**

ML

Couette flow between flat plates, top one moving, bottom stationary; top one at some temp  $T_{hot}$ , bottom one at  $T_0$ .

First, I am asked to draw the velocity profile (just linear) and then solve for it (standard N-S since they confirmed that I could treat it as Newtonian with constant properties).

Next, they ask me to draw the temperature profile with viscous dissipation, which I think I draw slightly wrong, but I note that I would be able to do it better after solving the energy balance. I go on to write the

energy balance but can't remember the form of viscous dissipation. That is OK though - they ask me what it depends on (viscosity and the shear stress) and then tell me just to call it some constant. Ask what would the temp look like without viscous dissipation (just linear, like the velocity profile). We talk through whether or not the profile with viscous dissipation made intuitive sense. They ask a few questions about heat flux at both surfaces (calculated with  $\rho \cdot C_p \cdot dT/dy$ )

They next ask what would happen if you changed the viscosity - how would the temp and velocity profiles change? I point to where viscosity showed up in both the temp and velocity profiles that I had solved for and talk about that.

Then they ask, if there were no viscous dissipation, would temperature gradient depend on viscosity? I say no. They ask, this seems to violate some of the transfer correlations, right? Following this, they ask me what correlations they might be talking about. I start saying something about Chilton-Colburn because I actually don't know the correlations that well, but they stop me and just ask which dimensionless group contains a heat transfer coeff (I say  $Nu = hL/k$ ) and what it depends on (I write  $Nu = Nu(Re, Pr)$ ). Then they ask how I would resolve the apparent contradiction, and tell me that it is a trick question (greeeeeeaaaaat). I say a few random things and then mention that the correlations come from boundary layer theory, which they latch on to. Where is the boundary layer? I say there would be one at both sides, but that is wrong. They tell me we are still assuming laminar flow so there is no boundary layer (or alternately, the whole thing is a boundary layer)

We have some time left so they ask another question - Colin talks about how this skydiver named Felix Baumgartner hit Mach 1.25, and then tells me he "has always wondered what the air pressure is at that altitude" (I'm sort of laughing because this seems like such a random way to introduce a problem... Colin and McCloskey are pretty amused too) Anyway, he asks me, how would you find the pressure as a function of height? This question isn't hard but I'm caught off guard so I have to be helped through setting up a force balance on a differential slice of air, and doing hydrostatics to calculate the pressure above and below a slice of air. I get to an integral expression that contains density (which is a function of pressure, making the entire integral a nonlinear expression) and time is up.

Overall: I went into this terrified that I would get some sort of reaction or phase change problem but it turned out okay - these two are also very helpful when you are lost and it seemed as if they liked hearing me think aloud even when I was on the wrong track.

NC

Clearly two really nice people and by far my nicest examiners and the most pleasant experience. Some nice chit chat about what kind of transport I had done. McCloskey tried super hard to be relatable to you in some way which was so nice of him! Colin knew me from my random rants in pedagogy so he just sorta smiled because now I had to be serious.

Basic couette flow between two plates with equal distance  $L$  with one moving at a velocity  $U$  and the two plates having a set  $T_o$  and  $T_L$ . They included a non-negligible viscous dissipation within the fluid. Asked for velocity profile. State all your assumptions (Newtonian fluid, constant viscosity and density. no gravitation or pressure differences. One direction completely ignored. Steady state.) then I found the linear profile. I also noted that viscosity doesn't change with temperature for this case if the difference between  $T_o$  and  $T_L$  are small enough (because it does change with  $T$ , even with Newtonian fluids).

Then they asked for the temperature profile. Viscous dissipation is dependent on the  $\tau$ 's I think...but ultimately depends on viscosity and the first derivative of the velocity. Since the velocity is linear, viscous dissipation is a constant in the heat equation (like a generation term). They asked for units and I fail boated

so hard. Ended up with the right answer, but with some help ( $W/m^3/K$ ). They also asked me for the temperature profile of the plates because I stupidly sorta started drawing one (doh!) which is just a parabola with the ends being at  $T_o$  and  $T_L$ .

Some of the next questions were things about maintaining the temperatures to be  $T_o$  or  $T_L$  at the plates (Fick's law) If you know the temperature gradient at the plate ends are, and you know the  $k$  of your material, piece of cake. Then they asked me why it's wrong to say that convective flow plays a part in the set up. It has to do with boundary layers and the velocity profile(?) Essentially, in couette flow, there's no boundary layer so there is no convection heat transfer...I kinda just nodded along and McCloskey finished that one for me. They let me go early because there wasn't enough time to do another problem.

Colin was the silent partner the entire time except for a couple hints. I think they were trying figure out how to do prelims since I was the second person to go. I wouldn't necessarily think that they'll give easy questions like this next year because they might have just been trying to figure out their groove this year. Basic prelim advice: try not to open doors for them to ask you harder questions. Anyway, this one I felt relaxed about but in general keeping your cool and stating what you know helped. I did decent on this one. Keep calm and prelim on.

MT

I don't want to repeat what has been said above. Same questions. Nice people. Fun and easy question- took me a while though as usual, because I'm slow. As always I tried my best to seem excited through the nervousness. I got a B. I thought I did better than that, but no complaints. I passed! We all passed ! It was freakin' awesome!

## **Radke / Graves**

JB

They gave the water-evaporating-off-an-eye problem that CH described above with Muller/Radke. Then, Graves took over by asking me about some mind blowing stuff. He showed me a book he had on his shelf called 'exotic animals', and said he'd been reading it (!?) and found a very peculiar animal that he wanted to ask me about. So there's a beetle that, when it makes a bubble of air, can go underwater and survive for very long periods of time. Two experiments were done, one where the air is replaced with pure oxygen and another where the air is replaced by pure nitrogen. In the latter case, the beetle dies almost immediately, and in the earlier case the beetle can live for some time but dies much sooner than with an air mixture. Why? Well... the bubble acts as a gill. When there is a low partial pressure of air in the bubble, but still enough for the beetle to breathe off of, oxygen diffuses from the water into the bubble fast enough to sustain the beetle. This can only happen because of surface tension effects and I had to write an expression for the partial pressure of oxygen in the bubble. Graves said, 'okay that one was too easy. Here's another one: there's a spider, which creates an air bubble on its back and the air diffuses directly through its skin into its bloodstream. The spider then goes into a river, and as long as the water is flowing at a sufficient velocity in the river it can survive indefinitely. Why?' Mind blown. It's because of an airfoil effect where the running water further reduces the partial pressure of  $O_2$  in the bubble so that there is even greater diffusion. All three of us proceeded to agree that this was indeed pretty insane, and then Graves started telling me about how his PhD advisor at Minnesota created a huge artificial gill which they put on a small dog and dropped to the bottom of a river where it survived for hours. I couldn't contain myself.

# Preparation Advice

CH

After New Years, I studied about 2-3 hours a day on whatever topic I felt the weakest in. This gradually ramped up to 8+ hours a day as prelims got closer. Take as many study breaks as you need so that you don't burn yourself out. A week before prelims, I made an effort to get as much board work as I could with other first years/older students. I think that board work is the best way to prepare for prelims since: 1) it forces you to solve problems and think deeply about subject matter that you might have just glanced over in a textbook, 2) it will rapidly improve your oral communication skills which is a must in prelims (talking + speaking + thinking all at once is hard!), and 3) it's a great way to rejuvenate yourself if you start to feel burnt out from individual studying. My advice would be that after you have gone through all your textbooks/notes, try to do as many mock prelims as possible. Also, ask the older grad students to make the mock prelims as tough as possible since that will best prepare you for the real thing.

Make sure to get lots of sleep the day before prelims (I forced myself to go to bed at 9:30pm) and try to remain calm and confident during each prelim! Being able to talk nonstop is a valuable tool, and saying a bunch of trivial (but correct!) things to is much better than saying nothing at all.

EB

Do not study more than 2 weeks for these. I started 4 weeks before prelims because I felt that I needed to catch up, having been out of school for 2 years, and the only time I was able to do anything productive during the last 2 weeks was during mock prelims.

ML

Main tips: Try to tailor your study plan to your work style, and study smart - not necessarily more.

I started studying on Jan 3 (prelims were Jan 16-17). My first day of studying I made a plan for the first week: study 2 topics each day, rotating topics, because I get bored of reading one subject for too long. I stuck to this until I figured out my weak subjects and adjusted accordingly. I did book studying almost exclusively in this coffee shop near my house (Jump'n Java, for any of you living in SW Berkeley... the owner started giving me free pastries and even remembered when the exam was!). Leaving home and going somewhere relaxing was crucial to working efficiently and not burning out.

I had my first practice prelim exactly a week after getting back to Berkeley (1 week before prelims) - I definitely did not feel prepared but the practice helped me figure out how to study better. I would recommend doing your first mock prelim around this time even if you don't feel super ready. I did several more practice prelims the second week, for a total of five.

Starting the second week I spent about two-thirds of my time working at the board with labmates/friends. We got problems from old transcripts and textbook examples, shared problems we'd done during mock prelims, and tried to make up our own problems (with limited success...). Don't feel stupid when you're working problems with other people. Everybody is going to feel stupid, just try to work past that and think aloud anyway so you get the practice.

First couple days I spent 2-4 hrs, then 5-6 hrs the next few days, and by the beginning of the second week I was doing a solid 7-8+ (harder to count when it was board work with other people). To relax at night, I watched lots of movies (the entire extended edition LOTR trilogy, and others) and read books. The night before prelims I saw Frozen and went to bed early. All of this helped me stay relatively calm during the entire process.

NC

I went in thinking I studied too little. This made me super nervous and I have a bad case of nerves. If you're like me, figure out how to minimize nerves, whatever that may entail. I got some help from alumni from my undergrad who told me where the weak points of our education is (super helpful).

I also did mock prelims before I was even close to finishing studying and that I highly recommend because it showed the gaps in my knowledge and also helped me prepare for speaking with a white board. I am lab-homeless so I emailed anyone who was willing to help. Someone in my year also emailed a large number of people that she had reserved hildebrand rooms and just a bunch of grad students came to test us. I went to 4 practice prelims and I think that each one had its own merits, even if it was just an ego boost for a subject.

I basically studied two weeks for this. First week, I woke up at noon, studied for four-six hours or so by hopping random cafes (I couldn't study more than 2 hours in one place for some reason. Recommend Asha, People's Cafe, and Au Coq if you live near university/shattuck intersection). Afterwards, I would eat dinner and watch movies until midnight. Rinse and repeat. The second week, I studied somewhat the same except Wednesday and Thursday night (Prelims were Thursday and Friday) where I crammed almost all day. I'm a hardcore procrastinator so I crammed in so much tidbits in those days. I also started bouncing off facts with people in my year the last two days after I felt I had a decent grasp on all the subjects. This helped a lot too. Again, work to what style suits you best. I just essentially reviewed my books and did practice prelims/looked at old questions.

I also studied with some strategy...but I don't necessarily recommend this route. I felt like my thermo exam was really doomed from the beginning. Even though I did well, that was probably from luck. I also didn't want to fail after spending 40 hours on the subject so I ended up just studying 4. This made me much more nervous for my other two exams though since I felt like I had to pass transport and kinetics.

In short: **keep calm and prelim on.** You will probably get nervous and have melt downs because lord knows I did. But the way you present yourself (aka filling the time with as much correct information as possible) has just as much influence as your actual knowledge. So feeling confident probably helps more than you think. To help you with that: *You're all smart, beautiful individuals with ridiculous potential. You're also incredibly good looking.*

KT

Ditto to most of the above.

Tailor your studying to your background. Don't study for more than two weeks unless (1) you really really feel that you don't have the necessary undergrad background or (2) studying early will help you stay calm throughout the process. You really won't remember what you learned two weeks ago anyway and you may burn out. You also may not need to reread all your textbooks. This really depends on you, but you can definitely tailor your studying to the professors testing you and to the commonly asked and important topics.



I only studied from notes, the already summarized and condensed textbook study guides, the things on the GSAC website, and transcripts of prelims. The only textbook that I opened was my transport book to 2 pages in order to memorize the mass and heat transfer and N-S equations.

Do as many mock prelims as you can. Do them before you think you know anything. Do them before you think you are ready. Do them when you think you know something. Do them when you think you have studied everything you can. Keep doing them even if you get bored. Just do as many as you can and start as soon as others are ready to quiz you, usually a week before. Most of them will be very helpful.

Don't stress out so much you go crazy. This is definitely easier said than done, it may feel next to impossible, but try to do things to relax yourself if you don't have the mental willpower to control your stress (I did not). Take breaks. Actively make time during the week to not think about prelims. Exercise, sleep, eat well, etc.

AH

Don't study the way I did. I started a little bit over break and then got back December 31st and studied straight until prelims. I put in a lot of hours... maybe not all of them were super productive (especially right at the beginning and definitely the last week before prelims), but I was definitely at my desk for the majority of every day. BAD IDEA. You'll burn out. I guarantee it. Do other things. Go for walks. Get a meal. Go to the gym. Take a day off. For thermo and kinetics, I fully read textbooks (and therefore was more confident going into those). For transport, I kind of skimmed BSL (sorry but I absolutely hate that textbook) and looked at questions. I had less time for that subject, and was therefore much more nervous for that test. It always took me a day or two to figure out what was important to study. I studied all of thermo, then all of kinetics, and transport last. I don't think I could have focused studying a different subject each day. The weekend before prelims I basically burned out. I don't think I got much of ANYTHING done the Monday-Wed before because I was so nervous, so tired and so burnt out. I did do quite a few mock prelims. I think those are only valuable if you memorize/study stuff BEFORE doing the mock. Otherwise it's a waste of time and you feel bad. I would get questions and think to myself "Oh I studied that but it was a week and a half ago", and then fumble through the problem. Take the time to review over before you do a mock. You'll get a better representation of how you can actually perform. I did not enjoy doing mocks, but I do think they are helpful. The first one will be rough - plan to do it a week before prelims, not any later.