

P R E L I M S 2 0 1 1

Compiled by DH.

T R A N S P O R T

ALEXANDER/RADKE

SK.

I was supposed to have Radke and Alexander, but Alexander didn't show up so Radke started alone, and Balsara showed up about 10 minutes into the prelim. First we had the usual chat about undergrad education, during which Radke seemed impressed that I had been a math major, too. (not that it helped in this prelim...)

We were waiting on a substitute, so we started out kind of late. Radke asked me to draw a closed tank with some water in it and a valve out the bottom, and said that the pressure in the tank was above atmospheric. He asked me to describe what happened. I said the tank would drain, and he asked if it always would, and I said no. He asked me to derive what the final liquid level would be in the tank. I had epic brain freeze about this problem (for some reason, hydrostatic pressure is hard for me??), so I started with the pressure of the air on top of the water. I used the ideal gas law, and assumed it was isothermal, and gave the pressure as a function of the liquid height, initial liquid height, area, and initial pressure. Then he asked me what the criteria for the draining to stop would be, and after lots of poking and prodding, I got that the pressure inside the tank at the valve would be atmospheric pressure. And then I was writing down the expressions for the barometric equation, but I think I did something wrong, so Radke told me to write down Bernoulli, and after that I got that the pressure inside the tank was the hydrostatic pressure plus the pressure of the air on top- so I had an expression for the final height, and whether the tank would drain all the way. Bleh. This took a long time, mostly due to brain failure on my part, and at the end of it, Radke said, THAT was the easy part. Now we're going to find how fast the tank drains.

So after some hemming and hawing about what kind of flow was occurring and where the resistance to the flow was I got that the resistance was in the valve, but couldn't remember the form of the "Engineering Bernoulli equation" (head loss in a valve), so Radke rather disapprovingly gave it to me, and then I had an expression for the velocity as a function of height. And he asked me if we were done, and it turns out, no, I needed height as a function of time, but then the prelim was over.

I did poorly on this one (I got a C), but it was a pretty easy question and Radke was full of helpful hints- I think I had just been expecting more of a fluids NSE type question or a heat/mass transfer question, and hadn't really studied practical things and so was thrown way off balance. Bleh.

SG.

My committee was supposed to be Prof Radke and Keith but when I was waiting outside Prof Radke's room suddenly prof Balsara opens the door and the first thing that comes to my mind was that prof balsara is famous for failing people ☹

Anyways.... I thought it doesn't matter who is there and I am ready. Prof Radke asked me my background and where is studied and also my name. It took him 1 min to understand what my name is but when he understand how it spells he said you name is very nice...i haven't heard such a beautiful name before ☺

Then he started with the flow in a tank problem. There is a close tank which is partly filled with water and it has some gas above it. What is the final height of liquid attained in the tank? And then transient problem... How the height of liquid in the tank changing with time? I finished the problem early and so they let me go 25 min early. It was my last exam so I was happy coming out.

CHU/GRAVES

DH.

This exam started out with a friendly greeting which set the tone for the entire experience. After discussing my previous transport training, Chu asked “I want to boil water with an electric spoon. How long will it take” What?! What the hell is an electric spoon? Fortunately he clarified: “It’s like a metal wire that you put in your coffee cup.” Ahh, gotcha Chu! I walked up the blackboard and started with a rough sketch and explained the system and what I knew. However, I drew a line to represent the wire. But Chu further clarified “No, it has thickness and is heated by an electric current. What does the temperature profile across the wire?” I knew exactly what he wanted—the BSL heat conduction problem. I explained that I will first solve for the temperature profile within the wire as steady state then switch to transient to find the time the water takes to boil. I performed the usual shell balance for a shell inside the wire, making sure I explain any assumptions and not skip any steps. After writing Fourier’s law and then assuming thermal conductivity was constant, Graves piped in “what is k a function of?” Luckily I had taken solid state physics the preceding semester AND read that first chapter in BSL which helped me provide a thorough answer. Graves then asks, “what if k is a function of temperature, can you still solve the temperature profile analytically?” I wasn’t sure since my diff-equs/calculus intuition is weak. He gave me a function: $k=\alpha T+\beta$. I reasoned that the constant, β , makes the differential equation unsolvable, but not very confidently. Graves then mentioned he was just “pulling my tail.” I finished finding the temperature profile of the wire and sketched the relationship. Then I moved on solving the unsteady state. I wrote the energy balance on the board and assumed I could invoke Newton’s law of cooling to relate the heat flux from the wire to the temperature rise in the water. Graves and Chu asked me a quick questions about which variables are time dependant: $T_{\text{wire surface}}$ and T_{water} (the former I thought was constant and still don’t know why it is not).

Since time was running out they wanted to move on. Grave’s pitched another problem: “I have two parallel plates in which the distance between the two is much smaller than the length and width. A (a gas) is flowed diluted with an inert and reacts with the surface and forms a solid layer. For example: oxygen forming silicon dioxide on silicon wafers). Using a back-of-the-napkin calculation, what is the function of the layer thickness with length?” Again I drew my system, assigned a coordinate system and stated what I knew and the assumptions (ie plug flow). I explained qualitatively what the profile looks like. “How would you allow for more even coverage?” Graves asked. So I drew the Arrhenius equation and thought “Hey, this is more of a kinetics problem!” and explained how k is temperature dependent and stated that you could cool the front of the reactor. “But what is the effect of heating or cooling the reactor on the gas velocity.” I tried to reason this from ideal gas law but made a few errors and then time was up. “We were looking for conservation of mass,” Grave stated. After making a few errors on that last problem I walked out feeling like an overall mediocre performance, but ended up doing the best in this prelim.

Take home: I performed my best—I spoke slow and articulate, sketched a diagram with a coordinate system, organized my work/equations, and wrote each algebraic step all while verbalizing my thought process. Also, know your shit—by identifying the first problem early I effortlessly solved it (ie I worked the BSL once or twice).

LL.

It was supposed to be Radke and Alexander, but Prof. Alexander was MIA that morning. But Radke’s usually the star of the show. The problem was a closed tank, isothermal and there’s a gas phase and a liquid phase. At time $t=0$, you turn on the valve that’s connected to the very bottom of the tank flowing out horizontally into atmospheric pressure ambiance. Gas can be described by ideal gas. He first

started with equilibrium conditions. Where would the water level be when it stops flowing and is it possible to still have some liquid in the tank when it stopped? Then he moved onto the dynamic part of it. Use Bernoulli's equation to connect things. Basically pull out some arithmetic Tai Chi and try to make your system of equations deterministic. He did mention head loss, which is something I wasn't exposed to in my undergraduate education. Then again, we didn't do much actual real-life chemical engineering in the classroom (unit ops? O.o). He then moved onto making the system non-isothermal by adding a jacket with a dry steam stream passing through. You simply do an energy balance and write out more equations. That modifies the Bernoulli's equation a bit. Radke liked to talk at me, so it left me little time to think quietly. Balsara was mostly quiet the whole time.

BE.

This was my last final and I was just ready to be done with the day. I thought I had done well enough on the other ones to be pass-worthy but still didn't want to blow this one off—good thing! Chu and Graves were both jolly when I came in and we started talking about Graves' chalkboard which was Lewis' chalkboard when he was in this office. After having a good time joking about using it, we got down to business. Graves decided to ask me a different problem because I am "smart," so he asked if I knew the oxidation of silicon question/ Deal-Grove problem. I said yes I did and started drawing out the system. When I started talking about some details of the system then Graves would ask how I know that assumption and I would have to give an answer that seemed to make sense but I had never really thought about. At one point I started to draw what the concentration profile would look like in the gas phase up to the top of the SiO₂ boundary layer and that's where this whole problem got diverted. From then on, they were asking me questions about how I knew that's what the concentration profile looked like and why I drew it flat in the boundary layer of gas and all sorts of things on this subject. They also asked me if it was flat or close to flat, what was the driving force. After a while, I had gotten to the point where I wrote out diffusion and convection terms and somehow set the fluxes equal inside and outside the boundary layer in order to get the ratio of diffusivities in the gas and in SiO₂. Chu asked what the ratio would be and I had no idea so guessed 10, then 100, then 1000, then 500,000 and then was told that it's about 10⁹... and that's why it's flat in the boundary layer so I was correct to begin with. They both laughed about the fact that I finished just on time to be done and seemed really ready for lunch. Overall this was a good prelim and they were both helpful and cheerful throughout, despite being hungry. I liked the way they asked questions to make me think about the problem in another way in order to answer their original questions. Great duo!

KATZ/RADKE

EY.

This exam was my first prelim and the best thing you can do as you approach your first exam is to hold your head high and smile as you enter. It may be worth mentioning that he still uses a chalkboard in his office (so don't wear black).

From Prof. Katz,

Heat transfer through a slab—draw the steady-state temperature profile? Why is it linear? Where is Fourier's Law from? (it's a scientific law, so it's not "from" a balance or theory, but rather that experiments have not proven it to be false). To get the temperature profile, set up a simple energy balance and plug in Fourier's first law for q.

$$q|_x \text{Area} - q|_{x+\Delta x} \text{Area} = 0$$
$$\frac{dq}{dx} = 0$$

$$k \frac{d^2T}{dx^2} = 0$$

$$T = c_1x + c_2$$

Prof. Radke asked for the assumptions of the analysis (steady-state, constant k-value, constant value for flux due to constant area). Prof. Katz then talked about a problem that is similar to the problems regarding the Arnold cell where there's a well and at the bottom is liquid A. Above it is air (B) and at the top of the well, there's a sweep gas such that the concentration of A is zero. He asked for the concentration at the interface (vapor pressure of A) and I discussed how the B is stagnant so it's A travelling through stagnant B. The profile will still be linear due to Fick's Law. Prof. Katz wanted to discuss if the profile may change if the molar fraction of A near the interface is close to one (or not close to one, I don't quite remember), and the correct answer has something to do to the fact that the following equation stands:

$$N_A = -\frac{D_{AB}dc_A}{dx} + x_A(N_A + N_B)$$

From Prof. Radke,

There's steam flowing on the left side of the slab and a well-mixed bath on the right side. How would you find the conductivity of the slab? First he had me draw the temperature profiles through the slab with respect to time assuming a constant steam temperature (this is a transient problem since as heat travels through the slab, the bath is being heated and thus the driving force between the two sides will be decreased). The profiles will be linear through the slab with decreasing slope as time goes forward with the same intercept on the left side of the slab. At the two interfaces, there will be the classic curves through a boundary layer and meets the ambient bulk temperature. He wanted some relationships, so I wrote the following (the second one can be written assuming pseudo steady state within the slab):

$$\dot{q} = hA(T_{wall\ (right\ side)} - T_{bath}) = \lambda \dot{m} \frac{dT}{dt}$$

$$\dot{q} = \frac{k(T_{wall\ (left\ side)} - T_{wall\ (right\ side)})}{L\ (thickness\ of\ slab)}$$

Then he asked if there were no boundary layers (i.e. very high mass transfer coefficients) to redraw the temperature profile (three straight lines, similar behavior to before but the function is no longer differentiable at the interfaces). You can combine the two equations from above.

$$\frac{k(T_{steam} - T)}{L} = \lambda \dot{m} \frac{dT}{dt}$$

$$\frac{(T_{steam} - T)}{(T_{steam} - T_0)} = \exp\left(-\frac{kt}{\lambda L \dot{m}}\right)$$

Professor Radke asked for experimental ways to find whether h is sufficiently high to ignore the boundary layer (increase the flow rate of steam and the agitation rate of the mixer in the bath). We finally discussed about Nusselt number being a function of Reynolds and Prandtl and how the Reynolds would be defined in this situation ($Re = \frac{\omega D^2}{\mu}$ since $v = \omega D$), where D is the diameter of the agitator.

Professor Radke may seem impatient at times and did tell me to "just write down the answer" at one point, but it's important to keep a positive attitude throughout and I ended up laughing along with him.

SS.

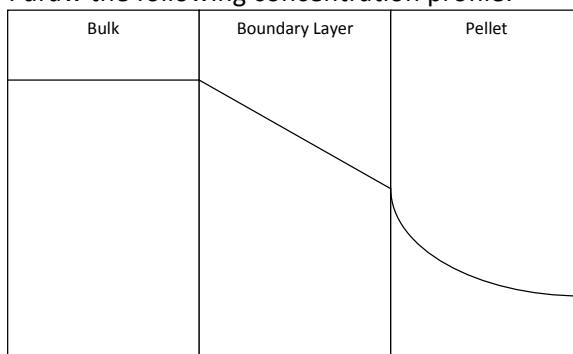
1. Katz - Given a solid object and ambient air at a higher temperature, describe heat transfer. What happens at the boundary? In which region does this boundary condition hold if warm air is not stagnant, but is flowing over a plate? What is boundary layer theory? What is the difference between Nu and Bi numbers?
2. Katz – brief derivation of mass transfer from bulk fluid A to fluid B (A soluble in B, B insoluble in A). Compare the boundary conditions here with those in heat transfer in the first problem above.
3. Radke – Given a spherical metal ball falling through a great height in air, with the air warmer than the ball, what is the temperature of the ball when it strikes the ground? Can we assume creeping flow to apply Stoke's law? What are the conditions for creeping flow? (very low Re) If we do not assume creeping force, how would you describe drag? How does drag coefficient vary with Re? (Remember, it is a log-log plot. He also asked me typical values of Cd/Re) Why does Cd flatten out at high Re?

KS.

This should have been really easy. They asked about lift on an airplane wing. I used Bernoulli to calculate the pressure change from the bottom to the top of the wing. Talked about what area I needed to calculate the force (I forgot the word for it...projected maybe?) Then we talked about a solid ball subliming in some light wind. I calculated the radius change over time and then he wanted to know how we find the concentration at the surface. He wanted a PV diagram for the temperature of sublimation (he said one for water would work) and a heat transfer equation. I should have gotten through all this in about 10 seconds, but it took me the full 45 minutes. Radke laughed a lot and Katz was really nice.

KJM.

We went over where I was from (UW) and what textbook I used (BSL). This fact struck their fancy. Professor Radke tells Professor Katz and me that he has a first edition McCabe, Smith, and Harriot, which must be pretty great to read. I just checked and the first copywrite is 1956. Anyways, we get started with a question from Prof. Katz. He wants to know about a reaction that is occurring inside a catalytic pellet. He adamantly won't tell me what the reaction rate equation is, but he will tell me that the reactant and the product are gas. I am asked to draw a concentration profile and calculate the rate of consumption of reactant. I draw the following concentration profile:



Prof. Katz wants to know why I drew a straight line in the boundary layer. I tell him the boundary layer is approximated as a slab because it is much thinner than the pellet. Right then, Prof. Radke jumps in and wants to know why I made that approximation. I repeat what I said. He replies that I just told him that, and he wants me to show him why. Basically, he wants me to prove it. I tell him I don't have spherical equations of change memorized, so he suggests a shell balance. We assume that there is no reaction in

the boundary layer, so rate in equals rate out. If the size of the boundary layer is small, then your shell balance reduces down to the 1D slab. Now, Prof. Katz wants to know why I drew the boundary layer/pellet interface as I did. I reply that it is a boundary condition. He wants to know what that boundary condition is. I reply that the concentrations have to be equal (continuous across hydrodynamic boundaries that are in the same thermodynamic phase) and that the fluxes are equal. Again, I have said too much. He wants to know if the flux is continuous. I said yes. We then match our fluxes and he walks me through, showing me that if the fluxes match and the diffusivities are different, then the concentration profile is not continuous. Finally, Prof. Katz wants to know the rate of consumption. He still won't tell me anything about the reaction; I try to find creative ways to get this information out of him. In a stream of consciousness, I keep babbling around, not getting anywhere, and I can tell that Prof. Radke is starting to get frustrated. He asks me what happens to the reactant that goes in the pellet. It reacts! But I only recognize this in retrospect. I say that there is diffusion of the reactant out. Both of them study me, and I am wholly unsure of myself. Prof. Radke directs me to my diagram. "What is the slope at the center line of the pellet?" he hints. Zero! Of course! What goes in reacts! Satisfied, it is now Prof. Radke's turn.

We now consider an infinite horizontal plate that has a uniform liquid on top. Prof. Radke then pulls the plate horizontally with a constant velocity. What does the velocity profile look like as a function of time? I try to impress them, asking if it is appropriate to assume that the shear at the liquid-gas interface is zero. "Is the viscosity of the gas much smaller than the viscosity of the liquid?" I ask, looking for a smile or a nod. The plainly affirm, and I am left wondering if that is a good thing or a bad thing. I draw to profile, with a flat velocity profile at long time. Prof. Katz nitpicks, and asks me if I am applying my boundary conditions correctly. I realize that the velocity slope at the liquid-gas interface should be zero, and accordingly modify my profile. Now, Prof. Radke wants to know the power required to pull the plate. "At steady-state, it is zero," I confidently state; I remembered this problem from undergrad. But now he wants to know the power before steady-state..... "Well, power is energy per unit time." I am clearly stalling, but they play along with my game. I keep trying to figure out how I can express power in a useful way. Purely based on units, the suggestion of power equals force times velocity comes up. I am not sure which of the three of us came up with this relation, but it was written on the board nonetheless. I know the velocity, which is the velocity that Prof. Radke is pulling the plate. But I have no idea what the force would be. Prof. Radke practically tells me outright that the shear stress is the force. So, $\tau_{yx} * v_0 = \text{Power}$. What is the power at Δt ? "Well, it would be infinity, because the slope of the velocity at the wall is infinite," I state frankly. Prof. Radke tells me that this actually isn't true and there are "other" effects that make the power finite.

This committee was really hard to read. I thought that they asked rather simple questions, but they would nitpick everything. Be sure to be able to draw concentration, velocity, shear, and temperature profiles and understand why everything is the way it is. Is your variable continuous across a hydrodynamic boundary layer? What matching conditions exist? If you know how to do this, and justify it using equations, you will do very well. I didn't have to know any dimensionless numbers, and they even seemed frustrated that I tried to bring in the Biot number and the Thiele modulus, because they were not relevant to my problem. Finally, verbally and methodically going through your units, sign conventions, and notation seems to make them happy. Good luck!

BR.

Radke did most of the talking during this session. You are given a tank of liquid with a gas head above it. The gas is not soluble in the liquid. The container is close at the top and has a tap at the bottom. First, I was asked to figure out what the final level of water would be if you open the tap, taking into account the pressure of the gas head and the changing pressure of the water column (Bernoulli's equation). I was asked to mathematically describe the conditions that would determine if any liquid remained in the

tank. Then the complexity of the problem increased! Now we add a saturated steam heating jacket on the outside of the tank. Assume vapor/liquid on the inside of the tank is uniform in temperature throughout, find the transient temperature profile in the tank over time. We went about setting up the Energy balance for this problem. Both Radke and Katz were very helpful and kind in guiding in the right direction.

GRAVES/CLARK

KM.

This exam consisted of one multi-part question. We were concerned about the design of a fluidized bed operating at steady state. The catalyst particles are spherical and the reaction A→B occurs homogeneously in each particle. I was asked how I would approach this problem:

- 1) We will treat the fluidized bed as a PFR. We can write a shell balance in order to find the design equation: $\frac{dF_A}{dV} = r_A$.
- 2) Write a mole balance around a single catalyst particle. Start with the molar continuity equation for a species in spherical coordinates. We can cross out many terms based on the following knowledge of the system:

- We are solving at steady state so cross out the time-dependent term.
- We can neglect convective transport terms since we have equimolar counter diffusion (since we have a reaction A→B). Even if we did not have equimolar counter diffusion, we could make this assumption if A was dilute.
- The reaction is described by the term $R_A - x_A \sum_\beta R_\beta$. Because we have the reaction $A \rightarrow B$ then $\sum_\beta R_\beta = 0$ and we can neglect the second term.
- We assume the diffusivity is constant.

We are left with:

$$D \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial x_A}{\partial r} \right) = kx_A$$

- 3) I wrote out the boundary condition, in which the flux at the surface of the particle (at $r=R$) is set equal to the mass transfer through the boundary layer:

$$Dc \left(\frac{dx_A}{dr} \right)_{r=R} = k_c (C_{A,bulk} - C_A|_{r=R})$$

I was asked how I would find the mass transfer coefficient; the mass transfer coefficient can be found using a correlation for the Sherwood number. I was asked to postulate the functional form of a correlation for the Sherwood number in terms of the Re # and Sc #. We approached this in part by rearranging the above boundary condition and non-dimensionalizing in order to demonstrate that the Sherwood number is simply a dimensionless concentration gradient.

- 3) I was asked what dimensionless group describes the processes within the catalyst particle. The Thiele Modulus describes the competition of reaction and diffusion. The effectiveness factor can be used to account for the geometry of the particle (spherical in this case) and transport limitations. We can find the effectiveness factor from a chart. We can also determine it analytically, although this may be difficult if the flow patterns are complicated.

General Comment: Both Professor Clark and Professor Graves provided useful feedback and as we went. A very friendly committee.

JW.

So before this prelim, I pretty much memorized every single problem Graves has ever given. While this is a good idea, you can be sorely disappointed when he asks a new question. And of course I was lucky enough for this to happen to me.

The problem consists of a fluidized bed with solid spherical pellets with substrate coming in as liquid. He wants to know conversion in this reactor. While this problem in retrospect is not that bad, at the time I freaked out because I wasn't prepared for this. I was ready to answer flow down an inclined plane!!! So I just started with a mass balance inside the spherical pellet to model concentration of A (in a first order reaction A goes to B). This is pretty standard mass balance that you can find in Fogler in Chapter 12. This is the same differential balance you start with in order to derive Thiele modulus. So after getting concentration of A as a function of radius in the pellet, I can write down the PBR design equation and find conversion from there. Next up, Graves asked about how to get mass transfer coefficients. So I mentioned Nusselt number and how it is a function of Reynolds and Prandtl. He asked for an explanation of each dimensionless number but I was not prepared for the question of WHY it is a function of those two. I really struggled long and hard with this until basically Graves told me the answer. It is because both numbers relate to the boundary layer thickness of momentum/mass. He asked me to write down the correlation and then Clark wanted to know why it was a 2 in the correlation. It is because minimum Nusselt number is always 2 and I explained how you would derive it. At one point, Clark also asked what are assumptions of PBR (or PFR). This is a straightforward answer in that there is no axial dispersion but then he asked how I would change my design equation to account for that. I was totally at loss and by this point, I just wanted this prelim to end. After a lot of prodding, it is that you add the diffusion term in the design equation. I probably would have come up with that easily any other day but just being asked a question that I wasn't expecting really threw me off so don't just count on being asked questions you have already read about.

Then Clark asked me about a water bubble falling and at what time it will evaporate completely. I first derived the terminal velocity (Stokes law, laminar assumption) and then did a heat balance on the drop where the volume is changing as a function of time. Instead of writing temperature difference, I wrote difference in concentrations in a heat balance. Wow, Clark must have thought I was a total idiot. After this, it was finally over and they actually were really nice at the end. I thought I might have failed because of their quiet demeanor during the whole ordeal but I still passed. They are tough and don't give much hints while you are working but just be confident and do not be thrown off. God, those people who got flow down an incline plane....so lucky.....

SP.

Graves started by asking me about my transport background. I didn't do a ChemE undergrad, so my transport background is lacking. Graves then decided to ask me what he called a "classic chemical engineering transport problem," namely predicting how much conversion you would get for a reaction A \rightarrow B in a catalytic packed bed reactor. I started by drawing out my understanding of the problem, namely looking at an individual catalyst particle and the internal and external mass transfer resistances. I stated the boundary conditions, fluxes between the external and internal boundary layers are equal, no flux at the center, and the concentration outside the boundary layer is equal to the bulk concentration. They stated that I was approaching the problem in an unconventional way, but they seemed to be fine with me continuing look at the problem in this way. I modeled the external mass transfer with a mass transfer coefficient, which they said was fine and then I started doing the shell balance to get the internal concentration profile with a reaction occurring inside the pellet. Clark doesn't seem to like to watch people slog through shell balances, and he said I could just write down the answer if I wanted to. I tried to write it from memory, but I couldn't get it quite right and he said if I needed to I could work through the shell balance. He didn't seem too upset by this, but I think I would have scored points if I had just written it from memory. They then had me talk about how I would relate the mass balance that I had just done on a single particle to the entire reactor. I talked about how the particles in a cross

section would all experience the same concentration assuming radial dispersion is high enough and we could use that to do a mass balance on the reactor and I wrote a few equations to describe this. We then talked about how diffusion in the reactor would affect the concentration profile and what the relevant dimensionless number would be for describing this (Peclet number). They asked how I could know if I could neglect the external mass transfer layer and after fumbling around and getting some hints as to what they were looking for, I realized that if you increase the Reynolds number, the external mass transfer layer thickness decreases. We talked about correlations between the relevant dimensionless parameters for this problem, (Sherwood, Schmidt, Reynolds) and how viscosity of the fluid (i.e. Schmidt number) plays into the boundary layer thickness. Clark and Graves we're cordial through the entire exam, but intent on probing what I knew. I didn't always get what they were looking for right away, but I kept talking and eventually I got to what they were interested in through some combination of hints and my own thinking. Know your dimensionless parameters for this pair and what they mean. I passed this exam, but I think I would have done better if I had come up with answers more quickly.

JS.

After asking about my classes and textbooks, they told me they would ask me the same problem they had been asking during the day: a packed bed reactor with pellets. I started to work on a balance similar to the one used in kinetics to derive the Thiele modulus for a slab configuration. But, they told I had spheres, so I started doing a shell balance in spherical coordinates. I was messing up, and they asked what was each term, what units did they have, where was I doing the balance (I said a pellet sphere). Then they said I needed to combine that with the concentration at the exit of the reactor, so I wrote the mole balance for a tubular reactor. They said that I was missing an additional term, and after awkward silences and help from them I added the missing term, which accounted for dispersion (they had also asked me to explain what dispersion was). Then they asked about boundary conditions in the shell balance (surface concentration at $r=R$ and $(dC/dr|_{r=0}) = 0$). They did not seem very happy, and time was running out, so they asked me about mass transfer coefficients. I talked about the analogies between heat and mass transfer, dimensionless numbers, and the correlation for a sphere in creeping flow. Then they asked what was the significance of the Prandtl and Peclet number, which dealt with how the boundary layers increased/decreased in thickness relative to each other. Then time was up, and I left the room.

K I N E T I X

REIMER/CLARK

BE.

This was my first exam and it was also the first exam time spot. When I walked into the room, Reimer and Clark seemed to be in good moods and asked me about my background, commenting on the fact that I'm one of the few people who did not use Fogler for undergrad. I felt great starting out and actually throughout the entire exam, however the grade did not reflect that at all. Clark started out by asking me a question about a packed flow reactor. First I wrote out the design equation of $dF/dw=r_a$ and then he asked me something about "is it?" and then I was going to start deriving it from a shell balance until he stated that he just asked and didn't need me to derive it if I knew that that's what it was. He then asked if I have 2 different reactors with same dimensions and everything and same weight of catalyst but catalysts in one reactor have half the diameter of the other, will there be one reactor with a faster rate. I initially said that these design equation only takes into account the mass of catalyst, so on that basis, they would give the same rate. Then he asked me to draw the catalyst particles and I realized that there would be issues with diffusion. I immediately started talking about how it could be diffusion limited in the larger one and then went into talking about the Thiele modulus and effectiveness factor. I described the general ideas of them and even drew out the plot of effectiveness factor vs. Thiele modulus. They then asked how this was relevant and what terms were most important. I couldn't remember the exact terms but knew that there was an r^2 in the numerator along with a $k^*C_a_{surface}^{(n-1)}$ and the denominator had diffusivity. We spent a while going through what terms go into the real equation in order to cancel out some of the r^3 and r^2 and all that in order to get the final equation that I had. After this, they kept asking questions about when it would be diffusion limited or kinetic limited and it seemed like there were a lot of these types of questions that made me keep giving very similar answers... Clark asked his initial question again and I had to talk about adding in the effectiveness factor on one side in order to show how the radius would make a big difference in the rate of one reactor as opposed to the other.

After this, they stated that they only had 5 minutes left for another question and asked if I wanted to answer another. I said sure and then joked about how I can't really say no to that question... Reimer ended up asking me a question about butane going to butene and then to butadiene after a long enough time and we want to know how long to let the reaction continue in a batch reactor to just get butene. I initially wrote this out as A to B to C and then was going to analyze the activation energies. Reimer stopped me and asked if this made sense since it was a dehydrogenation reaction and I said no, they would have about the same activation energies, so I moved on. He said this was a textbook answer and not what he was looking for, but apparently he says that to a lot of people. I then proceeded to draw a graph of concentration vs. time in a batch reactor and said that the longer you run the reaction the more of the butadiene you will get, which you don't want. At this point, they said that was enough and let me out 5-10 minutes early. They were both smiling and seemed in good moods still when I left. I thought this exam went well and was even told that I had a huge smile after finishing, however I ended up barely passing this specific prelim. I can't pinpoint what went wrong in this exam or how they thought I didn't understand the fundamentals, or how I might not know how to present myself since I did everything that I was advised to do in an exam and even felt good about it. I was told by many people that they will keep you as long as they need to up to/over time limit if they're not sure you're going to pass, but that wasn't the case for me. Needless to say, don't take a smile and an early let-out as a good sign, or that you think you did well...

LL.

Personality wise Katz was very nice and was always maintaining a smile. Smit offered a blank expression most of the time. Katz was doing most of the questioning, while Smit, is apparently a freestyle master. So be ready for what he throws at you.

After inquiring about my background, we began with pretty much a freebie question with Katz. What's the residence time of an inert substance in a CSTR (V/v) and PFR (L/u). He didn't display a satisfactory gesture when I wrote that out, so I said more about residence time distribution. But apparently that's all he wanted, so he cut me off and moved onto the next question, which was a spherical catalytic particle with no internal diffusion limitation. Draw the concentration profile of the reactant A, etc. I got really hung up on this question about why my concentration profile inside the pellet is constant. He insisted that there should be a concentration gradient since there's no source inside the pellet and mass has to be consumed by the reaction at every point. But I kept thinking to the definition of effectiveness factor, which equals to 1 when there's no diffusion limitation. That also implies that every volume element is reacting at the surface concentration \rightarrow CSTR with a defined non-zero concentration.

Anyways, that sort of distracted me for the remainder of the exam. One other mini question he asked associated with this system was why at the pellet's outer surface, there's no convection. And that's due to the no-slip boundary condition. There's also a series of questions on the slope of the concentration gradient at the boundary.

Smit then had the floor. You have a protein in conformation A, that always screws up and folds into conformation B. Write the rate expression. $r=k Ca$ by law of mass action. Draw out the exponential decay with respect to time. Now your colleague says that the cell cannot survive if number of A conformation proteins drops below 10% of its starting value, and let's say that occurs at the 10th minute. So it should be okay if he takes it out at the 9th minute. But when he actually took it out at the 9th minute, all the cells have died. What happened? (I know it's a long background story). At first, I blanked for a second. I said that maybe it's due to the distribution of k, the rate constants? Since it's sort of a stochastic process how these proteins fold? I should've known better not to delve into stochastic processes, because he somehow got excited, even though at the end it was not the answer he sought. He made me write out what's called the master equation given that there's a fixed probability for a protein to fold into B conformation in a tau time interval. $N(t) * P(folding) = N(t+\tau)$. Something like that, don't blame me if I remember it wrong. He then had me draw out the number of proteins in a cell if there are only 10 proteins in a cell (at t=0) with respect to time (step functions like stairs stepping down, with the highest step the shortest and lowest step the longest). He then assures me that it's not due to stochastic process (I wasn't very convinced by his argument, but I went along with it). Back to the drawing board, so I guessed because the process is nonisothermal and k's temperature dependence is exponential. He seemed to accept that and said time was up.

REIMER/CHU

JW.

This was my first prelim so I wasn't sure what to expect. Standard chit-chat ensued followed by Reimer flipping the coin to see if he or Chu will ask questions first. Chu called heads and it was heads. So Chu asks me to write out general steps and derive the rate equation of a Michaelis-Menten. Thank god that coin was heads. This is a very standard prelim question so obviously I had studied it over and over again. Chu then asked about the affinity constant which is explained in Fogler. He then proceeded to ask me to draw an energy diagram along a reaction coordinate. The key is to draw two activation barriers, with the middle "valley" corresponding to the substrate-enzyme complex.

Next, Reimer asked me how rate constant depends on temperature. He then asked me to graph $(1/T)$ versus $\ln k$ which is just a standard Arrhenius plot. He then says that one time, a student asked him how

two reactions with the same activation energy might have different rates. The answer obviously lies in the frequency factor (A). He asks what does it mean for the frequency factor to be different. I started to talk about collision theory but he stops me and wants another kind of explanation. I kind of struggled with what they wanted until it was clear he wanted to go to a stat mech/TST explanation. So writing K_{eq} in terms of ΔG and then also utilizing that $\Delta G = \Delta H - T \Delta S$, you can arrive at a TST expression for the rate constant. So the answer is differing A's is in the difference in deltas.

With some time left, Reimer just asked me a softball question about reaction series where A goes to B goes to C. This is very generic question and he wants to know how do I get the most B because it is the desired product. By assuming constant volume batch reactor, I wrote out simple design equations and then find the rate of dC_B / dt and where $dC_B / dt = 0$ is the optimal time where concentration of B is the highest.

Very standard questions. I felt lucky that I got these not so difficult questions but I didn't get as good of a grade as I thought I would. You never know with these things.

KJM

Prof. Reimer begins by describing the reaction in a catalytic converter. Perfect! I have done a report on catalytic converters before. I am asked to consider the reaction of nitrogen oxide and carbon monoxide to nitrogen and carbon dioxide. I am told that the reaction occurs on the surface of the catalyst. I am asked to describe the reaction rate as a function of carbon monoxide concentration. Reaction rate increases with CO concentration until a certain value, when there is not enough surface occupation of nitrogen oxides and the reaction rate slows; this problem follows Langmuir-Hinshelwood kinetics. I am told that we will model the catalytic converter as a CSTR and I am asked to give the steady-state reactor equation. Then, I am asked to overlay this plot with the previous plot I made. This plot looks like a line with negative slope intersecting a Gaussian distribution in three points. Then I was asked about the steady-state operating points, and which ones were stable and which were unstable. Using careful reasoning, I used the fate of perturbations from each of the steady-state points to argue the stability. Prof. Reimer then asks me a CSTR catalytic converter is a good idea. Because the catalytic converter has a stable steady-state point at low conversion, a CSTR is a terrible idea in this application. A PFR is more appropriate. I then go through the design equation for a PFR, we talk about how catalytic converters require "start up", where there is no conversion until the exhaust heats up the catalyst to the operating temperature. This goes briefly into the temperature dependence of a reaction rate.

Thus far, Professor Chu has said little, and he now takes the reins and offers his question. I am asked to consider another surface reaction that is occurring between two parallel plates, where the product deposits on the surface, causing an accumulation. He tells me that there is a concentrated inert gas and a reactive, dilute gas flowing through the reactor. Prof. Chu affirms my assumption of a PFR and I am asked to describe the rate of accumulation on the plate surface. He is very vague about this problem; I am not told the reaction order, just that the reactants are gas and the products are solids. I write the PFR design equation and struggle with the reaction term. Methodically, I am checking my units verbally, because I want to give the rate per unit surface area. Prof. Reimer pipes in and asks me to do a shell balance. When I voice concern that the volume is changing as we move down the reactor, Prof. Chu tells me to remember what he told me at the beginning. Of course! I cut him off with a very loud "ohhh!" The concentration of inert gas is much larger than the concentration of the reactant, and volume is essentially constant. Once we get the correct design equation, I am asked to draw the concentration profile. I drew exponential decay from the inlet to the outlet. Then, Prof. Chu tells me that this would be the "thickness" profile of the solid layer. In other words, more reaction would be occurring at the inlet and more solid would deposit there as a consequence. We, I am told, don't want this. We want an even

layer. I offer a thermal gradient, in which the temperature increases as the gas moves down the reactor. I then, stupidly, overstate my point and say that this would be true only if we have an exothermic reaction. I see both of their eyes light up; they have caught my weakness. I am asked to restate my point. I make an $\ln K$ vs. $1/T$ plot, which I do correctly (but for K_{eq}). The only issue, of course, is this is a non-equilibrium reaction. We continue down this path, and I am asked for the temperature dependence of the reaction rate constant. I write an Arrhenius relationship. I then write, in large, dry-erasable writing, that the reaction rate will increase for all reactions, because the value of E_a is always positive. Of course. I am then asked for what 'A' is in the Arrhenius relationship. I reply it related to the change in entropy for the reaction. He likes this answer and asks me how we can change A without changing E_a (on the $\ln K$ vs. $1/T$ plot, this would translate to a different y-intercept but the same slope). After pausing for a thought, I argue that a phase change in the reaction would like result in a different entropy change, but, as long as the transition state is the same, the value of E_a should be identical. I can tell Prof. Reimer wants to interject, and he tells me that enzymatic reactions are another example, due to conformational changes that change its solvation. I nod, unsure what I should say. After resolving my gaffe, we can now return to Prof. Chu's problem. He asks me to consider a new orientation of the reactive plates. They are now closer at the inlet than the outlet. What is the thickness of the deposits as a function of distance? I state, "we will need to return to the fundamental equations that I had wrote earli..." "There is no time! What is your intuition?" interjects Prof. Reimer. I then say that the concentration will be much larger at the inlet, as the volume decreases. Thus, I reason that the problem of uneven depositing will be exacerbated. I am told to clean the board and to not tell others about my exam. I thank them and leave. When I check my watch, I see that there is still 15 minutes in my time slot. I am elated; I felt really good about this one, as I was able to catch a lot of my mistakes quickly.

Overall, this committee is really enjoyable. I get the feeling that both Prof. Reimer and Prof. Chu wanted to share their knowledge and talk about science. I never felt that they were prodding me for answers. They seemed to really like that I was very verbally careful with my units. After my under whelming performance in Thermo, I was really pleased after this one. Most important of any advice is to remain confident that you know the material (because you undoubtedly do know it). Don't let a bad performance bring you down.

BR

Chu led most of this discussion. We focused on the Michaelis-Menten Problem. Setting up equations, plotting the free energy versus reaction coordinate for reactants and products. I was asked to use transition state theory to derive and explain the nature of the reaction rate constants.

Reimer- tube reactor problem from his days at IBM in which there is a non-uniform deposition of silane on wafer. What would you change to make the deposition uniform? (the problem has to do with diffusion limitation of the reacting material onto the wafers. Without changing the spacing in between wafers, you can adjust reactor size to improve diffusion to the surface. We didn't get to this problem until near the very end; see notes from previous years when it has been considered in depth.)

SS

1. Reimer – A liquid-phase reaction occurs in 2 different solvents with different rates. The activation energies are the same. What is different? (pre-exponential factor) How can you determine this factor? (not collision since this is a liquid-phase system) – Transition state theory. What part of the rate expression in TST accounts for the pre-exponential factor? (Entropy change, which I did not remember, and hence they made me derive from scratch)
2. Reimer – Batch reactor with $A \rightarrow B \rightarrow C$. Sketch rough profile without solving. Then write governing equations, and determine operating conditions (i.e. time) to obtain maximum B.

3. Reimer – Langmuir-Hinshelwood in a CSTR. Sketch flow/rate vs. conversion. Multiple steady states are possible in this case. Define stable and unstable points. What must be the starting point to obtain maximum yield? The answer to this shows that CSTR is a bad idea to run this type of a reaction
4. Chu – Catalytic converter. $\text{CO} + \text{NO} \rightarrow \text{CO}_2 + \text{N}_2$. Balance reaction. Reaction occurs between 2 flat plates. Write governing equations and obtain the profile wrt length of the reactor. If one of the product/condenses or deposits on the surface, find the film thickness wrt length. How can you obtain a uniform rate of deposition? (run the reaction non-isothermally, increase T at higher lengths)

KATZ/SMIT

SG

Prof Katz asked the first ques. It was about the differential reaction. He asked what is differential reactor and what is special about differential reactors? What are they used for? What is the design equation and rate law expression for the elementary reaction $A \Rightarrow B$. Which concentration do you use in the rate law? Does that matter which type of reactor you use i.e. CSTR or PFR? And why? Discuss the heat transfer in Differential reactors? I told them that temperature inside the differential reactor remains const and explained why this is so. Then he asked me to draw a plot for rate with temp whichever way I want. So I drew $\ln(\text{rate})$ Vs $1/T$. He then asked what the slope is and says that while checking that experimentally he finds that at high temperatures the curve become flat. He asked me to explain what would be happening. The reason is mass transfer limitation. He then asked me to explain what internal mass transfer and external mass transfer limitation means. How the above curve changes in the two cases. In the discussion the obvious parameter that show up was Thiele Modulus so he asked what does this represent and what is the significance of its values high and low. Then after this Prof Smit's turn... "you have a first order reaction going on ...write the rate law and draw concentration profile. I asked which reactor is it ..he didn't give me the straight answer and he start asking about all the reactors and when they are used . Then finally he agreed to assume this as batch reactor. He then added that after 10 min you have some conc in the reactor which can be obtained from the plot. And the problem with our cells is this that if the conc goes below this value then all our cells will die which we donot want. But when after 10 min this conc reached and we stoped the reaction ..we found that many of our cells are already died. What do you think is happening and give me solution for this problem. This followed by some weird question answers : Why all the molecules doesn't reactor at the same time when they are well mixed. Give the microscopic and macroscopic view of the problem. Some other protein folding and cell questions...I donot exactly remember...I think he asked same ques to others as well so take a look at those ans.

SK

This was a really strange exam. After the usual chat where I told them that MIT only had $\frac{3}{4}$ of a semester of kinetics (plus I had taken Iglesia's class, which I feel has all the kinetics you might ever want to know...) Smit told me that everything I had studied was fair game, including thermodynamics. I should have realized that this was foreshadowing for the horror to come.

So we started with Katz asking me questions about an unknown reactor with an unknown reaction. You want the activation energy of this reaction. What do you do?

So I first talked about probing the reactor with tracers and what that would look like for CSTR vs PFR, but that wasn't what he wanted. But he let me explain. Then he said, suppose you find that your reactor is sadly non-ideal, full of dispersion but not a CSTR. I indicated that I would be sad.

Then he gave me a hint about differential reactors. Aha! I had just done this the day before, so I explained how it worked for PFRs (small amount of catalyst, very little reaction, so you assume that the concentration is constant at the mean of the inlet and outlet concentrations) and was briefly confused about how it works for CSTRS/general flow reactors, so Katz prompted me by asking about the flow rate. So I figured out that to have really low residence time (and thus “differential” concentration changes) you need epic flow rates, and after that I wrote down the expression for the reaction rate with the Arrhenius expression for the rate constant, and also what the overall change in moles per volume per time was equal to this. So then if you plot $\ln(-ra)$ vs $1/T$, you get a straight line and the slope of that line is $-E_a/R$. And he also asked me how to get reaction order, and for that you keep the temperature constant but vary inlet concentration so that you can plot $\ln(-ra)$ vs $\ln(C_a)$ and the slope of that line is N , if your rate is $-ra=kC_a^N$. This part went pretty well, and Katz seemed pretty happy with my answers and how quickly I got to them.

Then Smit took over, and drew this setup on the board where you have two chambers connected by a small passage. In one chamber you have pure gaseous A. When A gets to the other chamber, it reacts immediately. He wanted a quantitative expression for the rate of reaction. Bleh. So first I thought that maybe this was diffusive and I wrote down that flux, but it turns out that there aren't concentration gradients, so that's not your driving force. ☹ So after several leading questions I got that the reason that the reaction rate wasn't infinite was because the particles had to go through the passage, and to do this they had to end up there by chance. So I suggested that collision theory could explain this and Smit was sad, obviously, and instead wanted me to talk about TST. So I wrote down the Eyring equation and Smit stared at me some more and I might have said something about partition functions, and then he said that (obviously) the driving force was ENTROPY difference between the chamber and the passage. Bleh. And then he wanted me to find this, and I said I remembered you could get this from the partition function so he asked me to write down the partition function of an ideal gas... at which point I was thinking to myself, “Really?? We didn't even have to memorize this for your class”. So of course I told him I didn't remember the form, so he gave it to me, and then asked me what the factor in front of the integral was, and seemed very upset when I couldn't remember the exact form of the de Broglie wavelength. At this point we had like, 15 minutes left, and he seemed to sort of give up on me in disgust and told Katz that he was done.

Katz decided that he had one more question, and asked me about the residence time distribution of a CSTR. I write it down, and then he had me derive it from the transient balance with no reaction. And I might have said something about convolutions and tracer experiments, as convolutions make me happy. I got out like 10 minutes early, utterly confused about what would happen with this exam, as I had completely nailed Katz's part and utterly failed at Smit's. I suspect that he took me sleeping instead of attending his lecture personally. It turns out, I got a B, so hurray for me!

DH

This was by far my worst prelim. I felt fairly prepared, but these two dudes managed to find the gaps in my knowledge and pry at these insufficiencies. Prelim write-ups from previous years stated that Smit and Katz love TST, so studied it quite a bit—apparently not enough. I walked into the room and both appeared comfortable but probably hungry (Smit was eating and peeling a tangerine). We shared a brief chat about my previous kinetic instruction. Then Katz informs me that he and Smit will ask me kinetic questions that will require me to wear an assortment of “hats” (metaphorical, I assume). “We have a reaction $A \rightarrow B$. What is the rate constant?” I assumed it was an elementary reaction and wrote the Arrhenius equation. “What are the units of A?” he followed up. I assume first order and find the proper units ($1/s$). “What is A?” he asked. “Frequency factor” I answered. “What does that mean?” My thoughts: hmm...usually in a bimolecular reaction it accounts for the frequency at which the reactants collide. But Katz presented me with a unimolecular transformation, ie isomerization. Unfortunately I did

not verbalize this and Smit interrupted and asked what the meaning of the exponential part of the equation. I explain that comes from transition state theory. "Is this a kinetic or thermodynamics property?" he asked. "Kinetic?" I unsurely answered provoking a strange face from Smit. Fortunately I knew the derivation of TST. Starting from a sketch of the reaction coordinate, I stated the assumptions and tossed in the necessary definition of equilibrium, Boltzmann equation ect ect to arrive at the TST equation for k. Smit seemed slightly pleased with this. So I explained the exponential from this expression and discovered: "oh, it's a thermodynamic property." "But what is A?" Katz asked again. I explained that it lumps the entropic properties (partition functions) of the transition state over the reactant. "What does that mean?" he continued. Aghhh! What does he want!! Flustered, I stared at my scribbles on the board. After a few moments Katz and Smit lead me bit by bit to the answer: the speed of reaction. I erased the board and Smit asks, "I want to measure the concentration of reactant A over time. How can I do this?" I waited for more information but he sat and stared at me. I asked what I had at my disposal. "Whatever you need," he said. Nice! This is easy with a batch reactor. I drew a batch reactor and began to describe my method of running the reaction with different time but I was interrupted by Smit: "Don't use a batch reactor. Use a CSTR." This should have been just as easy. However, I was mentally fatigued and dismantled from the first question, compounding with the first two prelims, my brain shut down and I struggled to answer this question. Because of the ill defined nature of this problem, it became a question-improve session for Smit and Katz. Fortunately, they were merciful and gave me hints to minimize quiet moments between my verbalized thinking. I don't remember the details of this question set. However, I remember feeling like I didn't know anything about kinetics much less chemical engineering at this point. I left the room exhausted and the feeling that bombed this shit out of this one.

Take home: make sure you verbalize and continue asking you panel to clarify/better define the question if you are unsure. If not, go ahead and start making assumptions and wait for them to interrupt and better specification in the problem.

BELL/SMIT

KS

This was my first and worst. Should have been easy, but I find Smit hard to follow. They asked about a reaction of A and B go to C. Talk about the rate of reaction. They wanted me to write the law of mass action for it and explain the assumptions in it. I forgot what all I said but I forgot that it assumes uniform distribution of A and B. So they attempted to make me say that for quite a while (I think Smit tried to give me hints but like I said, hes hard to follow). Then Smit said he had some protein and he wanted to know about the rate of its degradation. He said I had a CSTR (a perfect one, we mentioned tracer studies during this). So i told him how to find the order of reaction and rate constant. Then he said he used my data and modeled some cells and some of them died before their protein should have run out. Why? I was supposed to realize that each cell only had 10 proteins and so that nice smooth exponential decay for first order degradation doesn't apply. Took me a while to get there. Then Bell piped up and asked about an adiabatic CSTR. By this point, Smit had me so flustered that I couldn't even get the equation correct. I told them to have a nice day on my way out and Bell replied "I'll try" in the most exasperated tone ever. Somehow, I passed.

SP

Smit and Bell started by asking me about my kinetics background. The first question (from Smit) was about how I would get a rate law for a protein unfolding reacting using only a CSTR. I set up mass balances, and talked about how I could plot k as a function of C, by rearranging the equations in such a

way that you could make a plot of the rate of the reaction for several concentrations of A. I had some trouble explaining this in the way that Smit wanted, but he eventually was satisfied by my answer. They then asked me about how I could get a relationship between k and temperature. Talked about the Arrhenius relation and making a $1/T$ vs. $1/k$ plot. They then asked me what each of the terms in the Arrhenius equation meant. The E_a term is fairly obvious, and they asked about what that meant on a molecular level. The A term gave me a bit more trouble and I talked about how one gets that from TST and with Smit's help we decided that was an entropy term. They then asked me to talk more about TST and I explained the assumptions that went in to its development. When I started talking about how the 2nd step is irreversible and they asked me if one could use TST if the 2nd step was not irreversible. I said no, but they kept asking me about this and I never quite got what they were asking for. The next question was an energy balance to find the exit temperature for a reactor. I set this up and had a little trouble remembering that $\Delta H = C_p * \Delta T$, but Smit eventually gave me a hint. I also didn't listen closely enough to the problem statement from Bell to hear that the reaction was 1st order, so they let me flounder around for a bit before reminding me that it was first order. After that Bell seemed satisfied. Bell then asked me how does a molecule know that it's experiencing a higher temperature. This lead into a discussion of the Maxwell distribution and temperature, but I never got quite what Bell was looking for and we ran out of time.

Tips for these professors: This pair is really good at finding what you don't know well and then zeroing in on that. If they could tell I got a question, they wouldn't let me spend much time on it and we would move to something else. I would say the best way to prepare for this pair is to practice with people (who don't give you many hints) asking progressively more theoretical and ill-defined questions. Listening very closely to these two is also very important, as they won't help you out right away if you've missed something. Smit wouldn't explicitly ask me a question, so I would repeat back to him what I thought the question was to make sure I was answering what he wanted.

JS

Bell began by asking me what a rate equation was, and what the order represented. Then, Smit asked what was the highest possible order. I answered that I thought order 3 was possible, although not very common, and that if order 4 was possible, it was probably the highest, since it was unlikely that four molecules collided with the right orientation needed to carry out the reaction. Bell then asked what the rate constant meant, so I wrote the Arrhenius equation and talked about activation energy, the fraction of molecules having enough energy, orientation, etc. He continued asking about molecules coming together, so I talked about collision theory. I tried switching to transition state theory, saying it was more accurate than collision theory, but they told me to go back to it. I drew the cylinder where you have molecule A passing through B, talked about reactive cross-section, and with their help got an expression for the volume it would displace in a given time interval. Then they asked me about the effects of mass and size.

We moved from collision theory, and they asked me to write the rate equation for a simple reaction of unknown order, in which $A \rightarrow \text{Products}$. He asked me how I would determine the parameters in the rate law (k and α , the order with respect to A) in a CSTR. I started with a mole balance and derived the design equation for a CSTR. Then, before proceeding, Smit asked me if I knew right away that I had a perfect CSTR. I then talked about residence times, and how I could determine the residence time distribution to see how ideal of a reactor I had. I drew the distributions for an ideal PFR and an ideal CSTR, and then Smit asked if there was any way I could put that into an equation. So I said I could derive the residence time distribution equation for a CSTR, and I started writing out the mole balance and crossing out terms. Then Smit said that I had determined I had a perfect CSTR, so I could continue with my previous analysis. I kept using the design equation I had from before, put it in terms of conversion (no idea why, it wasn't

necessary), and after some hints I had an expression that could be rearranged and plotted, after taking logs, to give out k and the order. I took longer than I should have in this part, even though it is a completely and elementary problem.

Then, Bell asked me how would I model the changes in the concentration of a protein within a cell. So I said we could use a batch reactor model, derived the design equation, and for a first order reaction (they said I could assume I had a first order one), derived the expression for concentration as a function of time. Then they asked me if I could draw it, so I did, explaining that we had an exponential decay. Then Smit asked what would happen if I had a very low number of proteins, what would the plot look like. I was unsure at first, but with their hints I drew what looked like a step function. Then they asked what would happen if I examined different cells, so I kept drawing more step functions, just not all exactly alike. Then they talked about probability, and even told me to compare the proteins with frogs leaping in a pond... This last part was just weird, but with their help I got (I think) where they wanted me to. Overall they were patient and eager to help, and even though the last part was rather odd, it was a good examination.

KM

This prelim consisted of three questions.

1) Professor Smit: Imagine you have a box which contains two regions (region 1 and region 2) physically separated by a wall. The two regions are connected by only a small hole in the wall. There is one particle (A) total in the box and it is located in region 1. When the particle (A) moves from region 1 to region 2 it is instantly converted to product (P). The particle can be treated as a hard sphere. Traversing the slit is an activated process. How do you describe this reaction?

Answer: Let us define a general reaction rate as:

$$r = S * p * N_A$$

Where

$$\begin{aligned} r &= \text{rate of reaction of } A \\ N_A &= \text{flux of } A \end{aligned}$$

S = ratio of the area of the slit to the total area of the wall between the two boxes

p = probability that if a particle makes it to the entrance of the slit,
it subsequently makes it through the slit

We can rewrite the flux as the product of a concentration and a velocity:

$$r = S * P * v * C_A$$

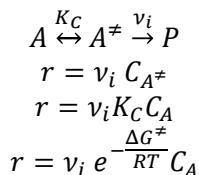
Where

$$\begin{aligned} C_A &= \text{concentration of } A \\ v &= \text{velocity of particle } A \end{aligned}$$

In this case, the concentration (C_A) refers to the inverse of the volume occupied by the single particle.

The velocity is given by a Maxwell-Boltzmann distribution.

Traversing the slit is given by an activated process, which we may describe using transition state theory. The reaction coordinate in this case can be thought of as a spatial parameter describing the position of the particle within the slit.



Where $\Delta G^\#$ denotes the free energy of the transition state compared to the reactant. We can rewrite this as:

$$r = v_i e^{-\frac{\Delta H^\ddagger - T\Delta S^\ddagger}{RT}} C_A$$

Because we have a hard sphere, there can be no enthalpic change. Hence:

$$r = v_i e^{\frac{\Delta S^\ddagger}{RT}} C_A$$

The equilibrium constant K_C can be found using a ratio of partition functions. Because A is simply a hard sphere, the only contribution to K_C is the translational partition function, which can be written in integral form; hence the equilibrium constant will be a function of the volume available to the particle.

2) Professor Bell: You have an exothermic, elementary, irreversible reaction $A + B \rightarrow C$ taking place in a PFR which has a cooling jacket. The reactants A and B are relatively dilute in the stream, so we can neglect volume changes. The reactants come in at a temperature T_o and we have a stoichiometric feed.

A) Draw the concentration profile in the reactor for species A and B.

Because the reaction is bimolecular, the reaction rate will decrease with increasing conversion, such that the concentrations of A and B will drop off sharply at first and then decrease more gradually.

B) Draw the temperature profile in the reactor.

We can consider two different scenarios. In the first case, we have a hotspot in the reactor and in the second case we have thermal runaway. If we have a hotspot, the temperature will initially increase, pass through a maximum known as the hotspot, and then decrease; this is because the reaction rate slows down as we move along the reactor such that we are able to more effectively remove the generated heat. If we have thermal runaway, then the temperature will not pass through a maximum and instead continue to increase along the length of the reactor.

C) Draw the concentration profile in the reactor if the inlet temperature is higher.

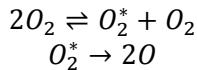
With a higher inlet temperature, we have a faster rate of reaction such that the reaction rates are higher and the concentrations of A and B drop off more sharply.

D) Find the concentration of A and B as a function of position down the reactor.

I wrote out the design equation for a PFR, and plugged in using the expression for concentration as a function of conversion. I then described how the energy balance would be done on a shell. The mass balance and energy balance are coupled since the temperature changes along the reactor.

3) Professor Bell: The dissociation of oxygen is found to be first order in the concentration of oxygen although it proceeds through a collision of two oxygen molecules. The process does not involve a catalyst. How is this possible?

This can be explained using the following mechanism, in which a collision leads to the generation of an activated oxygen molecule:



We assume the first step is quasiequilibrated such that:

$$K_c = \frac{[O_2^*]}{[O_2]}$$

The rate can be written based on the second step:

$$r = 2k [O_2^*]$$

Plugging in:

$$r = 2k K_c [O_2]$$

General Comment: Both Professor Smit and Bell were very helpful in asking questions which could help guide the next part of the answer. When you finished one part of the question, they would then provide

additional details in order to gradually build up the difficulty of the question. They were a very helpful and kind committee.

EY

This was my last prelim exam. In the beginning, Prof. Bell asked about the ‘order’ of reaction. I drew some generic first order and second order rate laws. Then I discussed how when you discuss order, it can be related to the idea of probabilities (see law of mass action). I mentioned that the order of elementary steps is associated with the stoichiometry of the reaction and how higher order reactions are unlikely to be elementary since it’s difficult to have multiple molecules come together simultaneously. Prof. Smit asked what the highest order elementary step could be. I didn’t get it correctly but apparently fourth order elementary steps have been experimentally confirmed. Prof. Bell asked what different type of reaction would give a zero order. I described how zero order would have no dependence on the concentration of the reactants and it could occur in catalysis. They then had me write the mechanisms and derive the rate law for a Langmuir reaction mechanism $A \rightarrow B$ with A adsorbing and reacting into B and desorbing (the latter two mechanisms occurring in one step) (correct answer being $r = \frac{k_2 K_1 [A]}{1 + K_1 [A]}$).

After that, I was asked about the differences between the Langmuir, Langmuir-Hinshelwood, and Eley-Rideal mechanisms (drew qualitative diagrams).

We back to the rate law and Prof. Bell asked about the k-constant, so I wrote out the version with temperature dependence (Arrhenius equation) and he asked what the activation energy was. I wrote out the equilibrium constant as an exponential with delta G. Since delta G is delta H minus T delta S, I showed that delta H is the thermodynamic energy difference between the reactants and the transition state. Here, we delved a little bit into transition state theory (drew the famous energy vs. reaction coordinate diagram) where I stated that the transition state is in equilibrium with the reactants and once you hit the top of the hill, it reacts irreversibly (with rate constant nu, representing the weak vibrational mode along the reaction coordinate—the bond forming/breaking). Prof. Bell then asked about what the delta S represented (preexponential factor of k) and how it would change (negative since the transition state is more orderly).

They then asked for the simple equation for the concentration of the elementary reaction $A \rightarrow B$ in a batch reactor as a function of time ($c_A = c_{A_0} \exp(-kt)$). After, Prof. Smit introduced a scenario where A is an enzyme and is being consumed in a cell and it has been observed experimentally that 90% is consumed by 9 minutes where my derived equation calculated that ten minutes would need to pass even though the reaction conditions and assumptions for the batch reactor calculations were accurate for the biological system. They had me draw the concentration profile of one cell (discrete step function where the time before another enzyme is consumed is longer as time goes forward). I was asked for the concentration profile of multiple cells (superimpose discrete step functions but they won’t overlap each other perfectly). The reason why the experimentalist observed the consumption at 9 minutes is because the probability that proteins in a cell would be consumed is higher at the beginning of a reaction since there are more of them at the beginning—some of cells will have less proteins, some will have more proteins at a given time, so it’s the average of them that the experimentalist observes and thus why it’s possible that 90% is consumed before the calculated expected duration for such a consumption.

There were some awkward silences during this exam but Smit and Bell were patient and provided enough hints (when I seemed completely stumped) that I was able to arrive at the correct answer.

THE R M O D Y N A M I C S

SCHAFFER/SEGALMAN

DH

This was my first prelim so I was pretty nervous since I wasn't sure what to expect in regards to question types and the overall experience. In addition, Segalman had no track record in thermo and was known to be intimidating.

When I walked up to Segalman's office Shaffer (who was running late) had been replaced by Balsara. This unexpected switcheroo definitely perpetuated my nervousness (Balsara is known to be rough). They asked me my thermo back ground and I told them about my one class at Texas, in which Segalman and I shared a brief connection (since we attended the same undergrad school.) Balsara asked the first question: "Show me how to obtain a relationship between the melting temperature of water and pressure". Perrrrf...I studied phase changes/equilibrium like a mofo. Started with a PT sketch of water phase diagram, I began to derive the Claperon equation. However, I skipped algebraic steps and confused myself even though I knew the answer to this softball question. But for some reason having those eyes stare me in the back vacated my brain of anything useful. I recommend taking it slow and writing each algebraic step (which will also slow you down and reduce mistakes.) After fumbling like an idiot, I came to the correct expression relating T_{melt} with P and described why this is negative for water (molar volume of ice is larger than water). Then Balsara asked me the sign of the enthalpy. I gave him a verbal qualitative explanation, but proceeded to confuse myself with sign convention while attempting to show this mathematically on the board. Again I fumbled and negative and positive signs flew across the whiteboard. After frustration I thought fuck it, I'll derive this from the 1st and 2nd laws. Balsara said "Woa, this way will take 15 mins. Look on the board, you've written it down. Just go slowly." Awesome hint. I traced my steps and found the equation he was looking for ($\Delta G = \Delta H - T\Delta S$, $\Delta G = 0$ for phase change). He said "enthalpy is hard to grasp, but reason from entropy. What do you know about the entropy of the two phases?" So I properly assigned equalities to the entropy of ice and water ($S_{ice} < S_{liquid}$) and found the proper sign (depends on which direction you go, of course).

Next, Segalman stepped up to pitch: "Let's stick with water. I dug a well and I want to know how the relative humidity changes with height." Luckily I brought my water bottle and took a drink and made a joke about wanting to stick with water. I didn't know how to do this at first. But I verbalized my thought process and drew a diagram, labeling a coordinate system, defined relative humidity and made a few assumptions. Segalman specified, "it's in the Sahara, so the vapor pressure of water at the top is zero." I explained what I know about the system. Before I could finish Segalman asks, "What is the effect of gravity." So I drew a gravity vector and started to derive an expression: $P = \rho g z$. Then I mentioned that ρ = molar volume (actually its molar volume divide by molecular mass, small mistake I discovered after I walked out of the room. Also, I forgot to add a negative sign, but this depends on how you draw your coordinate system. At this point Shaffer opens the door and apologizes for being late and Segalman said to him "you can take a 20 min break while we finish up here". Shaffer: "No, no, I shouldn't be rewarded for being late. I'll sit in." Oh man, now I have three of profs staring me down. Oh boy. I took a deep breath and explained to Shaffer the problem I was solving (he ended up not saying a word). Picking back up, I wrote: $P =$ and stood there thinking. We continued and Segalman hinted, "I actually want dP/dz ." So I took the derivative of the equation above, made the ideal gas assumption, substituted in for ρ = molar volume and integrated. I then converted water partial pressure back to relative humidity. Segalman asked me one more question on the same subject, but it escapes my memory. Nevertheless, I ran out of time midway through, thanked them for their time and left.

Take home: work slowly, remember to breathe, be mindful of sign conventions, and verbalize your thought process so the profs can hint you into the right direction. Also, once arriving at an equation,

check the extreme cases. For example, I should have checked $z=0$ (well water level) and $z=\text{well height}$ and make sure my equation punched out P^{sat} and P^{sahara} , respectively.

SS

1. Schaffer - Given a hot object of a finite volume, how can you define maximum work obtainable from it?
2. Segelman - Derivation of Clapeyron equation. Name one fluid which behaves differently from others during fusion (water). What term in the Clapeyron equation is different? (ΔV is positive since ice occupies more volume than liquid water)
3. Schaffer - In an isolated system consisting of subcooled water at $T_w < 0$ deg C, a very small fraction of the water freezes. Find the entropy change and lost work associated with this process.

SG

Both prof Segelman and Prof Schaffer were very good and they explain very well what the problem is and what they want to know.

Prof segalman started with the mixing of two gas problem. There is a box that has two compartments and one membrane in between. When the Membrane is removed what would be the entropy of mixing? What would be enthalpy and gibbs free energy of mixing? What would be their signs? Give physical explanation why these are so? Give an example when entropy of mixing is not favorable and what would happen in this case. Can mixing occur in this case? (When entropy of mixing is not favorable then also it is possible to get mixing. If the enthalpy of mixing is –ve then we can get $\Delta G < 0$ and we can get mixing. And the example for this is when on mixing A and B gas...A molecules are surrounded by B molecules and form cage like structure then entropy of mixing is not favourable.

Then Prof Schaffer's fav ques: U have a hot block at temp $T(H)$ in the atmosphere. What would be the maximum work that you can get from this system and what would be that work. So u need to do integration to get the work and then discussion of carnot cycle as that max work would be that obtained from carnot engine. He asked me to derive the carnot efficiency. I did that using secong law of thermodynamics. Then he asked for Full derivation of efficiency by considering individual processes one by one.

You have a subcooled liquid and you are making solid + liquid from this in an adiabatic environment. What would be the ΔS for the process. This was a nice tricky ques..... I had to analyze each process by my own and give reasoning why this is so. Would ΔS be +ve or –ve? And where is the chance that you can extract work out of it? This leads to discussion about water going to ice and what happens when water freezes? What is ΔV and why it is so? Then the P Vs T Curve and how it looks for water?

KJM

This was my first exam of the day and I was feeling very confident. I entered the room, and we started with the typical formalities of where I did my undergrad, what textbooks I used, etc. It must have been very obvious that I was nervous, because I was talking so fast that Prof. Segelman made me repeat myself several times. Abruptly, I was told to go to the whiteboard. Prof. Segelman started, and asked me the change in entropy of mixing two equal volume reservoirs of A and B, both ideal gases at the same temperature. I thought, "Perfect!" I had done this problem so often that I could have done it in my sleep. "Are A and B distinguishable?" I ask, trying to build up some suspense. "Yes, but what would be the entropy of mixing if they were indistinguishable?" asks Prof. Schaffer. "It would be zero; that is

Gibb's paradox," I reply, trying to show-off. I then turn to the board....and I freeze. I had forgotten how to do the problem. I first try to do the problem classically, but I jump into the problem in the middle when I really should have started from the first law. Essentially,

$$ds = \frac{1}{T} du + \frac{P}{T} dv - \sum_{all i} \frac{\mu_i}{T} dn_i$$

Assuming ideal gas, the change in entropy for each component is:

$$ds_i = \frac{R}{v} dv$$

$$\Delta s = R \ln\left(\frac{v_2}{v_1}\right) = R \ln(2)$$

The change in entropy for the system is then just the summation of the change in entropies for each of the individual components. However, I couldn't get anything remotely close to this. Prof Segelman asks me "to do this like Prof. Smit would." She is talking about using the microcanonical ensemble, which I then solve, although I didn't have the right sign, and I stumbled through the algebra. At this point, I felt like those Southwest commercials, because I really wanted to get away. Nothing was going right on the easy problem. I am stumbling, and it shows.

We then transition to Prof Schaffer. He asks me what the change in entropy is in the system when a subcooled liquid is perturbed and ice forms, with the final state in solid-liquid equilibrium. I have no idea how to do this problem and I am so disoriented from the mixing problem that I can't think. He keeps repeating "if we can't measure entropy changes in this system, what else can we do?" I repeat several times that volume is changing during the phase change, but he wants me to say the magic word - state function - but I bumble around and don't get anywhere. Both the professors want me to use the fact that entropy is a state function to measure the change in entropy for a path that we do know that has the same initial and final state as the path that we can't calculate. Prof Segelman asked me to write the first law, and I write that U is minimized (this isn't the first law). I eventually get that the entropy change can be thought of as a heating of the subcooled liquid to 0°C and then a phase transition from liquid to solid. All the heat of freezing goes to heating the water, as the system is adiabatic. I wanted to use the heat of freezing, which is hard to do, and I hard-headededly and wrongly fought to do it this way. I eventually got there, but I needed a lot of help. We have time for one more question, and Prof. Schaffer wants to know if we will get out work from this system. I say that we will, as the volume change is positive. I am not sure if this is the correct logic, but they are definitely ready to let me go.

I was most surprised by this exam. I was very prepared for the questions they asked me but I was very nervous. I felt terrible about my performance at the time, but I did get a passing grade and both the professors were helpful. The two worst things you can do are: not say anything or say things that are wrong. What I did, and what I think saved me on this exam, is that I kept writing the definition of dS and trying to reason from there, showing my understanding of the fundamentals of thermodynamics.

SP

Segelman started by asking me about my thermo background. I had only taken Smit's thermo course the semester before in addition to a half semester physics/thermo course as part of my Environmental Eng background, so my background is fairly weak. Signalman started by asking me what the entropy of mixing for two ideal gasses would be. I think since this my first exam of the day; I was a bit on edge and not coming off as very confident. I knew how to get this from calculation of the Gibbs energy of mixing, so I started with that even though it's a backward way of getting there, but that wasn't what she wanted. She started by leading me towards getting the entropy of mixing from the stat mech perspective, which I had done before, but hadn't studied for this test and I stumbled through. She

eventually cut me off, and I think I lost a lot of points for that. It was then Shaffer's turn, and he asked me his standard question about the hot metal bar in the reservoir. I had done this before and I worked through it fairly easily. He then asked me why I could make the assumption that the max differential efficiency for the bar in the water was the Carnot efficiency ($1 - T_c/T_h$). I talked about Carnot's proof with the Carnot refrigerator and the engine more efficient than Carnot violating the second law of thermodynamics. He then asked me to derive the Carnot efficiency. There are two ways you can do this, as this is an ideal engine, you can look at conservation of entropy for the isothermal steps, or you can go through and relate the hot and cold temps to the different volumes at different points in the cycle. We went through both of these, but he didn't make me do the entire math for the 2nd method. He seemed happy enough and it was Segelman's turn again. She asked me about calculating the weight of the atmosphere. Once again, two ways you can do this. You can just multiply atmospheric pressure by the area of the earth, or you can integrate the density of the atmosphere. I started with the easy way and then she asked me to do the hard way. With some hints I found a way to use Bernoulli to get an expression for the density of the atmosphere as a function of height and then plugged that in to my integral expression for the weight of the atmosphere. Finally, they asked me to write the Classius equation and how one could derive it. We then talked about the slope of the Classius equation and why water is different than most materials. Segelman wanted me to explain this in terms of molecular mechanisms and I had some trouble with this. I eventually got where they wanted with a lot of hints and we didn't have enough time for another question so they let me go 5 min early.

Overall, this pair wasn't too bad, but I sensed that Segelman wanted me to work faster and pick up on their hints faster.

PRAUSNITZ/SCHAFFER

BR

Shaeffer – you start with supercooled water; you then add some ice, which causes the contents of the beaker to crystalize. How do you determine if this is a reversible process or not (heating container to lq/solid equilibrium and then see if you can get back to supercooled lq state). Second question was about calculating the weight of the atmosphere. We discussed two ways: (1. Force=pressure*area, so weight of earth is product of Patm (1atm) X earth's surface area. 2. A more involved way to do it would be to take into account the density of the atmosphere and integrate it as a function of height above the earth's surface(using ideal gas assumption $P=\rho\cdot RT$))

Prausnitz –How do you calculate delta S and why is the third law important (helps define standard state). Liquefaction process – Linde Cycle, how to cool below 5K (magnetic cooling), what is O₂ used for (steel, medical applications, AND in oxidation chemical processes).

EY

This was my second prelim and I was a little nervous right before going in since I didn't feel too secure about solution thermodynamics. But I think it's extremely important to appear confident (preferably throughout the exam but especially right when you enter the room).

The first problem was from Prof. Prausnitz where he asked about possible ways to separate two components (distillation if they have different volatilities). “What if there's an azeotrope?” (introduce a third component that is miscible with the first two and does not form an azeotrope with them). Make sure to draw the introduction of this third component at the top of the column and not in with the feed. We then discussed various other methods (I mentioned absorption, evaporation, solvent extraction) and he then started relating the process to the removal of toxins

from the air and so through that we had a four minute discussion until I finally came up with the separation technique he wanted (aDsorption). Then he asked how the adsorption process worked in industry and how to design the process (two parallel columns so that as one is being cleaned, the other one is in use).

Prof. Schaffer then asked his classic problem regarding the most work you can get from a hot object. Here you define the Carnot engine and write down the instantaneous efficiency as:

$$\eta' = \frac{dW}{dQ_H} = \frac{Q_H - Q_C}{Q_H} = 1 - \frac{Q_C}{Q_H} = 1 - \frac{T_C}{T_H}$$

where T_H is a function of time (since the hot object is not a large reservoir and thus will not have constant temperature). Then,

$$dW = dQ_H \eta' = c_P \left(1 - \frac{T_C}{T}\right) dT$$

We had a discussion about how it didn't matter whether c_P or c_V is used since the heat capacity is that of the solid object and thus they are approximately the same. Integrate and find the solution.

Prof. Schaffer asked how to find the expression $1 - \frac{T_C}{T_H}$ and on the Carnot cycle PV diagram that I had drawn before, I went down each leg of the process and derived the expression. He then said that was a more difficult way of doing it (purely from the first law) and asked for the way you might do it from the second law.

$$dS \geq \frac{Q}{T}$$

Where the law would be equal for a reversible process (Carnot) and through one cycle of the Carnot, $dS=0$. Then you get the same expression as you would with deriving it from the first law:

$$\frac{Q_H}{T_H} = \frac{Q_C}{T_C}$$

Back to Prof. Prausnitz, he asked about how one would get equilibrium data on a ternary system (1,2,3) if you had binary mixture data on 1-2, 2-3, and 3-1. He hinted at Gibbs Excess so I scribbled something (you may want to check the accuracy of this) that looked like

$$G_i^E = RT \ln(\gamma_i)$$

And he asked me to define chemical potential $\mu_i = \frac{\partial G}{\partial n_i}$ Through some (a lot) of guidance, I reached the conclusion that you needed to sum the excess Gibbs of the three components and take the derivative with respect to the component in which you're interested.

Lastly, Prof. Schaffer asked how I would find the weight of the atmosphere on the Earth. The easy way is to state that you would need to know the atmospheric pressure and the surface area of the planet. He then asked me to do it the "difficult" way. The weight would be

$$\int \rho dV = \int 4\pi r^2 \rho(r) dr$$

I had a tough time coming up with how to come up with the density as a function of r , and Prof. Prausnitz asked what it would be for a gas ($\rho = \frac{P}{RT}$ where $P = \rho gr$) and Prof. Schaffer said that would basically solve the problem.

SK

This was by far most enjoyable prelim of the three, even though it was at 4:30 in the afternoon. Schaffer and Prausnitz were both really happy, and gave hints, but alternated in giving them and generally seemed very pleased whenever I answered anything correctly.

So we started out with the usual introductions. After that Prausnitz asked me about a 2 component VLE, where one of the components in the liquid was very dilute. How would I describe the vapor fractions of each component? So I wrote down Raoult's Law and Henry's Law, respectively. Then he asked me if Raoult's law had to be true if Henry's Law was. After some hinting, I said in this case the activity coefficient for the dilute component was fixed, and for the other component it was 1, and this was governed by the Gibbs Duhem equation – so the fact that one component had a specific fugacity determined the other. But would it be Raoult's law? So I wrote down Gibb's duhem, differentiated with respect to liquid phase mole fraction, and then Prausnitz pointed out that since the Henry's law component had a constant fugacity coefficient (at least for some range of compositions), the other fugacity coefficient must also be constant for the two derivatives to equal zero. And since the limit of activity coefficient is 1 when it's a pure substance, it has to be equal to one to stay constant.

The next question he asked me was about a three component VLE. He wanted to know what the equilibrium composition of the gas and liquid would be, and eventually I gave him an answer involving excess gibbs free energy and activity coefficients. Then he said, suppose we only have excess Gibbs free energies of the binary mixtures- how do you find it for the ternary system? I had no idea, but it turns out that you just add them and this gives you a reasonable approximation. Apparently this is important in industry.

Then Schaffer stepped in and asked me about a system of subcooled liquid water. Somebody upsets it and adds heat, and it partially freezes. Is this process reversible? I said no, because it seemed like the intuitively correct answer, and there was no driving force for the process to go the other way. With some more prodding, I eventually said that this was a non-equilibrium process, so it wasn't reversible. Then he asked me about the entropy change. Since it wasn't reversible, obviously it is positive, and after poking and prodding, I said to use $dS = dQ_{rev}/T$. Since entropy is a state function (this statement made them happy), you can invent arbitrary paths to get the entropy change- so first the heating up of the subcooled water to its freezing temperature, where $dQ = CpdT$, and then the phase change, where $Q = \Delta H$ of freezing (and T is constant at $T_{freezing}$). So you add these guys together to get the total entropy change. I needed some prodding through this but they seemed pretty happy with me when I got the answer. Then they looked at the final expression (which had an \ln in it) and asked how I would check if it was actually positive, and I said you would use a Taylor expansion. Luckily Schaffer said he trusted that I knew how to do this and didn't make me because I didn't remember off the top of my head...

Then we had some extra time left, so it was time for PRAUSNITZ TRIVIA!!! Basically he asked me about how to make liquid helium, so I talked about J-T inversion temperature. (Bonus- why do you need liquid He? Some sensitive sensors need to be that cold, as do superconductors...) But the J-T inversion temperature of Helium is like, 30K! So first you have to make liquid nitrogen from air (Linde process) and then liquid oxygen and at this point I forgot what came next (oops, this is in every past writeup ever) so he told me to think about the periodic table... Voila, liquid hydrogen, which has a J-T inversion temp of a balmy 100K or so. So liquid hydrogen makes liquid Helium. And then he asks... what if I wanted SUPER COLD He, like a couple of Kelvins? I actually kind of knew this because Jeff Reimer had told me about his NMR quantum refrigerator (and also it was in Matt P's writeup), so I said, something with magnets and maybe spins but I'm not sure exactly how it works. So Prausnitz told me all about how this was worked out at Berkeley and one of the labs in the Chemistry quad that I walk by every day regularly works with things at fractions of a Kelvin and the three of us have an amiable discussion about how ridiculous this is. Then they tell me to enjoy my weekend and when I respond that I see worry in my immediate future, Prausnitz tells me not to worry, and that I did "well in here." So hurray! I got an A in this one. I don't

actually feel like I was super on top of things the whole time, but the exam went well because they were happy and didn't seem to think that their hints and prodding were giving it away.

KS

Standard trivia questions from both (see old write ups for answers). Three laws, why its important to be able to calculate an absolute entropy. How you measure c_p at temperatures near 0K. Work from a hot object, a skier's watch measuring vertical feet skied (measure pressure changes and calculate height changes). Weight of the atmosphere. Both guys were really nice. I think I talked a little too fast for Prausnitz though.

TULLMAN/PRAUSNITZ

GJ

KM

This exam consisted of a series of short questions, which I have listed out below:

- 1) Professor Prausnitz: State Henry's Law. What is the physical meaning of the Henry's Law constant?

The partial pressure of a species in the gas phase is equal to the liquid-phase mole fraction times the Henry's Law Constant. The Henry's Law Constant takes the place of the saturation pressure for a supercritical substance; it has the units of pressure.

- 2) Professor Prausnitz: State Raoult's Law. If one component of a binary mixture is known to obey Henry's Law, must the other component obey Raoult's Law?

Using the Gibbs-Duhem equation, we can interrelate the chemical potentials of the two species. Hence, we can demonstrate that if one component obeys Henry's Law, then the other component must obey Raoult's Law.

- 3) Professor Prausnitz: What is the Van der Waals equation? Provide a physical interpretation of the parameters which appear in the Van der Waals equation.

One form of the Van der Waals equation is:

$$\left(P + a \frac{n^2}{V^2} \right) (V - nb) = nRT$$

The constant a accounts for the intermolecular forces. The constant b accounts for the excluded volume of each particle (the product nb is the total excluded volume of all particles).

- 4) Professor Prausnitz: A substance is taken from an initial temperature T_1 and pressure P_1 to a final temperature T_2 and pressure P_2 . Calculate the change in enthalpy of the substance assuming you are provided with the Van der Waals equation and the ideal gas heat capacity at constant pressure.

In order to calculate the overall enthalpy change, we will use transformations involving both a) changes in temperature at constant pressure and b) changes in pressure at constant temperature.

The enthalpy change is given by:

$$dH = TdS + VdP$$

Divide by dP at constant T:

$$\left(\frac{\partial H}{\partial P} \right)_T = T \left(\frac{\partial S}{\partial P} \right)_T + V$$

We can apply the Maxwell relation $\left(\frac{\partial S}{\partial P} \right)_T = - \left(\frac{\partial V}{\partial T} \right)_P$:

$$\left(\frac{\partial H}{\partial P} \right)_T = -T \left(\frac{\partial V}{\partial T} \right)_P + V$$

We can find $\left(\frac{\partial V}{\partial T} \right)_P$ using the Van der Waals equation of state, such that the enthalpy change for a change in pressure at constant temperature is now known.

We can find the enthalpy change for a change in temperature at constant pressure using a sensible heat integral (integrate the heat capacity over the temperature change).

With the above information, we can now define the process we will use for the transformation. We will use a process in which we first reduce the pressure at constant temperature until we reach a low enough pressure at which the ideal gas heat capacity is valid. Then we will increase the temperature at constant pressure (from T_1 to T_2), making use of the ideal gas heat capacity to calculate the enthalpy change. Then we will increase the pressure (to P_2).

- 5) Professor Tullman-Ercek: Why do proteins fold? What should the system be defined as in order to fully understand the thermodynamics of a folding process?

Discuss the entropic and enthalpic contributions to protein folding. The system needs to include both the protein and solvent, since they both undergo entropic and enthalpic changes.

- 6) Professor Tullman-Ercek: What kind of experiment can be used to measure the thermodynamics of folding?

A temperature-jump experiment can be used to collect the necessary data to apply the Van't Hoff Equation, which is used to connect the rate of change of the equilibrium constant with temperature to the enthalpy change associated with the folding process.

- 7) Professor Tullman-Ercek: How do you measure the equilibrium constant?

Use Circular Dichroism to measure the ratio of peaks associated with the unfolded and folded proteins.

- 8) Professor Tullman-Ercek: How can you use calorimetry to measure the enthalpy change?

Describe the use of a calorimeter and the assumptions used to measure the enthalpy change for a process.

- 9) Professor Prausnitz: What is an azeotrope?

The point at which two phases in equilibrium have identical composition.

- 10) How do you break an azeotrope?

Many techniques are possible, including pressure-swing distillation, membrane separation, and extractive distillation. Professor Prausnitz preferred extractive distillation.

- 11) Draw a process flow diagram for a process in which extractive distillation is used to break the azeotrope.

Draw a distillation column, including the reboiler and condenser. Draw a stream containing the entrainer which enters near the top of the column.

- 12) Do we want a more or less volatile entrainer? How much entrainer do we want to use?

We want a less volatile entrainer so that it exits from the bottom of the column. I guessed that only 10% entrainer would be used, but it turned out that the entrainer has to be added in vast excess.

- 13) How else can we separate two liquids, other than distillation?

Using a membrane or crystallization. Draw a phase diagram to demonstrate how two liquids can be separated by reducing the temperature. We can also use a liquid-liquid extraction. Draw a ternary phase diagram to describe this process.

General comment: This committee was very friendly and helpful. They would never leave you hanging and provided useful feedback along the way.

BE

This was my second exam and definitely the worst. I started a little late because the person in front of me went over on time. I thought I was prepared for this exam and had looked over everything that Prausnitz normally asks and also some bio stuff for Tullman-Erceck, however this did not really prove helpful during the exam. First I was asked by Prausnitz why there are holes in plugs you put into the wall and I said something to do with electricity...and then he was like "this isn't a prelim question, I've just

always wondered." So then they had me answer who I had for thermo and what book I used and all that jazz and then Prausnitz immediately went into it asking if I knew the van der Waals equation. I said yes, I remember it and went up to his tiny board. I first wrote out the ideal gas equation and said that for van der Waals we add in an a term for attractions and a b term for repulsions, which I think is true and then wrote one version of it that was slightly incorrect. When I was trying to fix it, Prausnitz immediately walked up and wrote out the real equation without giving me a second to change what I originally wrote—that's kind of scary! He then said that he had a refrigerant and he wants me to draw a P-H diagram for this refrigerant going from one point to another. He also said I know the heat capacity for it, but that's only good an ideal gas. He also talked about some other stuff that I don't really remember and wanted me to draw on the P-H diagram how I would get from one point to another. He mentioned that I couldn't get from one point directly to another but had to go another route. I started writing the equation for enthalpy and trying to get to pressure and some other variables that might be helpful and the whole time he was trying to give me guiding suggestions like "what is heat capacity" and "you have enthalpy with pressure, but what is it with temperature," and other random things like that which really only got me more confused as I went through. There were some other things told to me by Prausnitz and somehow I was able to get the idea that you go straight down to low pressure, over to directly under the higher pressure point and then straight up. I don't know how I was supposed to automatically know that giving his hints, but maybe I just didn't understand what he was asking.

After this, Tullman asked me about protein folding and asked me to describe the thermodynamics of protein folding. I started talking about how you decrease in free energy and it's like TST and you have to get over an activation barrier to get to the folded state. I initially said that the entropy of it would increase and then wrote the delta g equation to realize that the entropy would actually decrease when its folded. I said something along the lines of entropy of the entire system plus surroundings must increase though and then she started asking me questions about why that is. After some weird questions and hints like asking what the protein is in, I said that it's in a solution like water. I knew the entropy of water had to increase for the total entropy to increase but wasn't really sure why exactly. I tried to work through it and then she asked me about solvation effects and I ended up saying that there is less surface area for the water to stick to the protein once its folded and the water has to go back into the bulk water, which increases its entropy. I'm not sure if she gave up after this or thought it was right. My final main question was by Tullman about refrigeration cycle. I drew the refrigeration cycle on TS and PV diagram and talked about difference between Carnot and adsorption-desorption and then couldn't remember what you use to expand. I said it was either a throttle valve or a turbine and they asked me why you would choose one over the other. We went through a very long discussion about how throttle valves and turbines work and which one is isentropic vs. isenthalpic and why they only use throttle valves in real refrigerators. I was a little flustered by the end of this because we went in circular logic for quite some time.

Another quick question by Prausnitz dealt with Henry's law and I don't really remember what else besides that he was asking how we relate that or Raoult's law to something that is different from normal. I don't remember his exact wording but had he said nonideal I would have known he was asking about the activity coefficient. He asked a lot of confusing questions on this topic and then seemed to be feeding me the answers because I couldn't understand his questions/comments. By the end, I had gone about 5 minutes over the time limit and Prausnitz told me to relax before my next final. I didn't think this went very well, but I didn't think that I had done poor enough to give the impression that I really had no idea about the fundamentals.

Both of them say good morning, then Prousnitz asks me to sit down and we talk about where I did my undergrad, how many thermo classes I took and what books I used. Then, after asking which professors taught me, he asked me what Henry's law was. I go to the small board and then I talk about Raoult's law, its assumptions, and how in order to use it we need to have a species with a critical temperature above that which we are considering. In the case that we don't (such as air, I used the water and air example), we need to use Henry's law, in which a species has a given Henry's constant. He asked me how would I study the air and water system, and so I explained that we could use Raoult's law for water in air, setting the fraction of air in the liquid water to zero, and then for air we would use Henry's law. Then, he told me how chemical potentials were involved in equilibrium, so I said that in equilibrium the chemical potential of any species is the same in both phases. He then asked if there was any way I could relate the chemical potential of the species, because what I had said was only good for each species. After thinking a little, I asked if we could use the Gibbs-Duhem equation and the summability rules for that, and he responded that we could. Then he asked Prof. Tullman-Ercek if she had a question.

I had taken her Protein Engineering class during the fall, so it was funny when she said: "So, you've taken my class so I know you know what proteins are. Describe thermodynamically their folding process". I hadn't really thought about studying protein folding, since she didn't ask any questions last year, so I was a bit surprised. I then told her that proteins explore configurations in space and fold in order to minimize their energy, so she asked me to write an equation describing that. I wrote the Gibbs energy equation: $\Delta G = \Delta H - T\Delta S$, and she asked me to describe the folding in terms of that equation. I then proceeded to talk about secondary structures, hydrophobic interactions, burial of hydrophobic residues and exposure of hydrophilic ones... to which she replied: "Yes, that's all fine, but you haven't said the words enthalpy or entropy once". I honestly wasn't sure how to explain it well in those terms, so she asked me to draw an unfolded protein with water molecules and then a folded protein with water molecules as well. She asked me to describe the interactions with the water molecules in both cases, but I wasn't really sure of where that was taking me. So, she asked me which state was more favorable in terms of entropy, and I said that the folded (and more organized) state had a lower entropy than the unfolded (and less organized) state. Then she asked what needed to happen in order for that to happen, so I said that the enthalpic interactions need to compensate for that in order for the total change in energy to be minimized. Then she said that there must be competing forces in order for that to take place. She said that had taken longer than expected, so it was time for Prousnitz to ask me a question.

He asked me how would I separate air and nitrogen from air. I told him a cryogenic distillation could be used, since the boiling points of both were really low. He then asked how would I cool my system, so I told him we could employ a refrigeration cycle, based on compression and expansion. He then asked me what the Joule-Thompson coefficient was, so I wrote down its expression and explained what was it. He then said that JT throttling could be used for cooling, and asked me what the coefficient was supposed to be like. I told him we wanted a positive coefficient, so that when we expanded, the species would be cooled. He then asked what would happen if I wanted to separate hydrogen, which had a negative JT coefficient at room temperature. I told him they vary with temperature, so at low temperatures the coefficient could be positive. So, he asked how would I cool down the hydrogen. I wasn't sure how to answer this, so he asked me if I had not just made liquid oxygen. So the answer was to use it to liquid the hydrogen and then pass it through a JT valve to get liquid hydrogen. He then asked how would I get liquid helium, which had the same problem of a negative JT coefficient except at low temperatures. He told me to think about what we had available, so I asked if we could use the hydrogen, and that was the right answer. He then said that liquid helium was a major breakthrough, as it allowed studies at really low temperatures, with superconductors being an example.

Lastly, they said we only had a bit of time left, so Tullman-Ercek asked me what would I use a P vs. x/y diagram. I told her it could be used to describe vapor-liquid equilibrium, and drew an ideal example.

Then she asked what was the purpose of the tielines, so I said they were horizontal lines drawn within the bubble and dewpoint lines that were used to determine the composition of the liquid and vapor in those regions. Then Prausnitz said that I had drawn an ideal case, and asked me what could happen if it wasn't an ideal case, if there was an azeotrope. So I drew an example of a curve with an azeotrope. He then asked me how would I separate those two. I answered that you could separate up until the azeotrope point, and then you could shift the point by changing temperature/pressure, or by adding either pure species or a third component. Then he asked me what the third component needed to be like, so I told him it needed to be easy to separate. He wanted more details, in terms of its interactions with the original two components, if they were to be similar. I told him that the third component could be miscible with one but immiscible with the other, and he said that we wanted a third component that interacted strongly with one species and very weakly with the other.

After that, time was up, so I erased the board, thanked them, and left the room. This was my first prelim, so I was a bit nervous when I entered the room. But, they created a nice and respectful atmosphere, and it was a good experience.

SEGALMAN/TULLMAN

LL

Last prelim! They didn't seem very grumpy, so that's a good sign. Prausnitz, as predicted, used process examples. How to separate N₂ and O₂? Liquefaction with Joule-Thompson and also pressure swing adsorption. How to separate compounds with azeotropes? Extractive distillation. What's the characteristic of the chemical you add into the azeotropic mixture for extractive distillation? Preference for one of the components in the azeotrope. How else do you separate stuff? Membranes. Where do people use membranes? Reverse osmosis. etc. etc. The first question he asked was process-independent. What was the third law of thermodynamics? And what is it used for? (0 point for entropy so that you can calculate Gibb's free energy associated with an equilibrium constant).

Schaffer then asked about a subcooled liquid in an adiabatic container. If you throw in a nucleation site, like dust, what happens? (Freezing). Is it irreversible? No. Prove it, mathematically. Go from the second law. So the integration path was raising the liquid from the subcooled temperature to the freezing temperature. The heat required to do this temperature change is drawn from other fluid, which is causing the freezing. The whole time I was thinking why isn't there an entropy change associated with the phase change, since, intuitively thinking, a solid will have much less entropy than the liquid and that was the part I did not know how to analytically find. Turns out in his analysis, there's no such term.

JW

Both were really lovely people and so nice. I wish every prelim was like this. Tullman started off with how a breathalyzer works. I gave a simple explanation of how you can apply Raoult's Law but in reality, you use Henry's law because alcohol is pretty dilute in your blood. I went through a quick derivation of Raoult's and that was the end of that question.

Next, Segalman asked about how to find difference in entropy after removing a barrier between gas A and B. This is pretty standard problem and as I was about to start the classical derivation, she said she wanted the stat mech explanation. By recalling that $S = k \ln W$, where W is the number of configurations, you can find the difference in entropy pretty easily.

After that, Tullman asked how a refrigerator works. Very standard problem and I threw up a diagram and a TS diagram. She asked what other thing could I use besides a throttle. The answer is a turbine to

make it more like a Carnot refrigerator but we don't use that because turbines are difficult to fix and expensive.

Final question came from Segelman and was about how do planes measure altitude. I threw up a Bernoulli relation to relate pressure and height. She then asked me to write down $dP = \rho * g * dh$. Density (ρ) can be estimated by ideal gas law and then you can solve for dP in terms of dh . You will be able to tell that a small difference in height will give you a large difference in pressure. That is why altitude measurements are pretty accurate.

Again, I didn't get as good of a grade as I expected but it was extremely pleasant overall and both were very helpful. It was a very practical prelim and got practical questions but I'm not complaining. Who wants to talk about fugacities and activities for 40 minutes?

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