

# Prelim Exam Transcripts (2013)

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# Thermo

## *Prausnitz / Schaffer*

LF

This was my first exam. I had studied all of Prausnitz's old questions, so that probably helped a bit. As in the past, this exam was more a series of short questions rather than long ones that lead to little tangents.

Prausnitz: We started with a question about Henry's law and Raoult's law for binary system. If the system, in VLE, obeys Henry's law, should we expect to obey Raoult's law too? I hadn't seen this question before, so I wrote the two laws up, assuming we had ideal gas and solutions, and basically after a bit of hemming and hawing, I got around to talking about Gibbs-Duhem and partial molar properties, which were the magic words that Prausnitz wanted to hear. Moving on. Next we talked about the third law and uses, which of course ended up me telling them to get things to super low temps, we would use... MAGNETS! Wooh. Next was a system with a reaction, how to calculate the concentration of reactants, use calorimeter and  $k = \exp(-dG^\circ/RT)$ . What is pressure swing adsorption --> uses? temperature swing --> need high or low temps to remove substance from surface? I thought at first he was talking about pressure swing distillation, so I talked about that for like 5 mins, before he stopped me. Whoops. Next he asked about the separation of nitrogen and oxygen in the air --> Linde process using JT coefficient. After this Prausnitz was done so HE FELL ASLEEP.

Schaffer: While Prof P was napping, he asked me the following: given an isolated system, piece of ice with supercooled water, reversible or not, how would you calculate the entropy change, where is the work lost? He's asked this question before, but stupidly I did not take the time to look it over, so I struggled even with the basic idea that before the liquid freezes, it must be heated back up to 0°C. Grr. I think he asked me another question, but I really can't remember it? Finally, the exam time was over but they asked me if I wanted another question. Said sure, I mean it couldn't hurt could it? So Schaffer asked me to draw the Carnot cycle (which of course I screwed up - damn the PV diagrams! I can't remember how those stupid lines curve to save my life). So after that little mishap, he asked me to show how that entropy is zero for closed process using only the steps of each cycle, not second law. Which I got around to after lots of confusion.

One note to make here, which makes prelims kind of stupid, is that certain profs tend to ask the same questions over and over, so instead of generally being knowledgeable about a topic, like I tried to be, it's probably good to take a bit of time to go over what the professor has asked before. These were two profs that have asked these questions for the past few years in many different exams, so it's probably good to know them. Like I said, I don't think this is a good system, because if they are trying to make sure that we all have a standard level of undergrad knowledge, it shouldn't matter who is testing us, but whatever. I passed.

AW

This was my first exam, as well. We went through the usual inquiries of where I went to school, what textbook I used, etc. Prausnitz asked the first question, which was his ternary mixture question. He wanted to create a ternary phase diagram, but he only had data on the three binary mixtures. Keep in mind with this one that the ultimate goal is to relate  $x$  and  $y$ . Those two can be related by a modified Raoult's Law (with the

activity coefficient). The activity coefficient is related to partial molar excess Gibbs, and that is the derivative of the excess Gibbs with the moles of a component of the mixture. The excess Gibbs of the mixture can be approximated by adding the excess Gibbs of each binary mixture.

Next, Schaffer wanted to know the maximum amount of work he could get out of a metal box taken from the refrigerator. This really threw me off because I was expecting a finite hot temperature reservoir instead of a finite cold one. I struggled with this problem a lot and ended up writing energy and entropy balances for the system as well as the Carnot efficiency. Schaffer said I had the right equations to solve the problem and that I just needed to put a couple of them together. I wasn't seeing it and after a while, Prausnitz decided that I knew how to get the answer (I didn't) and made us move on.

Then it was back to Prausnitz and he asked me if I knew the third law ( $S = 0$  at  $T = 0$ ) and what it was good for. I wasn't sure, so he gave me a general reversible reaction and asked me to find the concentration of the product, assuming I know how much I put into the reactor. This led me to the equilibrium constant and  $\Delta G$  for the reaction, which I could relate to the heat and entropy of the reaction. Heat is easy to measure, but entropy isn't. However, using the third law, we can  $dQ/T$  from  $T = 0$  to the temperature of interest to get entropy. How do we get the heat capacity at low temperatures for  $dQ$ ? Use magnets.

We had about 10 minutes left at this point, so Schaffer asked me his subcooled liquid question. There's an insulated container with water at 1 atm, below 0 C. After he places a little piece of ice in it, what happens? The ice acts as a seed crystal for the water to freeze. We talked about whether or not the process was reversible, then he had me write out the energy balance. The heat of freezing should balance the amount of heat required to raise the temperature of the system to 0 C. I left out the mass of the ice in the freezing term, so Schaffer asked me what big assumption I made. I didn't get it for the longest time, but when I finally realized what I left out, I explained myself and he seemed pleased.

I felt pretty bad about this prelim by the time it was over, but as I left, Prausnitz complimented me. Maybe these prelims are supposed to make you feel bad, but I figured I did well enough to pass after he said that. I did end up passing, and actually did better on this than another exam, which I felt pretty good about.

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## ***Balsara / Head-Gordon***

### **Nutella**

I went in thinking that Balsara would be asking me most of the questions so I had looked over most of the things he asked before. The only history I had on Head-Gordon was that she asked about the limitations of transition state theory in a Kinetics prelim and expected a complicated answer that included quantum tunneling. So I brushed up a bit on stat mech in case she asked a random question about it.

I go in and Head-Gordon tells me that she's going to describe a system and use that to ask some questions. So she told me to draw a piston with an ideal gas. She then asked me what I should expect to happen if I pushed down on an equilibrated piston and then stopped pushing down. I told her that it'd return to its equilibrium state and pop back up. She then asked me which thermodynamic state function would be minimized if the process was adiabatic, and later isothermal. I didn't get what she was asking at first and after fumbling awhile starting from  $dU = TdS - PdV$ , I just asked her if she was asking me something much simpler, to which she said yes. Balsara then told me to think about the properties of an ideal gas. The rest

is a bit of a blur to me now, but I remember answering a bunch of short conceptual questions that seemed more like basic high school physics/chem questions about the properties of an ideal gas. I think she was a bit annoyed and disappointed with this first part.

She then asked me to write down the second law. She then asked if I was familiar with the statistical mechanics definition of entropy. I started smiling a lot and wrote down  $S = k \ln \Omega$  and explained the concept of microstates. This made her really happy so she asked me if the classical and statistical definitions were the same and to show they were the same. At the time I was thinking that since entropy can be derived from the analysis of a Carnot cycle with an ideal gas, and that both of them had asked me a lot about the properties of an ideal gas, that I should try to write a partition function for an ideal gas of arbitrary volume. I asked for a suggestion on how to partition the gas, and she just said use a grid-lattice model. So I then proceeded to explain permutations/combinations of placing  $N$  particles on  $M$  lattice sites and ended up with something with factorials. Both of them were pretty happy that I understood that I'd need to use Stirling's approximation at some point, but Head-Gordon told me to just use  $M^N$  instead so that math would be simpler. In the end, I ended up with a ratio of volumes to the  $N$  power, which was close enough to the classical expression I had. Since time was running short, Balsara asked how I'd reconcile the different between the  $k$  and  $R$ , which is just Avogadro's number.

tl;dr  
Ideal gas adiabatic reversible expansion. What's the relevant state function that describes this process if it is spontaneous? What is physically happening to the ideal gas particles during this process? What is entropy in classical thermodynamics? What is statistical entropy? Are these the same expression? Derive using an ideal gas.

KG  
My thermo prelim was quite similar to the one above, so I'll just outline the questions:

Questions: You have an ideal gas that is compressed at time  $t=0$  and then allowed to expand back to its equilibrium state. (1) You do this adiabatically - What is the thermodynamic driving force or what thermodynamic state function represents this system? How would you calculate changes in temperature, pressure, and volume for this isentropic system? (2) You now do this isothermally - What thermodynamic state function represents this system? (3) For the isothermal case, start from the statistical mechanics definition of entropy to get the expressions from part 2. Explain the meaning of microstates and the meaning of number of sites. Draw a lattice-grid of the initial and final states of the system.

Notes: (1)  $dU = dQ - PdV$  or  $dU = TdS - PdV$  where for an adiabatic, reversible and steady state process we can also say that it's isentropic and therefore  $dS=0$ . Head-Gordon wanted to hear that internal energy,  $U$ , is driving this process. You can also solve for the expressions of an isentropic process with an ideal gas that relate changes in  $T$ ,  $P$  and  $V$ . (2) If you do this isothermally, then  $dT=0$  and for an ideal gas  $dU=0$ . So now entropy,  $S$ , is the thermodynamic state function and can be solved as  $dS = (P/T)dV$  where  $PV = nRT$  for an ideal gas. Then integrate to get an expression for  $\Delta S$ . (3)  $S = k \ln(\Omega)$  and subtract the final and initial states to get  $\Delta S = k \ln(\Omega_{\text{final}} / \Omega_{\text{initial}})$  where  $\Omega$  can be approximated as  $M^N$  for an ideal gas (any of the  $N$  particles can go to any of the  $M$  sites) and  $N$  is proportional to volume  $V$ . Putting this all in and keeping in mind the relation between  $R$  (per mole,  $n$ ) and  $k$  (per molecule,  $N$ ) you get to the same result as part 2.

Overall Head-Gordon and Balsara were a good pair and quite nice during the entire exam. Head-Gordon did some talking when I fumbled, which helped me understand what she wanted. I was a little worried going in

because I didn't know what to expect from her, but I was happy with the outcome! :)

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### ***Balsara / Maboudian***

ED

Definitely my worst prelim, really not that bad but was not what I was expecting... when we got started, Balsara told me that they wanted to make a process to remove carbon dioxide from air (everyone's favorite topic these days) using a stream of NaOH in water. They started by asking me how I would estimate how much carbon would be removed by the water. I said that normally you could use Henry's law, but in this case the equilibrium would be shifted because of the reaction. Then they handed me a sheet with five equilibrium reactions ( $\text{CO}_2$  dissociates into water,  $\text{H}_2\text{O}$  acid-base dissociation reaction, aqueous  $\text{CO}_2$  forming various species by reacting with  $\text{OH}^-$ ), listed out of order, and Gibbs free energy of formation listed at the bottom. Now, they want to know how I would calculate the 'total amount of carbon that can be removed'. Basically they just wanted me to say, "for a given equilibrium stage, if  $x$  is the  $\text{CO}_2$  concentration and  $y$  is the  $\text{OH}^-$  concentration at equilibrium, we can relate all of our other unknowns via equilibrium constants from our  $\Delta G$  of rxn's (which you calculate from formation Gibbs), and an overall charge balance on the system." And of course you could relate initial to equilibrium values via stoichiometry, and end up with a set of equations you could solve. Really not a very difficult problem, but I got frazzled a bit with units (make sure you know how to move between dimensionless equilibrium constants and equilibrium constants in concentration and pressure) and then with the charge balance. Anyway, after lots of hints and writing clearly wrong constraints on an  $[\text{OH}^-]$  species I get it. There are only about ten minutes left now, and Balsara says, "okay, now we figure out the equilibrium curve, trust me on this" and draws it on the board. "Explain how you would figure out how many stages you would have for your unit". I draw a stripping column and explain where enriched and dilute streams of  $\text{CO}_2$  in gas and NaOH solution would be, and where those would translate to on the diagram (operating line above the equilibrium line for a stripper). I explain how you constrain your operating line with the  $L/V$  ratio from a mass balance, and how given one you would step between crossing streams (operating line) and stages (equilibrium line). Balsara and Maboudian are nodding their heads and Balsara says "that's good, we're out of time" Pretty sure I passed this one only because I explained the stripping column so cleanly. Thankfully I had taught stripping columns while I was a GSI for 140 the previous semester, so I had them down

CMS

Given a solution of NaOH in equilibrium with a gaseous mixture exhibiting a given partial pressure of  $\text{CO}_2$ , calculate the amount of carbon that is dissolved in the aqueous solution. It isn't a simple  $x_i P^{\text{sat}} = y_i P$ , because there are reactions going on in the liquid phase. A list of the five reactions is given to you, along with the Gibbs energy of formation of the involved chemical species. With the Gibbs free energy of formation, we can calculate the Gibbs free energy of reaction for each reversible reaction. Then, we can write an equation for the equilibrium constant  $RT \ln(K) = -\Delta G$  for each reaction. It turns out that one additional equation is needed to determine the values of the unknowns, and that is a charge balance. For every negatively charged ion that exists in solution, there needs to be a positive ion(s) accompanying it. Then, one can solve for the moles of carbon that are absorbed into the solution-- this includes the  $\text{CO}_2$  in solution as well as any ionic species that contain carbon.

So now we have the concentration of carbon as a function of partial pressure of  $\text{CO}_2$ . I.e. a  $y$  vs.  $x$  diagram for the equilibrium line in a McCabe-Thiele diagram for a stripper. Know how the operating line for a stripper is derived and how to step off the McCabe-Thiele diagram-- not just going through the motion of drawing the

stepping lines like you could teach a first-grader, but actually understanding what is happening for each line drawn and what each point on the op. line / equilibrium line represents.

The very last question was witty.

NP

I was the first person to take this prelim (I had the 8:45 AM slot) . So naturally, I was anxious and nervous that I would have to bear the full brunt of the professors' grilling. So I'm waiting outside and I see Balsara and Maboudian grabbing coffee and breakfast. He seems surprised to see me. I am then invited in by Maboudian and the prelim begins. Basically, I was asked the exact same problems that ED and CMS have talked about above. It took forever for me to figure out that you needed the charge balance to complete the problem. I was pretty nervous initially and ended up counting the wrong number of variables. Over this, all three of us had a good laugh and that made me feel a little more at ease. I can't understand why previous testimonials of Balsara prelims are so negative. There is plenty of awkward silence to go around but he is extremely friendly and keeps encouraging you, trying to get you to go in the right direction. Maboudian was pretty much quite the whole time although every time I looked at her, I got the feeling I was doing something terribly wrong. In any case, we got through the first problem and then I was asked about designing the stripper. We got through this super quick. We then moved on to the carbon dioxide cylinder problem. By this point, I was pretty sure they were asking me this question just for the heck of it since we were almost out of time. Basically, you have a CO<sub>2</sub> cylinder. When you open the valve, the pressure goes down but when you close it, the pressure returns to the original value. You pretty much have to realize that the CO<sub>2</sub> passes the vapor-liquid phase envelope. You come to this conclusion by drawing isotherms on a PV diagram for CO<sub>2</sub>.

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### ***Smit / Schaffer***

EC

I was very nervous going into this one as I felt like thermo was my weakest subject and I knew Smit had a reputation for being a wild card. The experience was more painful than I could have imagined. I hadn't had a thermo class for 4 years and it showed. Shaffer started off by asking me to describe what would happen if you had an adiabatic vat of sub cooled water and introduced an ice crystal into it. The question wasn't especially difficult but I struggled throughout while they provided hints that were just not helping. He first wanted the phase diagram of water and I spaced on the axis, which was embarrassing and set the mood for the remaining 40 minutes. He asked where the initial state was and I put a point to which he replied how could I possibly know since I wasn't specified a temperature. Basically he wanted me to say it was a reversible process and calculate the change in entropy for the process. The final state composed of subcooled liquid and ice at equilibrium. He then asked where the lost work was going. There were two places, one of which was the volume expansion of the water, the other had to do with the relative magnitude of the heat capacities of water and ice so that the final state would not be the same as the initial state (this is vague I know – I don't remember exactly what he said). Smit then asked me the difference between the ideal gas law and VdW equation. I discussed gas molecule volume and interaction. He asked why when the gas molecules have a volume does the pressure decrease. I started explaining the phenomena without looking at the equation while Shaffer was nodding like I was speaking some insightful truth. Turns out the pressure actually increases and Smit tricked me. About 5 minutes later he tried to pull the same trick but with the molecular interaction term. I caught it and explained it correctly. He asked when the V<sup>2</sup> term comes from. I believe one was from the density of the gas and the other I forget. He then asked me to draw the VdW equation on a PV diagram and was asked to explain why there could be 2 different molecular volumes at a given pressure and explained what I thought was the answer but clearly was not. Awkward

fumbling ensued for the last 5 minutes of the exam. I left feeling that I probably failed. Turns out I did.

LL

We chatted about my undergrad and its policies for a bit, and then about the East Coast (Schaffer is from Jersey). So that was nice. Schaffer decided to go first which may or may not have been a good idea.

Schaffer: It was his classic subcooled liquid  $\rightarrow$  solid problem and I paced through the question at a good pace to explain my thought process. I asked him if I can assume an adiabatic constant pressure process, and showed him what the relations to  $dS$  were (doing a total differential on  $dS$ ). I calculated the  $\Delta S$  of each step (heating liquid, heat of fusion) and then a final step to either heat or cool the liquid. We talked qualitatively about the different scenarios possible and how it won't be reversible. We discussed how to obtain work through this process. Where is this lost work (since it's irreversible). So he seemed relatively happy, and did some iPad work when Prof. Smit took the stage.

Smit: Not quite sure what his exact questions were. He led off from Schaffer's problem of "if you were a water molecule in that tank, what do you know?". And it led to discussions of reversibility, statistical mechanics, and the van der Waals equation of state. I described the assumptions in the ideal gas law, and then how the VDW EOS accounts for it. But I shot myself in the foot when I wrote  $+a/V^2$  instead of  $-a/V^2$ . So we proceeded to show I was wrong. He has a habit of making statements that are actually questions in disguise. There were several points I just stopped and asked him what he wanted and where was he going instead of fumbling about. Overall the mood was friendly enough, made some jokes and banter that seemed to keep them happy.

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### ***Prausnitz / Smit***

CE

How is liquid hydrogen produced (liquid nitrogen). Why do we want liquid hydrogen (because it is denser and can therefore be transported more efficient). What is the van der Waals equation, and what do the correction terms represent? Ideal gas law assumes particles with no mass/volume that have no interactions and collide as hard spheres. van der Waals term  $a$  takes into account attraction between particles and  $b$  accounts for volume occupied by molecules. It makes sense that volume decrease should lead to an increase in pressure, since with the same amount of energy and with less volume to fly around in, the particles will be hitting the wall more (increase in pressure). Further, attractive forces will decrease pressure since, since any given particle trying to hit the wall now has other particles "pulling" it back. We expect the strength of the attractive forces to increase as volume decreases (particles will be closer to one another, so attractive force felt by one particle from all other particles will be greater). Draw an isotherm of the cubic EOS, derive Maxwell's equal area rule using equal chemical potentials in the vapor-liquid coexistence region. Show that given two components A and B if A obeys Henry's Law then B obeys the Lewis-Randall rule. Can be done using the Gibbs-Duhem equation. Also makes sense qualitatively (Lewis-Randall applies for solvent, or high concentration, Henry's Law applies for solute, or low concentration).

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### ***Maboudian / Head-Gordon***

GN

Head-Gordon: ideal gas isothermal reversible expansion. What's the relevant state function that describes this process if it is spontaneous? Derive an expression for it from classical thermo and from stat mech. Are

these the same expression? Now derive  $\Delta S_{\text{mix}}$  from stat mech. System had large excess of solute compared to solvent.

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DG

Head Gordon asked all the questions. Maboudian only spoke a few sentences.

First questions (Head Gordon): IG in a piston. Pressure inside is greater than that outside. "What is the thermodynamic state variable that leads to equilibrium isothermally". I answered with pressure but they were looking for entropy. Basically I was getting tripped up by what they were looking for is, "In an isothermal system, what is the change in thermodynamic state variable to a local extrema that describes this process."

The answer: isothermal -  $de = 0$  for an ideal gas because  $E = 3/2RT$ . so  $Tds = PdV$ . use  $PV = NRT$ . This integrated will maximize entropy.

Question 2 (head Gordon): same thing for adiabatic:

Adiabatic -  $dE = dq - pdv$ ,  $s = dq/T$  for reversible.  $de = -pdv$ . This is an internal energy minimization problem.

Question 3 (head Gordon): Use thermodynamics to model the entropy change in isothermal expansion. I used a lattice gas. Lattice gas has possible states of  $M^N/N!$   $M$  is the number of spaces (proportional to volume). She didn't like the  $N!$  for some reason, I said it wouldn't matter since it will wash out anyway. Use  $S = k_B \ln(\text{number of states})$ . Use log rules to make the entropy make sense,  $\Delta S = R \ln(V_2/V_1)$

Question 4 (head Gordon): Model a dilute number of sugar molecules in water. Membrane permeable to sugar. Maximize entropy to find the flux across the membrane. I didn't finish the problem

KS

Head-Gordon did most of the talking, Maboudian would make occasional clarifications. I was the last time slot on the last day so they seemed tired of the whole process by the time I got there. H-G seemed happy that I had some stat mech background.

I went over the laws of thermodynamics, there were some questions that asked about an enclosed ideal gas that had a piston at one end. What does the system do if you disturb the equilibrium by pushing down on the piston, etc. What is the state variable that drives this behavior (I blanked and kept thinking about state functions here - state variable is entropy fyi)/why does this happen?

I had to derive what the change in entropy was from the expanded state to the compressed state in two ways. First, she told me the temperature was constant, and I had to go through and explain why this means that the change in energy of the system was zero (ideal gas internal energy depends only on  $T$ ). 1st Law then tells us that  $Q = W$ . Add in 2nd Law (make some statement about why this situation is reversible) to get  $TdS = PdV$ . Solve for  $dS$ , substitute  $P = nRT/V$ , to get entropy change:  $\Delta S = nR \ln(V_1/V_2)$ .

Next I had to write down the "stat mech" definition of entropy (uses multiplicity) which is  $S = k_B \ln(\omega)$  where  $\omega$  is the multiplicity or number of arrangements. She then asked how I would find out "omega" or the number of microstates for a specific macrostate. I started off by describing how to break up the volume into a grid that has spaces that can hold only one particle ( $M$  spaces,  $N$  particles, # of arrangements is given



by  $M$  choose  $N$  and the factorial business). After trying to reason it from this way, she eventually reminded me that we are dealing with an ideal gas and one of the assumptions of that is that they are point particles with no volume. So eventually she leads me to writing out  $\Omega = M^N$  for an ideal gas - I don't remember where that is derived from though. Once you have that you can put that into your entropy equation, take a difference, and you get  $S = Nk \ln(V_1/V_2)$ . This is the same as the earlier result since  $Nk = nR$ .

H-G then asked about an ideal solution system. I struggled here because I only remembered ideal gas things and started to panic. Apparently I was supposed to know that change in enthalpy is zero for an isothermal system here, but I would check that because I could be wrong still. Anyways, you have two ideal solutions separated by a permeable membrane, one side has a different concentration of particles. She asked me about the state variable again, then what is chemical potential in terms of Gibbs free energy. I ran out of time around this point because she also asked about the "probability form of entropy" earlier and I wasted time trying to figure out what she was talking about. All she wanted was for me to say that  $S = p \ln(p)$ .

# Kinetics

## Clark / Zhang

ED

Zhang started out by asking me about transition state theory for enzymes. I have no idea why professors always ask about TST since as far as I can tell nobody studies it in undergrad, but they all seem to love it. So learn this, and how to explain things with it. Anyway, I fumbled through this. Then they asked me to write down the M-M rate mechanism (yes, you should just have this memorized, thankfully I did). Then Zhang said, "now we have another substrate and want to find the relative selectivity of the enzymes." I interpreted this as an inhibition question where we wanted to find the relative binding constants (no, we know all the rate constants for both reactions, but want to find the relative selectivity). Then they asked me if I would do my experiments at low or high substrate concentrations... I said 'low because then the rate will be linear with substrate concentration'. Anyway, it turns out they just wanted me to take the ratio of two M-M rates, assuming low substrate concentration so that the substrate and enzyme concentrations cancel. I still think this question is stupid, because if you know all of those rate constants from other experiments, why would you do a separate experiment/why would the low substrate concentration matter in that case? But whatever, I think they were just trying to bend the concepts around M-M. Then they started asking me questions about 'why I was writing my rates the way I was' and we went around for a few minutes before I realized they just wanted me to say that they're valid for a batch reactor. If you have these guys, the hardest part is just realizing what question they're asking. Anyway, it got better after this... we discussed that now we had our enzyme tethered to catalyst particles in solution in a stirred tank reactor (CSTR, whatever, they didn't care). They wanted to know how we would predict the product concentration that came out... I discussed external diffusion (it's stirred, minimal external diffusion), internal diffusion limitations (modeling via an 'effectiveness factor, thiele modulus, explained how the effectiveness factor scales with values of the thiele modulus). Make sure you both know how to derive the thiele modulus but also have it memorized. They seemed happy with this, so I got one last question before time was up: you want to see how well-mixed your tank actually is, what would you do? I say I would put a tracer in and see how it comes out. I start out by saying something like, "If you had a perfect CSTR, it would be instantaneously mixed as soon as you insert it, but of course that's ridiculous" and Clark interrupted me and said, "let's assume it is, draw a graph of the distribution on the board". So, I quickly drew the exit concentration profile with time and explained that for a perfect CSTR I would see exponential decay and how I would derive that via a mass balance. Clark briefly asked why I wouldn't have a reaction term in my mass balance, and I basically said that it would be really dumb to choose a tracer that would react... Anyway, this one was a bit frustrating but I passed!

NP

This was my first prelim. I had the exact same questions that ED talked about above, so I won't go into too much detail on them. Yes, if you have these guys, figuring out what you're being asked can be the hardest part. What's good though is that what they're looking for is usually something very simple. Know the assumptions that you have to make for Batch, CSTR, and flow reactors like your life depends on it. As ED mentioned, for some bizarre reason, Transition State Theory seems to be a hot favorite with most prelim examiners. This is strange considering you don't cover it in undergrad (atleast I didn't) and the graduate kinetics course I had to take here was pretty useless for this (and for most other things lol). In any case, Zhang managed to combine a Michaelis-Menten question with TS theory. Clark then asked me how I would use the MM reaction in a packed bed flow reactor. We then dove into effectiveness factors and Thiele modulus. I didn't have to derive a single equation. Overall, I thought this one didn't go particularly well but I

ended up doing the best on it. Goes to show again that prelim grades can be pretty arbitrary. I would say be an effective listener and try to keep the dialog between you and your committee open by constantly asking questions about things you don't understand. Clarity is key.

KS

Zhang asked the questions and was frequently interrupted by Clark to either clarify or expand on the question. The first question was about transition state theory which people were saying was not going to be on the exams, so I almost didn't study it. Thankfully I had memorized the equations right before the exam on a hunch, because I definitely had to write out the reaction rate thing that involves the change in Gibbs free energy. I had to write out the energy diagram/reaction progress graph as well. I went through M-M assumptions to get to the final equation, but didn't have to derive it. They asked about the significance of  $V_{max}$  and  $K_m$ , does it depend on  $[S]$  or initial enzyme concentration?

We then moved on to talking about different reactors that you would choose for a M-M system. We talked about the design equations for the batch and CSTR relating that to reaction rate  $r$  (then what if there is a catalyst in the mix) and dealt with the units of  $r$  for a while (eventual conclusion, it doesn't always have units of concentration/time). Back to the M-M equation, if you have two substrates the enzyme can react with, how can you tell what the enzyme selectivity is? (or something along those lines). Basically if you know  $V_{max}$  and  $K_m$ , you can look at the substrate concentrations in the limiting cases (low or high) and figure out from that... I'm still confused from that prelim. I had a hard time understanding what they were asking and as you can tell from these notes, still have no idea.

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### **Katz / Ciston**

EC

Katz started the prelim with a fairly simply question about a clear bath and at time zero a dye solution was added to it at some constant flow rate. It was also being drained at the same rate. Basically he wanted me to model it as a CSTR and plot the concentration of dye in the water leaving the bath as a function of time. I jotted down the mole balance of a CSTR (he didn't explicitly say CSTR). I forgot to turn auto-pilot off and accidentally wrote the balance at steady state and didn't catch my error until a few lines down. However, I corrected the error without them bringing it to my attention so I doubt I lost points. Next Ciston said we would talk a little about heterogeneous catalysis and said we had a reaction  $A \rightarrow B$  occurring on some catalyst sphere and wanted me to write down the steps of the reaction ( $A+S \rightleftharpoons AS \rightleftharpoons PS \rightarrow P+S$ ). I briefly explained why certain steps had double arrows and others did not. She then told me to write the rate law for the formation of the complexes so I did (I also said I would assume rapid equilibrium for the double arrow steps). She then asked me to now add the diffusion part. I was thinking I was screwed but didn't want to look like I had no idea what she was talking about so I just continued the dialogue as if everything was okay and drew a circle stating it was my catalyst and then drew an "A" about a foot away from it and explained it would need to diffuse to the surface in order to react as I drew an arrow from the "A" to the circle. This was more of a way to buy time as I thought but she said "Good." At some point I wrote down the equation for the rate constant and Katz asked if it would always take that form and I said no that if the reaction was mass transfer limited that there would be a  $\frac{1}{2}$  in front of the  $E_a$  term. Katz remarked that this was clearly too easy for me. He then asked me a question that went something like this: You have a Bunsen burner and you turn the gas down so that the flame is very small. You keep turning the gas down until it is almost off and notice

the flame volume is constant (albeit small) until it finally goes out. He wanted me to describe this phenomena. I was clueless as what he wanted me to do. He asked me to draw a plot of  $X = f(T)$  for an adiabatic reactor in which an exothermic reaction was occurring. I explained that as the reaction proceeded that heat would be liberated that would in turn heat the reactants and increase the rate (positive feedback loop). He asked if the energy balance knew about the increase in reaction rate to which I responded it did not. He then asked me to plot this on the graph and I was still very unsure what to do so I drew a concave down curve from the origin to  $X = 1$  at high  $T$ . He asked if this made sense to which I responded it did not (the temperature barely changed until conversion as very high and then suddenly jumped). I redrew essentially the same trend but this time concave down. He again asked if the energy balance knew about the increase in rate and asked me to write the energy balance. I finally realized he wanted me to plot the energy balance alone (for some reason I didn't think of this before). I drew a straight line at roughly a 45 degree angle and he said that the  $\Delta H$  was very high so I drew the line again with a very small slope. He then asked me to add the mole balance to the plot. I finally began to realize this was a steady state problem. I began to derive the mole balance (I was a little rattled at this point) and he told me to do it without equations. I drew the same concave up trend that I had draw earlier and he asked if it made sense that it shot up to infinity and I said no it wouldn't do that and that it would stop at  $X = 1$ . He then asked if the trend made sense and I realized that the trend should plateau near  $X = 1$ . He asked me to identify the SS point and there was only 1 intersection between the 2 curves, near the origin. He asked if this represented the flame off or on. I was a little confused and began to say that there was some conversion (albeit small) before he cut me off and said it was small enough to assume no conversion and that the flame was off. He said we would move on and Ciston asked a question about parallel reactions with a desired and undesired product. She asked me to write out what the selectivity was. I wasn't sure so I wrote  $D/(D+U)$  to which she said that was okay but to use  $r_D/r_U$  she informed me that we did not know the rate constants or order of the reaction and wanted to know how to get them. I said I would use a batch reactor and take liquid samples at a specific time interval to get the concentration profiles wrt  $t$  and then use finite difference to get the rate of formation of the 2 products as a function of  $A$ . I suddenly forgot what to do next and stood there for a few seconds before she said let's just assume the desired product is 2nd order and undesired is 1st order. She wanted to know how to maximize the desired product. I went through the whole explanation of why a PFR would be best and they ended by asking me if the reaction was gas phase would the conversion be increased if pressure were increased. I should have immediately said it would increase but my mind went blank and I jotted some things on the board and responded a few seconds later that assuming the  $y_A$  remained constant that the rate would be increased, which made since there would be more molecular collisions between the reactants.

I felt like I knocked this one out of the park upon leaving Katz's office but the more I thought about it the worse I felt. Ends up I got an A.

Nutella

Katz offered to let me go early, but I figured it couldn't hurt to answer more questions. IT'S A TRAP! He gave me a hard time for not being able to finish his extra problem in the time I had left. He's actually pretty nice though when giving prelims.

TL;DR

Katz: Draw a differential reactor. The outlet flow is the equilibrium concentration for the 1st order reversible reaction  $A \rightleftharpoons B$ . What is the apparent activation energy of the reaction? Use the Van't Hoff equation in your explanation.

Ciston: Given a generic  $A \rightleftharpoons B \rightleftharpoons C$ , write down rate expressions for each species. What is the pseudo-steady state approximation? How do you solve for the concentration profiles after assuming PSSA for species B (batch)? What does the concentration profile look like in a batch reactor if it was really

A→B→C?

Katz: Under what conditions will the measured activation energy of a reaction be less than what it should be? Derive the Thiele modulus for a generic  $r=k[Ca]^n$  rate expression. What is effectiveness factor in terms of the Thiele modulus. Show how the effectiveness factor influences the apparent activation energy.

CMS

Ciston: A question about selectivity in parallel reactions. See section of the book in Fogler. Know both the local and overall definition of selectivity. Know how temperature influences selectivity (depends on activation energies) and how reactor types can be exploited to increase selectivity. Know the [sometimes] trade-off between selectivity and conversion.

Katz: A question about 'apparent activation energy'. 'Apparent' because this is for when you have a rxn  $A \rightarrow B$ , but this is not elementary to your knowledge. Think  $\text{rate} \sim \exp(-E/RT)$  where E is the apparent activation energy. One can then take the log of both sides and get that  $-1/RT$  is the slope of  $\log(\text{rate})$  vs. E. Thiele modulus question, which he asked in previous years. Know what it is, where it comes from. Difference between internal and external diffusion limitations for spherical catalyst particles. Straight out of Fogler's book.

DG

Maximize selectivity of parallel reactions. Use the correct concentrations and temperatures  
Catalysis particles - how to know whether the particle is internal diffusion limited, external diffusion limited, or reaction kinetic limited. Remember people, if the reaction is externally limited you can check by upping the flow rate, this will decrease the bulk flow boundary layer (by a factor of  $re^{1/2}$ )  
Thiele modulus and whether the rate is limited by reaction or by diffusion

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## **Reimer / Zhang**

GN

Zhang: transition state theory with MM. Draw reaction coordinate with transition state. If you know  $k_{cat}$  and  $K_m$ , can you determine the activation energies ( $ES \rightarrow ES^\ddagger$  and  $E + S \rightarrow ES^\ddagger$ )? Write down the final rate law expression. What assumptions did you use about  $[ES]$ ? Which reactor type do you have to use for this mechanism?

Reimer:  $A \rightarrow B \rightarrow C$ . Talk qualitatively about which reactor type to use to maximize production of B. What if you now have a competing parallel reaction? Don't write down equations. Okay, so now you've immobilized your enzyme within the pores of spherical pellets. You have two CSTRs that are equivalent in every other way except one of them has free enzyme and the other has these "catalyst" pellets. How are they different?

AW

Reimer asked his question first, which was the formation of silicon from silane. He told me that silane is in equilibrium with silalene and hydrogen, then silalene reacts irreversibly to form silicon and hydrogen. That silicon is to be deposited on wafers. He asked me to design a reactor for the process. I ruled out a batch reactor for efficiency's sake. A CSTR didn't seem like a good idea to me (I didn't have to explain why I thought that) so I went with a PFR where the wafers were placed next to each other down the reactor with the thin direction being perpendicular to the flow. We then talked about wafer thickness as a function of length down the reactor. We first ignored temperature effects, so I sketched concentrations of silane, silalene, and silicon as a function of length. I looked at what would happen for the cases of a reversible and irreversible first reaction. He then told me that the reactor actually had wafers stacked the other way, so the

thin direction was parallel to the flow direction. Each wafer also takes up nearly the whole cross section of the reactor. With this configuration, Reimer noticed that the wafers were thicker towards the outside than the inside. We talked about why this could be and how to fix it.

When Reimer was satisfied with the production of silicon, he asked me about the Arrhenius law and the pre-exponential factor. He basically just wanted me to tell him that that factor comes from an entropic effect.

Zhang then asked her question, which I had a little trouble understanding. It boiled down to spherical pellets in a CSTR, which had a catalyst on the inside. We talked about diffusion limitations and how they affected the reaction rate. This was a Thiele modulus/effectiveness factor question. I hadn't heard about those two until about a week prior, since my copy of Fogler (Essentials, not Elements) came without that information, but I was still able to answer their questions. The Thiele modulus compares diffusion rate with reaction rate (I currently can't remember which over which, but I would know that for the prelims) and the effectiveness gets you a reaction rate that includes diffusion limitations. They asked me to plot a relationship between Thiele modulus and effectiveness factor. After that, I was free to go about 8 minutes early.

I was pretty pleased with this prelim and they seemed happy, too, but I ended up getting my worst grade in this subject. Not sure why.

CE

You have reaction  $A \rightarrow B \rightarrow C$ . You want to optimize for product B. What type of reactor do you want to use? PFR which is continuous and will maximize intermediate. Assume that the first reaction  $A \rightarrow B$  obeys the law of mass action. Discuss the meaning of the rate constant  $k$  from the standpoint of physical chemistry (a.k.a. discuss transition state theory). Transition state theory assumes formation of a transition state (draw reaction coordinate vs. free energy plot) which is in equilibrium with the reactants. The reaction of the transition state to products is assumed to be the same for all reactions and to occur with rate constant  $k_b T / h$ . The equilibrium constant between the transition state and reactants  $K$  can be written in terms of  $\Delta G^\ddagger$  which can be written in terms of the product/reactant partition functions, which allows the rate constant  $k$  to be predicted. What is the dependence of the rate constant on temperature. It is given by the Arrhenius equation, where  $k_0$  can be thought of the rate constant observed if reaction rate is determined solely by collision events (all molecules collide with sufficient energy/correct orientation for a reaction to occur). Suppose you wish to carry out an enzyme catalyzed reaction. You have two setups. In the first, you have enzymes in solution while in the second you have enzymes distributed within the two setups. Discuss diffusion limitations in the second setup (Thiele modulus, effectiveness factor). Draw a plot of the effectiveness factor vs. Thiele modulus. Estimate the value of the Thiele modulus at which you expect the effectiveness factor to demonstrate an observable decrease (I didn't remember, just tried to make some argument about how I expected to see significant decrease if  $k$  is say 100 times larger than  $D$ , and plugged that into the expression for Thiele modulus).

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## **Bell / Ciston**

XZ

Bell:

(1) Derive Michaelis Menten, what is  $V_{max}$  in terms of total enzyme concentration. (2) elementary reaction:  $A+B \rightarrow C$  (in gas phase), what is rate equation, how to get rate constant theoretically? use collision theory. derive it while explaining each term, draw speed distribution, what is root mean square speed (it's the

square root of the integral of  $v \cdot v \cdot f(v) \cdot dv$  from negative infinity to positive infinity). (3) PFR,  $A \rightarrow B$ , exothermic, adiabatic, sketch conversion vs volume, sketch temperature vs volume (both look like a "S"). in temperature profile, there is  $T_{max}$  and  $T_0$  (initial temperature), what is the name of the temperature difference? (it's adiabatic (combustion) temperature? obviously I didn't know the answer, and obviously Bell knew I didn't know the answer, but I guessed "adiabatic..." Bell was excited when I said that word, and said "correct!"). then calculate the temperature difference.

Ciston:

(1) parallel reactions:  $A \rightarrow D$ ,  $A \rightarrow U$ , how to maximize D? talked about each scenario (if  $k_1 > k_2$ , PFR or BATCH; if  $k_1 < k_2$ , CSTR; if  $k_1 = k_2$ , PFR, BATCH CSTR). temperature dependence.

(2)  $A \rightleftharpoons B \rightleftharpoons C$ , in a batch. write rate equations of each species. using quasi-steady state assumption, explain how to solve the equations orally. if  $k_{-1}, k_{-2} \gg k_1, k_2$ , sketch concentration profile vs time. I made a guess, and I was not sure whether it's right or not. Fortunately, they told me it's correct before I wanted to erase my guessed profile.

KG

Ciston started by asking about a reaction of A going to B occurring on a surface. She asked to write out the reaction mechanism:  $A + S \rightleftharpoons AS$ ,  $AS \rightleftharpoons BS$ ,  $BS \rightleftharpoons B + S$ . She asked me to solve this single-site Langmuir-Hinshelwood adsorption problem, but she also asked about the form if two sites were needed, etc. Fogler has a nice schematic of this. Then Bell asked me to talk about the different steps that may occur prior and after reaction on a surface -- diffusion of the species through the solution and in the pellet. I verbally described each step and drew a concentration profile of the reactant in the bulk, boundary layer, and pore for external and internal mass transfer limitations. There's a good drawing of this in Hill. We then talked about the effectiveness factor and how to derive it. Bell asked me to give the expression for the ideal reaction rate (no m.t. limitations) for a spherical particle and he then asked me to set up the mass balance and describe how I would solve for the reaction rate in the pore. Bell then asked about how we can determine the rate constant,  $k$ , of a reaction. From the Arrhenius expression, he asked about what goes into the pre-exponential frequency factor,  $A$ , and the activation energy,  $E$ . He asked how the factor  $A$  may vary, say with particle mass or diameter. He then wanted this related to collision theory. By this point, the time was almost up and I was quite exhausted and ready to be done, so I said a few things that I remembered from my notes and that was the end of that one!

In general, the exams were less scary than I thought they would be. That said, I'm glad they're over though!

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## **Clark / Katz**

LL

This was the my last final and also their last one of the day. The set up was a bit strange & unconventional since they both knew I had taught undergrad kinetics. Prof. Katz didn't ask me any questions and Clark said they are just going to 'wing it' since I should know my kinetics pretty well. We spent while comparing my undergrad Levenspiel background to the way kinetics was taught here. I had brought up PSSH as one of the examples so we got into an in depth discussion on PSSH. We focused on what really makes this assumption hold true, when does it hold true, how do we know it's true? So the main point is talk about relative time scales. We also went a bit into M-M kinetics showing how PSS applies.

Then we got into some residence time discussions. We talked about the expectations for ideal reactors, and

then non ideal reactors, and all the scenarios that affect a non-ideal reactor. CSTRs is an exponential decay (how do we know it is exponential? do a mass balance). Is mixing good or bad? Do we want to use CSTRs and PFRs? Why do we need RTDs? Depends on the reaction kinetics. Case: PFR then CSTR, and CSTR then PFR - the residence time distribution looks the same. So we get the same conversion/results? To which I say no, no, no no no. He then wanted to get into RTD models, to which I admit that I knew of them, but I didn't know much more than that since I never covered RTD in undergrad nor in the class I taught so we spent some time discussing about how the material emphasized in the chemical engineering course changed throughout the years... Then they sent me off and told me to have a good weekend, so it was nice to end with Kinetics. Clark does get very impatient with questions in the sense that you may not always be able to finish your explanation/thought process before he wants to move on.

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## **Reimer / Bell**

LF

Reimer: Start with a series reaction.  $A \rightarrow B \rightarrow C$ . which type of reactor is best for this? talked about the design equations for each Batch, CSTR and PFR. I drew rough concentration profiles for each of the species in the reaction and then talked about how batch has a maximization with time, but the other two maximized versus space time. Defined space time. Talked about some assumptions we make for ideal reactors. At the beginning I said that I would chose the PFR for this reaction. Explained why a batch reactor was no good but couldn't give the reason they wanted for choosing a pfr over cstr, so we then talked about residence distribution functions, but i still wasn't getting there, so Reimer told me to talk about it with my "friends."

then we talked about the first part of the series, simply  $A \rightarrow B$ . They asked me to draw the energy profile of the reaction along the reaction coordinate and this lead to a talk about the arrhenius equation and about TST. I wrote the eryleng equation and discussed its connection to the pre-exponential factor and the exponential factor. I talked about how A could be found experimentally and how from there the entropy of the pre-exponential factor could be found by varying A with temperature. They then asked if my free energy profile was in G or in H. and I didn't know so I just guessed, but then we moved on.

Bell: Then we used the same equation ( $A \rightarrow B$ ) and talked about it with surface catalysis in a PFR. I discussed the langmuir-hinshelwood mechanism. I wrote up the elementary reactions and I talked a little about the pseudo steady state assumption, and derived the rate equation. He then says that a friend has observed that as the velocity thru the reactor increases, the conversion also increases, until at some point it plateaus off. Why could this be. First I thought it could be thiele modulus so I wrote it out but then of course it has no velocity terms, so that wasn't it. Then I drew the concentration profile of A as a function of distance from the catalyst. I talked about the boundary layer and then explained that as the velocity increases, the boundary layer should decrease, increasing conversion, until at some point, the reaction becomes diffusion or reaction limited and then the Thiele Modulus comes into play. Then we talked about the efficiency and then bell wanted to know what the rate would be in terms of one catalyst pellet. It was really confusing and i had absolutely no idea what he wanted me to do, so I struggled a lot for this part, which turned out me just writing that without diffusion,  $r_a = -k_1 \cdot Ca \cdot (\text{vol of catalyst})$ . Now with diffusion, the equation becomes  $r_a = -\int_0^R (-k_1 \cdot Ca(r)^4 \cdot \pi \cdot r^2 \cdot dr)$  from 0 to R. This basically shows that Ca is varying from 0 to R because of diffusion limitations, so you have to integrate over the volume instead of just multiplying. What? Anyways, at that point, we ran out of time and so I left.



I felt the worst walking out of this prelim, but didn't end up doing as badly as I was expecting. Bell and Reimer were smiley, but they seemed a little harsher than my other examiners in that they would really focus on what I couldn't figure out and then smile like "Haha you're a real idiot" as I struggled to grasp at any sort of truth. I think my tendency for these exams was to basically jump on anything that they said that I knew a bit about and explain as much as I could about it. This was probably both helpful and slightly detrimental because although it showed that I knew what I did know pretty thoroughly, often times, my little tangents were quite off topic and burned up unnecessary exam time. Anyways, I passed this one so yay!

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# Transport

## Graves / Chu

SS

Chu: You have a flat plate and have water flowing over it. Derive the hydrodynamic boundary layer thickness as a function of the flow velocity.  $\delta \sim L \text{Re}^{-1/2}$

Graves: Now consider that you have a concentration profile of A within the BL. Outside you have bulk concentration  $C_{A,bulk} = 0$  and on the plate the species gets adsorbed ( $C_{A0} = 0$ ). Find dimensionless groups which can describe the mass transfer coefficient as a function of the flow properties. Assume only diffusive mass transfer takes place within the BL.

First you need to solve  $d^2C_A/dy^2 = 0$  with BCs, equate  $k_m(C_{A,bulk} - C_{A0}) = -D_{AB}dC_A/dy$ ,

Show  $k_m\delta/D_{AB} = 1$ , plug in the value of  $\delta$  from 1st ques. Final answer is  $Sh = \text{Re}^{1/2}$

How does  $k_m$  vary with flow? Decreases with increase in flow velocity (No?)

What are the assumptions involved? Mass transfer BL and hydrodynamic BL have the same thickness or  $Sc = 1$ . Draw the profile for  $Sc \gg 1$ . How does  $Sh$  depend on  $Sc$  for this case? ( $Sh$  proportional to  $Sc^{1/3}$ ).

Chu was very jovial during the whole exam and Graves was very grave, he didn't smile at all. I was getting confused with the symbols for velocity a bit, which irritated Graves. So its better to explain the symbols you are using to them before you start solving. But they gave me useful hints when I needed them.

CE

Derive the expression  $\delta \sim \text{Re}^{-1/2}$ . Start with Navier-Stokes, observe that  $v_z = 0$ . Consider a balance over x-momentum and non-dimensionalize your equation using  $\tilde{x} = x/L$ ,  $\tilde{y} = y/\delta$ ,  $\tilde{v}_x = v_x/U$ ,  $\tilde{v}_y = v_y * L / (U \delta)$ . You can find your characteristic velocity in y using continuity (assume incompressible, Newtonian fluid). Because  $\delta \ll L$  you can see from your characteristic  $v_x$  and  $v_y$  that  $v_y \ll v_x$  so only consider x-momentum. Non dimensionalizing your equation, you will see that you can neglect the viscous term in x, and rearranging will yield  $\delta/L \sim \text{Re}^{-1/2}$ . Express the bulk mass transfer coefficient  $k_m$  as a function of D. Write down the two expressions for flux and set them equal to see that  $k_m \sim D/L$ .

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## Muller / Blanch

GN

Muller: resistive heating in a wire. What is the temperature profile?

Blanch: packed bed reactor filled with ice cubes (approx as spheres). Blow air to melt them. Determine design parameters. Don't write down equations.

LL

Some usual chitchat on my transport background. I felt fairly confident with the transport material at this point since we've exhausted pretty much most of the complex transport scenarios to death.

But all Muller wanted me to do was heat conduction from a wire... assuming that there is a conduction within the wire. I drew some profiles, wrote the boundary conditions, fixed my profile to account for the fact that there should be no heat flux at my center. I did a quick shell balance so I wouldn't drop by r's and my source term. Set it up, filled it in but she did not need me to do the math, which was fine. Talked about where to get

the heat transfer coefficient. And then the case where we have a stagnant fluid outside... here is when I forgot about the natural convection - too much mass transfer in my brain but we got to it and concluded that's why at a certain point there's going to still be  $T(\infty)$  and not infinite conduction possible.

Blanch: Process design for gaseous dissociation of HCl in water. I drew the reactors with a feed of gas and water. I was waiting to talk about the mass transfer in the bubbles and how it will shrink as it passes through the reactor. That aspect of transport never came... His questions really threw me off because I was in a transport mindset, and he was in a design mode and we were pretty much on different pages. Asked me what spargers were? How the gas should be introduced into the reactor? What size would I make my reactor? How concentrated can HCl be? Do we want large bubbles or small bubbles? How do we get small bubbles? Trick question, I was thinking higher velocities but turns out that pumping the bubbles too quickly, they will coalesce and form big bubbles. What holds the bubble together? Surface tension, yay! What causes the bubbles to leave the pipe? buoyant forces... Some questions were actually really trivial and I over complicated things... No equations were necessary. He just wanted a description on how the reactor was designed industrially... and what industrially makes sense. They are very nice and quick to help you, maybe a little too quick such that they would point out really obvious things that you could have gotten yourself. Oops. But overall, it went well.

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### ***Muller / Tullman-Ercek***

LF

Muller: She likes to ask about viscometers, and I had studied some of them, but hadn't refreshed my falling-cylinder viscometer knowledge, which is the problem she asked about. Thankfully, we had done this problem in 250, so I went with what I remembered from it. I went through and explained a rough picture of what the velocity profile looked like and explained the boundary conditions. From there we went through Navier Stokes and solved for the velocity profile in terms of a  $dP/dx$  term. Next, you need to solve for the  $dP/dx$  term. I knew it came from the mass balance, but like I said, this problem happened at the beginning of the semester, so I started to get a bit fuzzy on the details. After lots of help from Muller, I eventually figured that part out. It's about the mass flow of the fluid ( $Q$ ) and the liquid displaced by the falling cylinder. After that they asked about how to find the viscosity. And from here, I got nowhere. It was a force balance and I really suck at them. This fact became apparent quite quickly. After a while of talking about these ideas of buoyant forces and pressure terms, we moved on.

Tullman-Ercek: She set up a problem that was solving for the mass transfer of some sort of cancer drug that is diffusing from a polymer into a tumor, where it is being consumed (reacting) and diffusing. This could be modeled as two adjacent slabs (polymer and tumor) in series. So, I drew up the problem and started to talk about how to approach it. Mass balance in the tumor, bounds are constant flux from the polymer and constant chemical potential, could be translated into some sort of solubility relation. From there I worked on the mass balance. When I had it in a solvable state, I froze, because I somehow had forgotten how to do any sort of math. When I told them I was a little stuck, they suggested that I nondimensionalize. After explaining what I would nondimensionalize it with, I quickly realized that this was a form of the thiele modulus. What?!? So I talked about that for a while, and then talked about how the concentration profiles would look in the polymer and the slab. We were running out of time, so I quickly talked about the lumped thermal capacity model for the polymer (the concentration would be changing over time) but only drew a steady state line for the tumor. They seemed happy about that.

I totally did excellent on the second part, but was kicking myself for screwing up the force stuff of first one so majorly. Either way, these people were a good pair of examiners and I passed this one!

Nutella

These two get annoyed with details and small mistakes very easily. They will also let you take their problem where ever, but will make you clean up the mess when you realize that you made the problem too hard for yourself.

TL;DR

Muller: Temperature profile in a hot wire (1D radial conduction in a cylinder, convection in the air). How do you get heat transfer coefficients? What if you don't have flowing air across the wire? Is there flow in free convection? What is the dimensionless number involved in free convection? Why does free convection happen?

Tullman-Ercek: Concentration profile for a drug diffusing from a polymer slab to a tumor. Cartesian coordinates.

DG:

Same as LF.

Falling cylinder viscometer, and drug delivery.

Briefly, drug delivery

Slab of drug, slab of brain matter. Assumed psuedo steady state. Assumed the slab all had equal concentration. Assumed the destruction of drug in brain matter was first order in concentration of drug. I had a hell of a time teasing out what assumptions I could make about this system were.

Non-dimensionalized the diffusion equation to pop out a  $(1/\text{thiele modulus})^2$

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## ***Radke / Chu***

NP

This was my last prelim. Having done well on the previous two (or so I thought at the time), I was quite relaxed when I walked in to Radke's office. If you read previous prelim transcripts, Chu/Radke are the funnest pair to have and like all the others before me, I would have to agree with that. The whole thing started out with all three of us laughing and Chu and Radke asking me to tell them about the grades I got in their classes (Transport and thermo). I was then asked to rate how they had done teaching wise but almost immediately, both of them burst out into a hysterical laughter before I could even answer. So, I'm guessing this question was rhetorical. Problems-wise, this was a really easy prelim. I was asked to derive the hydrodynamic boundary layer relations using an order of magnitude analysis. Before I could start, Chu wanted to know how the thickness of the boundary layer correlates with the Reynold's number. I wrote down the good  $\delta = x/\text{Re}^{0.5}$  where  $\delta$  is your boundary layer thickness. I was then asked to draw velocity profiles for developing flow. This is where the nut busting began. I drew my profiles but Radke kept picking on little, irrelevant details of my drawing. As for Chu, I couldn't for the life of me, figure out what he wanted me to tell him. Also you have to make the assumption that  $\delta \ll x$  and then you need to invert that to put it into your Navier-Stokes equation. After the electrocution session that Radke and Chu gave me because I drew my profiles wrong, I got nervous and made a mistake inverting my  $\delta$ s and  $x$ 's. To this, Chu very snidely remarked how it was strange that I was an engineer and did not know how to invert numbers. In any

case, we got through the problem and then Radke proceeded to ask me what I wanted to do next. What did I want to do?! I was totally thrown off by this. Did he mean what I wanted to do in a general sense? If that was the case, I wanted to wrap up the prelim and get the heck out of that office! That wasn't an acceptable answer though and Radke shook his head and then proceeded to ask me how I would calculate the power needed to overcome viscous forces on an airplane wing. I was to use the boundary layer thickness I derived. Basically,  $\text{Power} = \text{force} \times \text{velocity}$ . You get the force by integrating the shear stress. You can get the shear stress by using Newton's law of viscosity and doing an order of magnitude analysis. This was pretty easy and we were out of time by then. Overall, this was a very relaxing prelim save for the few moments of terror that Radke and Chu delivered to me. All in all, I was quite happy and ended up doing pretty well.

KS

Radke did most of the talking. Chu would occasionally chime in but he mostly just sat there and laughed. Question: hot copper ball falling distance  $H$ . What is its temperature as it hits the ground. We discussed macro vs micro approach, dimensionless numbers and their appropriateness ( $Nu$ ,  $Bi$ ,  $Re$ ,  $Pr$ ),  $Nu$  correlations, temperature profile, Newton's law of cooling, units of " $h$ ," boundary layer things, terminal velocity and its derivation (know Stokes law and where the  $6\pi$  part comes from), also, skin friction and form drag, substantial derivative (know what each term in the N-S equations means). Also, it was helpful to know the N-S equations in different coordinate systems even though memorizing them was a huge pain. Radke's time to shine is in these prelim exams, and he's pretty good at taking a problem and turning it into a question that addresses almost all aspects of transport. He just asks rapid questions constantly, jumping around, throwing out ideas and promises of coming back to address certain things later. It was hard for me to think through the problem because of this. I think it would help to practice with someone who purposefully asks you questions like this so you can get used to it.

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### ***Radke / Tullman-Ercek***

CMS

Radke: Hot, spherical ball of copper falling in space. What is the temperature before it hits the ground? Think of Biot number-- answers question "can we assume that the temp of the spherical copper is uniform?". Yes, then we have  $T(t)$  where  $t$  is the time that the ball has been exposed to a flow of air that is carrying heat away from it (forced convection).  $Nu = 2 + \frac{1}{4} Re^{1/2} Pr^{1/3}$  for the heat transfer coefficient  $h$ . Then  $\rho V c_p \frac{dT}{dt} = -h(T - T_{\text{air}})$  subject to  $T(t=0) = T_0$ . Can solve this simple ODE for  $T(t)$ , then find the  $t_h$  at which the sphere hits the ground. For this, we need the initial height above the ground and set up a force balance that includes buoyancy, drag force, and weight due to gravity.

Tullman-Ercek: Diffusion of a drug from a polymer material into a tumor. Pretty simple 1-D reaction-diffusion in both the polymer gel and the tumor. The drug is degraded first-order homogeneously in the tumor. The only tricky question is with the boundary conditions. Be able to draw a concentration profile for the two phases. Remember that concentration can (and almost always is) discontinuous between two phases. By a mass balance, the flux across a particular phase boundary must be zero, and with different diffusion coefficients, the slopes at the phase boundary will be different via  $\text{flux} = -D \frac{dc}{dx}$ .

EC

This was my last prelim and I was feeling very nervous after most probably failing thermo. It was the last prelim slot on the last day and was by far the most enjoyable experience I had over the 2 days. He said we

have a drop of water at a higher temperature than the environment and that the  $RH < 1$ . He wanted to know how far the drop would fall before disappearing completely. I had studied this problem extensively and knocked it out of the park. Basically do a balance for the heat, mass, and momentum. Pretty straight forward. He asked how to get the convective heat transfer coeff and the overall mass transfer coeff. I said the Nu and Sh, respectively. He asked what they were and how to get them. I wrote the correlations for Nu for a sphere which I had memorized ( $Nu = 2 + 0.6 \cdot Re^{1/2} Pr^{1/3}$ ). He asked me to explain the exponents. I knew it must have something to do with the boundary layer that the individual dimensionless numbers were describing. For the  $1/3$  I was fairly sure that the reason was that the heat boundary layer was getting lost in the momentum boundary layer (momentum BL is bigger). For the  $1/2$  I wasn't really sure but concluded that it was a result of wrapping the momentum BL around a sphere. He asked me to derive it using the equations of motion and continuity. I was a little nervous because I didn't really know how to do this but using some scaling arguments it was actually a really easy thing to prove and Radke was extremely helpful throughout the entire process. The atmosphere was very laid back and there were several times when Radke laughed about one thing or another. Tullman-Ercek didn't speak a word. I left feeling like I knocked it out of the park but wasn't sure if it was good enough for Radke to give me an A. Turns out it was.

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### ***Graves / Blanch***

Easily my most enjoyable prelim. Blanch asked me to discuss (no equations on the board! I like his philosophy...) a problem in which I have tank full of ice pellets and I'm blowing saturated water vapor through them (top of the cylinder down; fresh water is drained out the bottom) to melt them. (context: we're in africa, we need fresh water, so we freeze ocean water, rinse off the salt, cut it into little round balls, and melt it to get fresh water back. unconvinced? me too, but he swears it's a real process). I forget exactly how the questions started, but overall we wanted to know how tall the cylinder containing all my ice pellets needs to be, and how much power is required to pump the air. We discussed how the rate of heat transfer is related to the temperature difference between the ice and the air blowing by it, and also to the heat transfer coefficient. Ice temp will remain constant, air temp will drop as it goes down through the cylinder. Heat transfer coefficient can be found from the Nusselt number which is a function of Reynolds and Prandtl... so since Reynolds is a function of radius, as the spheres shrink over time, the heat transfer coefficient will be affected. Now he goes back to "why do we use saturated steam". When it gets cold, steam will condense; condensation is an exothermic process, so this will release additional heat for the process. Okay, how would we find the pressure drop? I bring up the Ergun equation for PBR's that we use in kinetics; discuss it in terms of density and porosity; apparently that's good enough. Okay, now I want to size this thing after all... I looked at the problem and wondered out loud why you couldn't just make the whole thing a wide, squat cylinder; Blanch pointed out that I would lose some of my Nusselt number. Then I said I would optimize between a heat transfer coefficient with the cost to pump steam over my pressure drop. Last question from Blanch was how would I calculate the power for the pump? I said it would be the pressure drop times the flow rate (which for some reason I had memorized, although it's easy enough to work out via unit analysis). Apparently Blanch was satisfied, because then Graves came in with his  $SiO_2$  question. We really dug into the assumptions, boundary conditions, and relative time scales on this; I lost my units of diffusivity for a few minutes and ended up re-deriving the Fourier number for mass transfer. Somehow in talking about the degree of internal diffusion limitations on this I ended up deriving a Thiele modulus for this problem in planar geometry. Eventually Blanch got tired of watching me do the problem and I just chatted with them for the last ten minutes or so. Graves and Blanch are a wonderful combination, very relaxing, and always joking with each other and you. This was a great prelim to end on after two that were a bit rougher, and I got an A :)

AW

These two were a great pair. They were great at making me feel relaxed and giving hints. Graves even gave me a compliment before he asked me any questions, which helped me focus more on the questions and less on the weight of these exams. Graves started by asking me about the velocity profiles for the startup of a flat plate. We talked about the no-slip boundary condition at the plate and we also talked about the stress continuity boundary condition. He then asked me to draw the velocity profile for Couette flow. At some point, I mentioned momentum diffusivity, so Graves had me explain the diffusion of momentum.

Graves was satisfied, so Blanch jumped in with his no equations philosophy. We talked about an HCl absorber using water. We talked about driving forces for mass transfer and concentration profiles and after a few minutes, he threw a chemical reaction into the mix. When the HCl becomes absorbed, it protonates the water. He asked if we add acid to water or water to acid and why, which led to the protonation being very exothermic. We then considered heat effect in the absorber, which could be countered by putting cold water in the top of the column. We talked about how to relate the temperature or amount of water required to the amount of HCl put in the column (an energy balance). Then he mentioned that the deprotonation of HCl is very quick. This changes the concentration profiles, so we revisited the driving forces. For a quick reaction, the liquid side interfacial concentration of HCl drops to 0, so the vapor side interfacial concentration does as well. This maximizes the driving force.

At this point, we still had 15 minutes left, but Graves wondered what the point in asking me more questions was if I was just going to get them all right, so they let me go. It was really nice leaving with that compliment. Took away my worries of passing this one. This was their second to last prelim on the second day of prelims, so I do wonder if that had any influence on them...

KG

This was the first afternoon prelim on the second day of prelims. Blanch started off with his no equations rule and posed the problem detailed above about removing HCl from water. They then asked about the Sherwood number correlation for mass transfer around a sphere. After Blanch was finished, Graves asked about heating a solid metal sphere with a hot air blow dryer. They asked for a sketch of the temperature profiles of this transient heat transfer problem and then for the equations and boundary conditions you would need to solve for the temperature profile. They then asked to discuss convection at the surface and conduction in the sphere, and they wanted to hear about the Biot number.

As others have mentioned here, these two were a happy pair. Blanch especially was very talkative and kept joking around.

XZ

Graves: poiseuille flow. spell "poiseuille"... how can we tell a flow is laminar or turbulent? Reynolds number, if  $Re > 2000$ , it's turbulent. before the fluid reaches steady state, what does the velocity profile look like? think about boundary layer! how long does it take to reach a fully developed flow? (think about units, or use  $Fo$ )  
Blanch: ice sphere in PBR, hot air flow in. how much does it cost to run a pump? energy balance, pressure drop, final state in the PBR? (ergun equation? I couldn't remember the exact form, but I told Graves that we could find that in folger's kinetics book. and he said yes.)

You can ignore the following part, it's not related to transport. Blanch tried to ask me some biochemistry questions (because I told them I was biochemistry major in undergrad, he was excited about that...I thought it just meant I've already passed transport) what are the base pairs? why do we have hairpin structure in mRNA? I tried to explain that using delta G or hydrophobic forces?...Graves said that should be biological

purpose which he couldn't understand. so I talked about specific sites for enzymes, regulation mechanisms (obviously, I didn't prepare for it and just tried to answer this question from three-years-ago memory). He just smiled. I asked him whether it's right or not. Then he told me the correct answer briefly. Graves said that he couldn't understand what we were talking about and then he told me i did well. I left 10 min earlier.

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## Preparation Advice

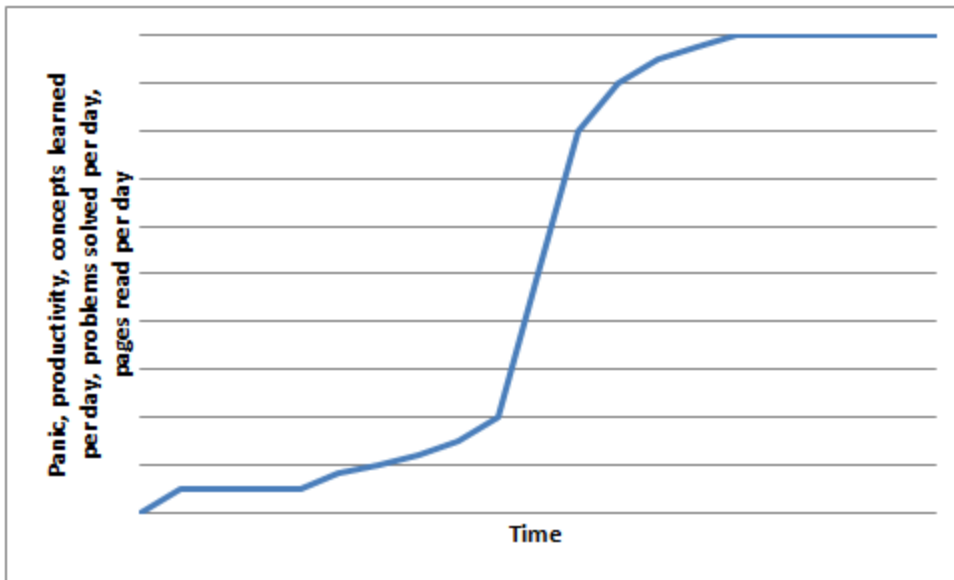
After a relaxing break with zero studying, as everyone suggested to me, I began studying January 3rd (prelims took place Jan 17-18), and I studied around 5 hours per day-- broken up into two sessions. I had three books: Fogler, Smith and Van Ness, and BSL. I went to Starbucks every day by myself and flipped through each book, copying down the equations on notebook paper and going through examples. When it came to thermo, I had to read some of the chapters thoroughly. I only had time to have mock-prelims with a classmate for two afternoons. I prioritized going through the books and making sure that I understood how each equation was derived and the concepts behind it. I glanced through a lot of worked-out examples in the book and made sure that I understood each aspect of the given example. Skimming through the questions that were asked in the previous years is essential because you can't know everything. But, I think the idea that you should have lots of mock prelims is stressed too much. My prelim grades were A, A, and A-, and I was in Starbucks by myself reading the textbooks and going through the worked out, in-chapter examples. I covered more ground more efficiently than I could have with a bunch of mock-prelims. The committee isn't likely to ask you some esoteric, tricky question at the back of some textbook, but rather some basic concept that you can pick up by reading the textbooks.

### NP

Number one thing to remember: Don't be nervous! I know it's easier said than done, but I feel like my performance was severely affected by the fact that I was nervous. The best way to approach prelims is to keep a positive attitude and go in and come out with a smile. Be very effective at communicating your thoughts--clamming up won't get you anywhere no matter how much you know. Also, make sure you don't waste time studying ultra specific concepts that no one cares about. What prelims should actually test is your ability to reason through a situation using first principles. Group studying is great but at the end of the day, keep in mind that on the test day, it's just you and your committee in that room. So try and spend time asking yourself questions and working through problems starting from very basic things like mass balances. If you can show that you can do this, your committee will be very happy. Also, get lots of sleep and also have fun. I would recommend putting in a good 6-7 hours a day 2 weeks before the exam but not more than that. Take Friday nights and the evening before the exam off and do something fun. I watched a mindless Mel Gibson action flick--trust me, it helps. Take a look at the recommended textbooks at the gsac website and go through them even if you didn't use them in your undergrad. Why? Because they use them here for Berkeley's undergrads, hence making them the "best" textbooks in the world. Definitely undergo mock prelims by senior grad students. You'll be surprised how much you forget when you are up on the board. The good news is, your performance will improve exponentially with practice. Honestly, as much as I hated the prelims experience, I'd like to think it leads to character building. That's the only way I could justify putting myself through this.

### AW

I definitely wouldn't try studying more than ~2 weeks before the prelims. A day or two before prelims began, I was so tired of studying that I was just wasting time. Also, the productive hours/day varies person to person. In the beginning, I could only focus for like 2 or 3 hours per day. As prelims drew closer, I became much more productive, though, and probably worked for ~8 hours each day. Could've been more than that. I think this plot accurately describes how things went for me:



Actually, panic might need its own curve, where it just continues to increase. Anyway, I did fine, but I would recommend trying to be more productive in the beginning.

I had all my old notes and textbooks with me, so I went through what I was familiar with when I studied. This made all that knowledge a little easier to swallow. Contrary to that person above me who studied at Starbucks every day, I found practicing to be much more useful for me than reading notes and textbooks alone, or at least it felt more useful. Definitely take some time in the beginning to read so that you actually have some idea of what you're talking about, but make sure you get lots of practice in. It's really important to be able to express yourself verbally and on the board. Teaching during the first semester helped with that. Our class was the first to teach that first semester, and I'm very grateful we did.

One more thing: for anyone who used the Essentials version of Fogler's book like I did, it's missing some concepts like the Thiele modulus and non-ideal reactors. Try to borrow an Elements version at least when you study those concepts. They seem to come up quite a bit.