Preliminary Exam Questions January 2000

Hi,

Here are some of the questions experienced by my class. These were sent to me by the people listed. I haven't really edited the questions for content, but they will at least give you an idea of what kind of questions to prepare for. I can't find mine, but there were pretty much repeats of other questions. Good luck!

-Jolene Ignowski (12/8/00)

Jason Voogt's Questions:

### Thermo & Kinetics, Petersen and Clark

How can you tell if reaction is occurring in a vessel & how to determine kinetics. How to account for liquid phase reaction volume change, some density stuff rather than concentration. What is Haber process and what are operating conditions. How to determine Keq at these conditions. What is Gibbs energy of nitrogen at these conditions (different from standard state). How can you calculate equilibrium conversion, i.e. w/ fugacities (high P). What determines change in T when the product ammonia is expanded (J-T coefficient).

#### Design, Prausnitz and Cairns

What was you senior design project? Cut short after a minute or two. Where does the reactant ethanol likely come from? How else is ethanol made (fermentation). What makes this method costly (eth-water azeotrope breaking). How do they do this. How do you make methanol? What is most common precursor. How can you make hydrogen feed gas from methanol for fuel cells (steam reforming). How do you get rid of the CO which poisons the PEM cell (preferential oxidation w/ stoichiometric amount of O2). What is thermal pollution? Why are we concerned about it? How does a cooling tower work? Where is most of the heat transfer (latent)? What about organic pollutants? What's better for biodegredation, pure O2 or air? List advantages and disadvantages. How do you make pure O2? How do you get rid of the CO2 in the air? What do you do with the N2 (Haber or inert blanket)? How do they make liquid hydrogen? What are you concerned with? What is it used for (rocket fuel)?

### Transport- Graves and Schaffer

What is Reynolds number? Ratio of what forces. For infinite liquid with flat plate moving below, how long would it take for a disturbance at the wall to be felt some distance up (distance squared, scaling arguments w/ diffusivity units). For plug flow in a pipe with steam condensing on the outside (heating pipe fluid) how would step change in inlet T affect transient outlet T profile. Set up equations to show. How is heat flux changing down pipe. What are relevant resistances? How would you estimate overall heat transfer coefficient. What is Pr, Nu number. Single ice cube in center of a glass of ice, how does liquid level change with time? Who first postulated buoyancy idea (Archimedies) and why (check gold crown authenticity)? Show w/ equations that the level stays the same.

Chuck Monroe's Questions:

# Design (Blanch & Lynn)

What was your senior design project? (it was acetaldehyde by dehydrogenation of ethanol)
Here I was accountable for all the flow stream compositions, temperatures, and pressures, as well as exact compositions of binary and ternary azeotropes. They wanted to know reactor type and the catalyst for the reaction, whether the reaction was endo- or exothermic, and how changes in T & P would affect the reaction. (I.e. was it kinetically limited or equilibrated, how do the constants depend on T and P, etc.)

How would you improve the process you've got here? (pressure-swing distillation, remove a compressor. The plant I showed them lost money.) How much did the input stream cost (in dollars per pound. They eventually told me it cost about as much as gasoline, and made me calculate it in my head. "How many pounds per gallon" was basically what this question came down to), and where did it come from? Okay, even if it were a "magical stream"

provided by your prof, where do you think it would have come from? What chemical reaction leaves byproducts like the ones in your input stream?

What are five other ways to get acetaldehyde out of ethanol without distillation? (Chemisorption, physisorption, react an alcohol with the acetaldehyde, size exclusion [chromatography]. They were looking for esterification of the acetaldehyde as an answer).

Why did you use H2 as fuel gas? (Economies of scale. It was good I mentioned this, because Prof. Lynn burned up the rest of the time telling me about trying to sell byproduct ammonia when he was working at Dow.)

# Transport (Graves & Schaffer)

What textbook did you use for undergrad transport? Was the class one semester or two?

Schaeffer started. Draw a slab on the board, thickness much less than length. Say it's under resistive heating with constant voltage and current (so there's a constant power output). There's air flowing over the slab.

What are the important factors in this problem? (convective & conductive heating, const. heat generation per unit volume in the slab) What does the temperature profile look like qualitatively?

Develop and solve a differential equation to get the temperature profile within the slab (they didn't make me finish the algebra, but they asked boundary conditions and made me get it integrated with constants in there so I could see the distance dependence).

Do you have to worry about conduction to the air? (no. Nusselt #) What's an empirical relation for the Nusselt number here? Why is the form  $(a + b*Re^n)$ ?

How would you look at an overall heat transfer coefficient for this problem if the thickness of the slab was 2B and you knew the temp in the center (convection dominant in the air)?

Now that you have the resistances - what dimensionless number relates them? (Biot number). What length would you want to use in the Biot number?

Okay, now say you have a race car moving on a road. What equation can we use here (Bernoulli's), and what assumptions are made in its derivation? What happens to the car as it speeds up? (There's lift on the bottom) What would you do to the car to resist this effect? (Put a fin on it and streamline the bottom)

Then Graves came out with: "I'm going to give you a mass transfer problem. You've got oxygen diffusing onto a silicon surface, where there's a first-order reaction to make SiO2. This SiO2 forms a layer which increases in thickness with time." Why at short times does the layer thickness increase directly with t, and at long times with root t? (rxn vs. diffusion dominated) Develop and solve (with the algebra) the differential equations that prove this. What assumptions can you make in Fick's Law? Show me the limits at short and long times. (BCs, math on the fly, etc. I suffered).

### Kinetics & Thermo (Clark & Petersen)

Thermo was mostly prof. Clark:

What is the Carnot cycle? What does the engine that this was based on actually do? Sketch a steam engine (ugh). What is the efficiency? Why is Qhot/Qcold = Thot/Tcold? (this involved proving that the ratio of the volumes was the same over both of the adiabats and solving the work over them and heat over the isotherms).

Say I wanted to use a solar pond to air condition my house. How would I do that? (use a heat engine to drive a refrigerator) Sketch a flowsheet for the process.

What's the equivalent of the efficiency for a refrigeration cycle? Why do we use the cold temperature?

How does this all relate to the second law of thermodynamics? (I said "you can't make a perfectly efficient engine" is another statement of the 2nd law, but they made me restate it in a couple other ways. Change in entropy >= zero didn't do it; they wanted "heat flows from hot to cold.").

What's the first law of thermodynamics?

What's the third law of thermodynamics? Why do we give a shit? (It provides a reference point for entropy was what they were looking for. I told them it gave entropy a zero, and they pushed me to "reference.").

Kinetics was both of them sort of trading off: How do we experimentally measure rate constants? (Batch reactor, integral method)

What does Fogler always assume in rate expressions? (density is const.)

Say density of the fluid in your reactor was changing. How do you need to modify what you've got?

How do you look at the temperature dependence? (change temp of reactor)

What is the dependence of rate constant on T? (Arrhenius)

Now say you had diffusion also going on in your reactor and your reaction was endothermic. How can you make sure that you're not measuring diffusivity by mistake? Draw a k vs. 1/T diagram and show me what the slopes would look like at high and low T. Which region is diffusion-dominated?

If I measured an activation energy of 80 kcal/mol, would that be a good value for a rate constant? Would it be a good value for diffusivity?

#### Wei Liu's Questions:

# Design, Prausnitz & Cairns:

How to synthesize ammonia, How to treat waste water with organic contaminate (aerobic microorganism activated sludge). How to make Lithium (where and what form of the original material, how to convert to molten salt, and what the cell looks like)

#### Kinetics and Thermo, Clark & Petersens:

What are the three laws of thermodynamics. What is the Carnot cycle, Carnot theormodynamics. How to collect the reaction rate data. (Here, I have to think about how to measure concentration. Anyway, I do not know too much of it. SO, I just try to try!) The apparent order in reaction rate with diffusion control. If the volume and density of liquid phase reaction changes, how to measure reaction rate.

# Transport, Graves & Schaffer:

What is Re number, physical meanings. How can an airplane to take off. How to measure the diffusivity (stagnant film experiment). How will the liquid level change if the ice is floating on the surface of water.

#### Baron Peter's Questions:

### Transport: Keasling/Radke

Keasling is a very nice man, and so is Radke - but his chatter can be a little annerving. My question dealt with just about every aspect heat transfer in an electrophoresis gel. They first wanted me to find the temp distribution for uniform resistive heating inside the gel. (If the gel is a thin layer over large area, this is a 1-D problem except for near the edges.) Speaking of edges, Radke may forget what he has allowed you to assume i.e. insulated edges, etc. Be prepared for this and just adjust as the problem evolves. I used boundary layer theory to solve the external heat transfer problem. (The gel was cooled by a flowing fluid) Equate heat flux at gel fluid boundary ~ convective = conductive. Be able to talk about the free convection solution as well.

### Kinetics/Thermo: Reimer/Katz

Katz was pretty intimidating for a first timer. Reimer asked a series of kinetics questions about a series reaction A>B+C and B->D. First I worked with a CVBR. Qualitative [] vs time profiles. What residence time is best to make which product. Solve the system of ode's. (sounds hard but actually pretty trivial.) Then wanted to know which type of flow reactor was best for making B. (PFR because initially pure A, so B->D only happening near end of reactor.) Explain how temperature affects these reactions. Had to talk about activation barriers and rxn coordinates. Katz then asked about supercooled water. Nucleation temporarily led back to activation energies, rate constants, and potential wells. After this he wanted the final state when the ice begins to form in an isolated (adiabatic system). I

said the ice formation would remove heat from the surrounding water and so the final state would be pure ice at T < initial temp = -10C. Fortunately I caught my own mistake here. The ice formation releases heat, so the final temp will be between -10 and 0 and we will have water and ice (0) or all ice (T < 0) depending on the energy balance. They didn't make me finish the calculation.

#### Design: Blanch/Lynn

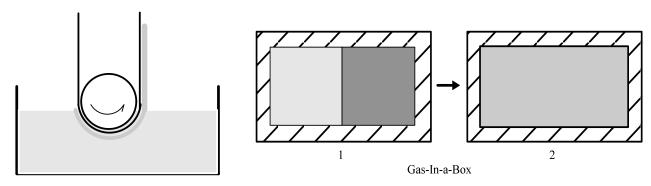
These guys weren't really to bad. I had to design a reactor for a rxn to avert formation of a byproduct formed by parallel & series mechanisms. (a triangle) The rxn required uv so use quartz PFR. (PFR because initial conversion is fast and because viscous oil carried the components. MANY small PFRs and very slow (laminar) flowrate to cut down pump work and maintain high. avg res time. Heat led to formation of byproduct so design cooling system. Baffles provide mixing for narrow res. time distribution and uniform temp in laminar "PFR". (Because plug flow can't really be laminar flow.)

Lynn wanted me to distill EtOH + H2O. Of course the azeotrope gets in the way of high purities. He wanted me to get around this obstacle using a third component. I didn't say much of anything smart beyond here, but they drug me through it and somehow I passed.

### Dave Lubertozzi's Questions:

# Transport: Goren and Newman

Goren was much nicer than I expected, but in a sort of condescending fatherly way. He kept giving me looks like he was very disappointed with me, as well he might be. I asked him for hints and clarifications, but he was no help. Newman was better, he was able to break things down into smaller pieces and walk me through a bit. The first problem was putting a liquid coating on a piece of film run through a bath. I still don't know how to find the thickness, but I drew some plausible velocity profiles (similar to the falling cylinder problem; linear from shear at the moving film, plus a half parabola from the falling fluid). I mumbled something about superposing two solutions; he said let's move on to another. He told me Ne and Ar had (roughly) the same atomic radii, so which would have higher viscosity and diffusivity, and why? I guessed the less massive Ne would be higher on both, since at a given temp it would have higher rms. speed. They then wanted me to derive the relation for temp dependence of gas viscosity; I had just looked at it in BSL the night before, but could only remember it had the  $\sqrt{kT/M}$  and  $\lambda$  in it, so I floundered until they gave up. Then they had me do heat transfer from a steam pipe in a tank of fluid. Showed the convection plus radiation terms, drew the laminar and turbulent flow profiles for free convection, and talked about the boiling curve for the convection h coefficient. I tried to show how the Graschoff number was defined and used,



Film Coating

but didn't quite get it right. I was worried I'd failed this one, but I didn't.

# Thermo/Kinetics: Maboudian and Iglesia

Maboudian asked me the three laws, then a gas in a box problem: one mole of each of two ideal gases, separated by a wall, whole thing in adiabatic box. Find  $\Delta S$  of mixing if both are at same temp initial and final. (=Rln(V<sub>2</sub>/V<sub>1</sub>) for each mole,  $\Delta S$  tot is sum) Then she asked me to write the Van der Waals EOS, and find the temp change of mixing

for the now non-ideal gases. I couldn't figure this one out; she led me by the nose to the Maxwell relation from  $dU = TdS -PdV \rightarrow (\partial T/\partial V)_S = -(\partial P/\partial S)_V$ , then sort of waved her hand like "the rest is simple", but I still didn't get it. On later reflection, it seems you want the temp change  $\Delta T$  for the (already established) entropy change  $\Delta S$  for the system as a whole at constant Vol; i.e.,  $(\partial T/\partial S)_V$ , but this is a bit tricky, requiring several other MRs. Then Iglesia gave me a rate expression and asked

$$A + B \rightarrow C$$
  $-r_A = \frac{k[A]}{1 + \alpha[B]}$   $A + * \rightarrow A * (RLS)$   
 $B + * \rightarrow B *$  where \* and B\* are the MARI  
 $A * + B * \rightarrow C + 2 *$ 

me for the mechanism. It took me a few guesses to arrive at the answer, but he was patient. He wanted some ideas on how to estimate the rate constants, so we got into TST, I sure didn't remember the partition functions, but I correctly identified the activation energy as the TS enthalpy change,  $\Delta H^{\ddagger}$ . Then he asked me some rather vague and general questions about mole balances on a PFR, what were the important variables to consider, when you could neglect axial dispersion, selecting an appropriate volume differential given different conditions, etc. I'm not sure he was satisfied with my answers.

# Design: Prausnitz and Cairns

By far the most pleasant exam of the day, they just let me blab about all kinds of stuff. Prausnitz never really stuck to one subject, kept interjecting little questions on tangents, trying to shake me up, but I fielded them well. Started with about 5 minutes of my design project, then methanol, then Cairns asked how you could burn it in a fuel cell (onboard reforming back to  $H_2$  followed by water-gas shift to get rid of CO, plus catalytic oxidation of the remaining CO 'cause it poisons your fuel cell). Got into organics removal from aqueous waste stream, BOD and  $LOX/LN_2$  manufacture, thermal pollution and cooling towers, but fortunately no control whatsoever. Cairns finished up with Zn process, which I didn't know well, but he led me through. My only flub was I got a bit lost for the oxidation half-reaction at the anode, but he clued me in.

# Dave Humbird's Questions:

#### Transport

This was with Keasling and Radke, though Clay did most of the talking. Actually, Clay did all of the talking.

Suppose we have an electrophoresis gel that is supported between two parallel plates. The current passing through causes a constant 1-D heat generation in the gel. Draw the temperature profile. Explain the boundary conditions if the thing is immersed in a moving bath of brine. Describe the dimensionless numbers involved in finding a heat transfer coefficient. Where do the exponents on Re and Pr come from?

### Kinetics/Thermo

I had Katz and Reimer.

Reimer asked me almost verbatim an old question from 1997 or so. I described reaction equilibrium using the equilibrium constant K, talked about Gibbs free energy, enthalpy and entropy of formation. Talked about how the activities in the statement for K are related to fugacity and how they can be calculated from VLE data or equations of state.

Katz asked me a long question about residence time distribution. However, this was one of his first prelims and the questions were quite silly. Rather than just ask me to derive the RTD for a CSTR (which is what he wanted), he made up something ridiculous about a reactor in which the fluid is so corrosive that one cannot insert a temperature probe, and that someone very intelligent has come up with a temperature transmitter that is roughly the same size as a molecule and is put into the reactor inlet and sends a temperature signal out for as long as it is in the reactor. These are naturally very expensive, and once they leave the reactor, we have to buy more. So, after one residence time,

what is the probability that this fabulous device still remains in the reactor? (It's 1/e, of course, but this took a long time to explain.)

### <u>Design</u>

Blanch and Lynn

This was pretty mellow, but I ended up getting the lowest grade in it. They asked me about my senior design project, but I didn't remember it, so I described something I had done at work. Lynn found a suspiciously superfluous exchanger in my design, and didn't like my reasons for having it. It wasn't until after I left that I realized there were other reasons for having it that I didn't tell him. Blanch then asked me to design a reactor for Ergosterol + UV light à Vitamin D. It's a clear, tubular reactor with baffles inside for mixing. This question basically consisted of me throwing out wrong answers for thirty seconds to a minute until Blanch gave me the right answer, and we moved on.

Di Gao's Questions:

## Thermo & Kinetics (Reimer & Katz)

Katz: A plant produces Sn at 1 atm when the temperature is above 283 K. The Sn is grey. When the temperature is below 283 K, the Sn is white. Now the plant wants white Sn @ high T. We know the change of enthalpy from white Sn to grey Sn and the change of density. Can we get white Sn @ high pressure and high temperature? (Clausius Equation) Derive the Clausius equation and some other small questions while deriving.

Reimer: Say we have the reaction:

$$A \xrightarrow{k1} B \xrightarrow{k2} C$$

If we like B, analyse how to get maximum B using a Batch Reactor. And choose a better reactor from BSTR, CSTR, and PFR.

### Process (Lynn & Blanch)

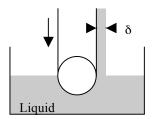
Lynn: Senior Design project.

Blanch: How to deal with SO2 in air.

Blanch: Analyse scrubber of HCl by water. (Azeotrope, heat generating...)

Transport (Goren & Newman)

Goren: Consider a roller like this:



We know the viscosity and density of the liquid. Calculate the thickness of the film  $\delta$  at steady state.

Newman: A heating pipe is in a liquid. T1>T2. As T1 increases, what happens to the liquid? Draw the graph of heat transfer  $(\theta)$  versus T1.





Analyse the three modes of heat transfer.

Goren: Compare momentum diffusivity (v), heat diffusivity k, and mass transfer diffusivity D of Ne, Ar, and Kr.

Phyllis Chen's Questions:

#### Kinetics/Thermo

Katz: What is the residence time for a reactor? Derive the residence time distribution for a CSTR. He was very helpful. As soon as I gave an answer, he would agree (or disagree) quickly. Also quick (maybe too quick) to help me out. I had to know the physical significance of  $\tau$ .

Reimer: The following reaction is in equilibrium:

$$A + B \Leftrightarrow C + D$$

Calculate [D]. He tried to get me to say "equation of state", and that took lots of prodding.

#### **Transport**

Goren: There is a 0.3m\*0.3m square duct, 50 m long. If the air velocity is 5 m/s, what is the pressure drop in the duct? Remember that Goren is infuriated quite easily. Keeping this in mind, I skipped the shell balance and used Bernoulli's equation. He likes the f versus Re plots. A lot.

Newman: A reacting tank is heated by an internal steam pipe. Discuss the heat transfer. I drew the boiling curve and jabbered about it.

Goren: Discuss the relative D,  $\mu$ , and  $k_t$  of Ne, Ar, and Kr. They all have about the same radius. I guessed my way through this one. Newman was helpful in reasoning things out. Then they wanted the statistical mechanics behind all of it. Thankfully, time ran out.

#### Design:

Blanch and Lynn: Discuss the ethanol-water azeotrope. Blanch just smiled and winked. Lynn was visibly upset. They helped me through some of this.