

Preliminary Exam Questions 2004
Compiled by J.T. Koerber

Transport:

JT Koerber (Graves/Bell)

Graves - Suppose you have a CSTR with flat plate in it. On the plate a catalytic first order reaction occurs ($A \rightarrow B$). What is the temperature dependence of the rate of reaction? Derive the relevant equation and discuss the limiting cases. Why does a boundary layer develop? How could you estimate k , the mass transfer coefficient?

Bell - Draw a velocity profile in the boundary layer. Write a mass balance on A in a differential element in the boundary layer using vectors. How can the equation be simplified for the boundary layer? Basically, non-dimensionalize the species balance and the corresponding continuity equation to make some order of magnitude arguments.

Graves - Suppose you have a thermocouple with a hair dryer nearby. If the hair dryer is suddenly switched on, write a differential equation to describe the temperature of the thermocouple as a function of time. Draw a qualitative plot of T vs. time.

Brian Bush (Muller/Balsara)

Dr. Muller – Basically she asked me to solve for the velocity profile of the falling cylinder problem, but she simplified it to be in Cartesian coordinates (i.e. an infinitely long flat plate sandwiched between two other plates). She had me solve for the velocity profile, this is very straightforward. Next she asked me to determine the terminal velocity of the falling plate. To solve for the terminal velocity all I had to say was that you would have to balance the forces being exerted on the plate (gravitational, buoyancy, and drag force). The drag force term is just the tangential and normal shear stresses (τ_{yz} and τ_{zz}) integrated over their respective cross sectional area. There were a few other minor questions she threw in during the discussion, but nothing too difficult.

Dr. Balsara – his question was this. “If I have two buckets, one containing water, and the other air (the air has water vapor in it), and I lower the temperature to some value below the freezing point, why will I get a single large ice cube forming in the bucket of water and snow flakes forming in the air.” My first explanation was nucleation theory. Basically you will get many snow flakes versus one or two ice cubes because of the nature of nucleation (I provided more details though). He didn’t like this answer, so he rephrased and I starting BSing. I never did answer it to his liking, but I heard later that he was looking for me to say that the ice in water is intrinsically a heat transfer problem while the snow in air is a mass transfer problem. I’m not sure how I was supposed to come up with that, but that’s what he wanted.

Marie Fojas (Bell and Graves)

What is a Newtonian Fluid? How does viscosity change with temperature and concentration. Graph time evolution of shear stress vs position. What is the shear stress at the wall at $t=0$. Plot τ at wall vs time. What is the steady state value of τ . Say you have a guy wearing clothes and it is cold outside and the wind is blowing. Describe heat transfer considerations. How does velocity of wind determine how warm guy stays. How would you calculate Re # for this. What is important length scale? We ended with them trying to get me to say the words boundary layer thickness and then describing what it is.

Brad Olsen (Radke & Newman)

Dr. Radke started by asking me the question about evaporation from a capillary where the liquid level is going down (BSL 2nd ed. p. 545-550). Second, Dr. Newman asked me a question where a fluid of ceramic spheres in water was being filtered, and the spheres were accumulating on top of the filter (all water passes through the filter; none of spheres do). I was asked whether constant pressure or constant flow operation is better. I chose constant pressure so that I would not overload the filter on accident and so that I could achieve maximum flow at all times. They asked about safety concerns with a positive displacement pump. Then they asked me to solve for the height as a function of time and solve for the flow rate as a function of

time. This required the Ergun equation, which I think they would've helped me with because they said they didn't remember it, but I was able to derive it from friction factor definitions and such. Dr. Radke was very engaging (I didn't go more than 30 seconds without being interrupted) and did most of the questioning, whereas Dr. Newman only jumped in twice.

David Moler (Balsara & Muller)

How to measure the viscosity of a fluid by measuring the velocity of a plate falling in the middle of a channel filled with said fluid? (similar to many of Muller's past questions)

Why does freezing water sometime form a "fluffy" substance like snow and other times form a rigid solid like ice? (this is not a nucleation problem)

Lisa Bergeron (Graves & Bell)

(Bell) You're standing outside on the east coast, where it is very cold, with the wind blowing on you. If you are a cylinder, and are wearing a thick jacket, how would you calculate the temperature of the outermost layer of your jacket? Write out the governing equations and boundary conditions. Draw the T-profile assuming no gradients in the body.

(Both) Independent of these equations, how would you find h knowing k ? They wanted $h = k/\delta$, where δ is boundary layer thickness if the changes in T cancel, and they were very pleased to hear the word "boundary layer" when getting the change in $x = \delta$.

You have a flat plate with air blowing over it at a velocity, v . I was cut short with this problem, but they generally asked many short questions about this, like for a plot of shear rate vs. shear stress (you can solve them by knowing all the different types), and for the direction of momentum. There was also something about the definition of shear stress/rate and what is really happening here. It has to do with one layer sliding over the layer below it...they wanted it worded very specifically or they weren't satisfied with the answer.

Josef Macht (Newman/Radke)

- the 1st question was about the Arnold cell -> how to determine the diffusion coefficient...We treated only the steady state problem.
I think the problem is discussed in BSL.
- the 2nd question was about a filter process -> Ergun equation, friction coefficient vs. Re
- general comment: If the last time you did transport problems is quite a while ago (about three years in my case), and if you were taught transport problems different from here, than two weeks of preparation might not be enough to go into the exam with confidence, as it was in my case. In the end the exam worked out alright, but a longer preparation period would not have hurt.

Thermo/Kinetics:

JT Koerber (Reimer/Katz)

Reimer - An enzyme denatures as you increase the temperature. Discuss how G , H , and S change during this process. Physically, do all your answers make sense and why? Basically talk about conformation changes and H bonds breaking.

Reimer - Draw P_{xy} , T_{xy} , and y_x VLE phase diagrams. Describe all information that can be obtained from these plots. How does the P_{xy} plot change as T is increased? What happens to the plots if the mixtures are extremely non-ideal? Very straightforward stuff

Reimer - Suppose you have an enzyme that reversibly binds to its substrate. How can you estimate the concentration of free enzyme in solution? Why is the equilibrium constant a function of activities rather than concentration? Where could you get the activity coefficients from? Basically talk about equil. Constant and activities and apparently you can just assume someone that knows to get the activity coefficient.

Katz - Suppose you have a black box with some 0th order enzymatic reaction occurring inside. If we know the thermodynamics of the reaction, the inlet T, inlet conc., outlet conversion, and that the heat capacity of the inlet and outlet streams are equal, how can we calculate the outlet temperature? How can the reaction be 0th order? Physically, what is occurring at each enzyme if the reaction is 0th order? Is the heat of reaction at standard state? Why or why not? Write out overall energy balance and talk about where you get various terms from

Katz - Suppose you have a paint bucket with a second order degradation reaction occurring inside of it. Consider the following two cases. First, the paint bucket is well-mixed at all times. Second, the concentration of the reactant decreases linearly from top to bottom of the bucket. In which case will the rate of reaction be larger? Why? Type of CSTR vs. PFR rate of reactions question

Brian Bush (Reimer/Katz)

Dr. Katz – He asked me to set up the design equation and the necessary equations to determine the conversion in a PFR reactor with holes in it (leaking PFR). He told me that the volumetric flow rate was linear in z , and that the flow out of the end of the tube was zero. This problem isn't that hard. I started with the generic equation governing any reactor (Flow In – Flow Out + Rxn term = accumulation). Then I had to do a shell balance over the length of the tube for any arbitrary point along the reactor. The main point was to recognize that the reactor had two outlet flows, but writing a shell balance around the reactor is straightforward since you know that the axial volumetric flow decreases linearly with z . The shell balance was in terms of concentration, so he had me convert the concentrations into conversions (very simple) and that was pretty much it.

Dr. Reimer – He asked me to draw P_{xy} and T_{xy} plots for a binary mixture. I drew them and he asked me to explain some of the qualitative aspects of the plot. Then he asked what would happen to the curves as he changes T and P , so I redrew them as necessary. I made sure to note how phase envelope narrows as the temperature increases to some value above the boiling points and/or a pressure below the vapor pressure of the fluids. He asked me to describe an azeotrope, draw one on the graph, and explain how they arise (activity coefficients, fugacities, etc.) He asked me if the “lips” (as he called them) are always symmetrical. Of course they aren't, except for ideal systems. Nothing he asked was really that difficult, I was kind of surprised.

Marie Fojas (Chakraborty and Peterson)

Chakraborty asked me what is the difference between a liquid and a gas, both above and below the critical point. He wanted the energy vs volume curves for above, at, and below the critical point, and then we spent a long time discussing how and why the liquid becomes vapor and what happens to the energy barrier between the two phases. Peterson had me write out the basic equation for conversion, which was fine, but then he completely confused me on how I would change it for the general case. It turns out the answer was to change the terms in the expression to mols/ kg instead of mols/vol. After I finally figured that out, I still couldn't figure out why that was so important and time was up so he gave me the answer... it is much easier to measure mols per reactant mass than to measure mols per reactant volume.

Brad Olsen (Chakraborty & Peterson)

Dr. Chakraborty led off with a series of thermo questions: if water vapor is cooled at constant pressure, why does it change to liquid below a certain pressure? (A: vapor has higher entropy but liquid has lower enthalpy, and as temperature is decreased effect of entropy in $G=H-TS$ becomes less important) If water is thrown into hot oil it splatters, but if oil is thrown into boiling water the reverse does not happen; explain. Draw several isotherms on a P - V diagram. Why does the tension in a rubber band increase when it is

heated? If a bag of fruit juice is placed into a concentrated brine solution, why does the fruit juice become concentrated? (A: the chemical potential of water in the juice is higher because there is a smaller mole fraction of solute, so water moves through the bag from juice to brine and the juice is concentrated) Then Dr. Peterson asked me some kinetics questions. How would I experimentally measure conversion in a reactor? What if there is a change in volume with reaction? (A: measure concentration and density at inlet and outlet because the moles per mass will remain constant with reaction) What does the reaction rate depend on? What about for a heterogeneous catalytic reaction? What are the units of the rate and rate constant? How do you make sulfuric acid? Is the reaction exothermic or endothermic? How does temperature affect the rate and equilibrium? During the kinetic discussions, I wrote up the Arrhenius rate law, so when there was extra time, Dr. Chakraborty asked me to explain why it was exponential. I explained about the canonical ensemble and Boltzman probabilities. This was regarded as a circular response, so I did my best in the last few minutes to try and remember how I could use the microcanonical ensemble and the postulates of stat mech to derive the exponential probability distribution, which I couldn't really do. Dr. Chakraborty let me off the hook. Both Chakraborty and Peterson were pleasant and fair. They would let me keep going until I completed my thoughts and then comment on whether they liked the answer or not.

David Moler (Maboudian/Clark)

Kinetics/Thermo

Thermo (Maboudian)

What are the three laws of thermodynamics? Explain them, write equations, etc.

What is fugacity? How is it defined? (I had some problems with this so we spent the rest of the time going over details).

Kinetics (Clark)

In the context of the reaction of $\text{H}_2 + \text{O}_2 \rightarrow \text{H}_2\text{O}$

How to find reaction order/rate constant from experiment?

How to measure temperature dependence of rate constant?

When to use PFR/CSTR?

Lisa Bergeron (Reimer & Katz)

By this time I was dazed, depressed, and ready to be done with it all. Reimer and Katz cleaned the dry-erase board right before I went in, so I think we were all a little distracted by the smell of the cleaning fluid. For these reasons, I don't remember as much about the questions I was asked here as I do about the other two sections....sorry.

They asked a lot of conceptual questions that were pretty basic (I don't remember having much difficulty on them.) I got the impression that they like verbal explanations of everything before you start writing stuff on the board; and when you start using the board, use different colors to label stuff.

(Reimer) There was a problem about a tank with a first order reaction going on inside and no concentration gradient in the r-direction (gradient only in the y-direction). How would you do a shell balance to derive equations for the flux?

(Katz) There was a catalyst problem with a suspended enzyme. They asked for equations for the equilibrium constant, and the activity coefficient. How would you measure these experimentally?

(Reimer) Draw P-T and P-V diagrams and label all parts. Draw the T tie lines on the P-V diagram. What cases change the slope of these tie lines (straight for an ideal case.)

Josef Macht (Reimer/Katz)

- draw a p-V, and p-T diagram, discuss the slope of the gas-liquid border line (Clausius-Clapeyron)
- protein denaturation; why do proteins denaturize at higher T_s ? $\rightarrow \Delta G = \Delta H - T\Delta S$

- another “problem”, which I do not remember any more in detail. I think it was again about minimization of Gibbs energy and the “enthalpy-entropy trade-off”
- kinetics was mostly about mass-, energy and species balances for a zero order reaction with the reactor treated as a black box. As far as I remember I had to draw an Arrhenius plot, too.
- general comment: this exam was pretty relaxed – nothing to be really scared about. Stay cool and apply basic knowledge (balances, etc.)

Design/Control:

JT Koerber (Keasling/Cairns)

Discuss your senior design project. What reaction governs the relative amounts of CO and CO₂ produced from combustion? (Water Gas shift $\text{CO} + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{CO}_2$) What reaction will result in carbon deposits in your reactor? (Boudart equil $2\text{CO} \rightarrow \text{C} + \text{CO}_2$) How can you avoid depositing carbon? LeChatlier’s Principle stuff

Design a controller to control the height of water in a tank if the exact height is not that important. How can one obtain the control parameters? From your response curve, what values do you need? What are you assuming about the process? How can you turn the values from the response curve into control parameters? Some of these questions from completely out of the blue. Somehow, I managed to derive/reason the important values on the response curve and come up with the ever popular Ziegler-Natta tuning method.

Design a plant to produce H₃PO₄ from Ca₃(PO₄)₂. How could you remove various impurities from the phosphate salt such as iron? What can you do with CaSO₄ produced?

Benzene and other aromatics occur in gasoline. Why is this bad from an environmental viewpoint and how do they get into the ground/drinking water? Design a process to purify the drinking water. How can you get it from the ground? What would you do when the activated carbon beds become saturated?

Marie Fojas (Schaffer and Lynn)

Described my senior design project (AiChE "polyether" semi-batch process)... Lynn started asking me details about viscosity and density of reactant mass in my semi-batch reactor, processing times, etc... he wanted numbers. He also wanted details about the choice of solvent used. Schaeffer asked me to draw the arrow pushing mechanism for how my polymerization was proceeding. They wanted to know what my product was used for and where I got my reactants. Lynn also wanted to know about the other steps in the plant that were not associated with my project. I had to optimize a part of my reactor that was inefficient. Schaeffer also asked me about the controls on my reactor and why I would choose one over the other. I had to go through the three basic P, PI, PID and also describe why I had cascade and feedforward vs feedback. I know they asked some other questions but I can't remember what they were.

Brad Olsen (Blanch & Wallman)

After asking where I went to school, Dr. Blanch asked me to draw the HCl process. He then asked me how I would do the process with only one absorber. How would I size the absorber? I started by drawing the diagram for stepping off stages, and then we discussed the mass balance and equilibrium line. The mass balance is horizontal and the PEQ is vertical along the $x=0$ axis due to the dissociation reaction, so there is no way to step off stages. I worked on falling film models for a long while, which led to the conclusion that the limiting mass transfer rate was the diffusion of Cl⁻ ions away from the gas-liquid interface but not before I said a lot of silly things. They then told me to use a CSTR and explain how to design it. (A: Use a sparge to send HCl bubbles through the liquid (bubbles mix the liquid) and recycle the excess HCl from the top of the column. Use a cooling coil to remove excess heat) Next, Dr. Wallman asked me to write the

reaction for ammonia synthesis. Explain how temperature and pressure affect rate and equilibrium. Explain how to separate out the products. What are typical temperatures and pressures used? What is the name of the process? After that, Dr. Wallman asked where I learned about the Haber process because they don't teach it in ChemE curriculums anymore. Before I said anything, Dr. Blanch replied that I learned it in the last 6 weeks studying for prelims.

David Moler (Wallman & Blanch)

How is ammonia made? (Haber-Bosch process - if you have Wallman, I think he would appreciate it if you pronounce this correctly)

Endo- or exothermic?

How will pressure affect conversion?

Where do you want to operate?

Then they walked me through the hypothetical design of a HCl from Cl₂ production plant. Stopped and asked questions along the way (mass transfer issues, controls that might be necessary, how to implement).

Lisa Bergeron (Schaffer & Lynn)

First they asked about my design project, which was making Ethylene Glycols from Ethylene Oxide and water.

(Lynn) Then they asked how I would estimate the melting points and boiling points of my reactants and products if I didn't know them from a table (they wanted pictures of the molecules showing dipoles and polarity.)

(Schaffer) Show the mechanisms of all reactions taking place in detail (electron pushing).

(Lynn) They gave analogous reactions and asked what reactant would be needed to make a different product. For example, one of the ones they asked me was:

If my reaction was: ETO + H₂O => EG

Fill in blank: ETO + ____ => HOCH₂CH₂NH₂

The answer is NH₃.

(You need to remember your nomenclature from organic chemistry so you know what molecules they are talking about when they give you the name.)

(Schaffer) They asked about ratio control systems – when you use it and how it works.

(Lynn) How do you make Ethylene Oxide?

(Schaffer) What controls should surround an ETO reactor?

(Lynn) Why do you drop the pressure in a system of evaporators in series?

When and why would you use vacuum columns for purification?

Josef Macht (Blanch/Wallman)

- the 1st question was about steam reforming (stoichiometry, endothermic reaction -> how do you heat the reactor? -> burn some of the methane -> how do you introduce the methane (staged); further conversion of the reactant stream by the water gas-shift reaction; how do you separate the products? -> absorption of CO₂ using a caustic absorbent)
- the 2nd question was about separation of a small amount of acetic acid from a pulp/paper plant waste water stream. -> use liq.-liq. Extraction, but acetic acid is present in form of acetate. Here, I had to discuss pK_a and pH. The ideal carrier is a so called "ionic liquid". I do not remember the exact chemical formula. I think it was an amine with a long alkyl chain.

- general comment: Again, this exam was pretty relaxed, just trust your common sense.