# 1999 PRELIM QUESTIONS

## KINETICS and THERMODYNAMICS

### Maboudian and Iglesia

Maboudian

What are the Three Laws of Thermodynamics?

Can you express the change in entropy for an ideal gas when:

1) Pressure is constant and temperature is changing? (just know it.)
2) Temperature is constant and pressure is changing? (requires a Maxwell relationship, unless you know it already. I kept fumbling with my Maxwell relations until Maboudian just gave me the one I needed.)

Iglesia

Consider the overall gas phase reaction:

$Q_t$ : molecular weight $A \rightarrow B + C$

If this is exothermic/endothermic, what happens as you increase the temperature? (I got confused initially between the activation energy and the heat of reaction, delta H.)

$Q_r$ : Moment of Inert Can you suggest how this might occur in elementary steps? (Unimolecular reaction - look in Atkins Physical Chemistry.)

linear: 1 non-lin: 3 Devise a reaction rate mechanism and an overall reaction rate expression. (It must be second order in A. I never figured it out and Iglesia looked like he just wanted to move on.)

$Q_v$ : $(1-e^{-h\nu/kT})$ How would you estimate the rate constant parameters? (You could use transition state theory and all the partition function stuff. You don't need to memorize the expressions, just know what the important terms are like mass, moment of inertia, etc.) Which partition function is probably the most significant? (translational motion)

Consider a recycle loop for a PFR:

What happens to the fractional conversion of the reactants as you increase the recycle ratio? (I didn't give him a straight answer because I didn't really study recycle reactors. Really I did not know where he was going with this question.) entropy: $ds = \frac{dQ_{rev}}{T}$ Calculate: $\int_0^{T_1} \frac{C_p}{T} dT + \frac{\Delta H}{T} + \ldots$

### Maboudian and Iglesia

Maboudian

1. What are the three laws of thermodynamics?

She didn't even want any of the equations that went along with the three laws.

2. What is entropy and how do you calculate absolute entropy? How do you calculate the change in entropy from $T_1$, $P_1$ to $T_2$, $P_2$, assuming ideal gas?

I got stuck a little with this one because I remembered a Maxwell relation wrong, but eventually figured out my mistake.

3. What is fugacity? $\mu = \mu_0 + RT \ln \frac{f}{f_0}$. physically. fugacity is the fleeing tendency of a substance
4. Using the virial equation of state, how does the compressibility Z change with differences in pressure?

$\frac{PV}{RT} = Z = 1 + B/V + C/V^2 + \cdots = 1 + B'P + C'P^2 \cdots$

Iglesia

I don't remember this section very well; that's why the questions are phrased so vaguely.

1. Discuss kinetics of a reaction of A -> B + C, an endothermic reaction.
   a. This reaction is second order. Figure out a mechanism.
   b. Some question about the pre-exponential factor of the rate constant. Had to say that the dominant term in transition state theory is the translational term, which is greater for two particles than one particle.
2. We have a PFR with a recycle. How does the PFR behave as recycle approaches zero? How does the PFR behave as recycle approaches infinity?

### Reimer and Schaffer

Reimer

$\frac{PV}{RT} = 1 + BP + \cdots$

$p = \frac{RT}{V-b} - \frac{a}{V^2}$

engineers adopt a sign convention that is much like the way we view a boiler/steam turbine system--work out of the system is positive, while any heat we add to the system is positive). Then he asked me about state functions. Afterwards, he asked me about the Second Law. Tell me about Entropy.

The rest of this portion was over the Carnot Engine. He made me draw up a P-V diagram and explain what each section was about. How are Pressure and Volume related? (Ideal Gas equation of state). Questions about efficiency and whether or not the Carnot cycle is reversible. I was asked if the cycle could ever be 100 percent efficient--I showed him the formula for efficiency [efficiency = $(|Q_H| - |Q_C|) / |Q_C|$ ] And I subsituted $T_C$ for $Q_C$ and $T_H$ for $Q_H$--mentioning that the only way that effiency could equal one is if $T_C$ was equal to zero.

He wanted me to show him how the $T_C$'s could substitute the $Q_C$'s. Other general questions about cycles.

## Clark and Reimer

### Clark

What are the three laws of thermodynamics? Explain them. Since you mentioned cycles, give us an example of one. (The Carnot cycle was an acceptable choice.) Sketch it on the board.

### Reimer

Your company has a very exothermic reaction A+B goes to C that makes millions of dollars. How do you maximize production of C? What kind of reactor would you use? Why? Tell me about rate laws. What is the temperature dependence of the rate constant? What is the pre-exponential factor? (Obviously, my feeble answer that the pre-exponential factor is also called the frequency factor and is related to the entropic change of the reaction was inadequate because the next question was:) No, what does it mean to you? (At that point, A did not have much personal significance to me.) Is it a big number; generally, what is its order of magnitude, 1 or 1 million? How do you measure it?

small $10^{-12} \sim 10^{-9}$

## Maboudian and Peterson

Both of them were really nice and guided me when I need help. Maboudian's question were much more to the point than Petersen's.

Maboudian went first and asked about the 3 laws of thermodynamics to ease me into things. Then she asked about changes of entropy with temperature and pressure. To my surprise, she did expect me to know the Maxwell relation for dS/dP. She asked about the compressibility factor and to give a graph of Z versus P at T1 and T2 where T2 was greater than T1. When I completely screwed this up, both of them walked me through the correct answer.

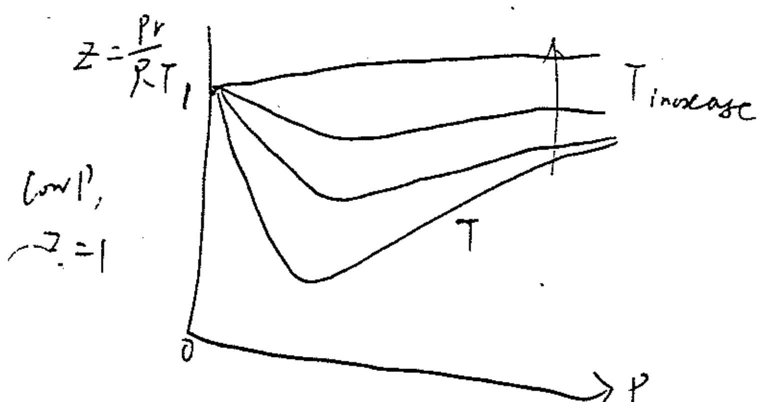
Petersen began by asking me about finding rate data in a batch reactor and units of rate of reaction, etc, etc. Then he asked me a very strange question about how you would determine the change in concentration with time if the volume were changing in a liquid reaction. He wanted me to say that the total mass of the reaction mixture remains constant and to re-express concentration ~~using density~~. I never really got what he was getting at, but after talking to others, neither did they.

Basic: $r = \frac{1}{V}\frac{dN}{dt} = kC_A^n$ → express $C_A$

~~for~~ Virial eq: $Z = \frac{PV}{RT} = 1 + B \cdot P + CP^2 + \cdots = 1 + \frac{B}{V} + \cdots$

truncated: $Z = \frac{PV}{RT} = 1 + \frac{BP}{RT}$   physically: Z: compressibility.

So high P, it is diff from to compressib



Have you ever heard of a hotpack or coldpack? For instance one of those heat packs that skiers use to keep themselves warm [you break the inner container on one and it starts to heat up]. Tell me what you would have to consider when designing one of them.

I thought about the five main issues:

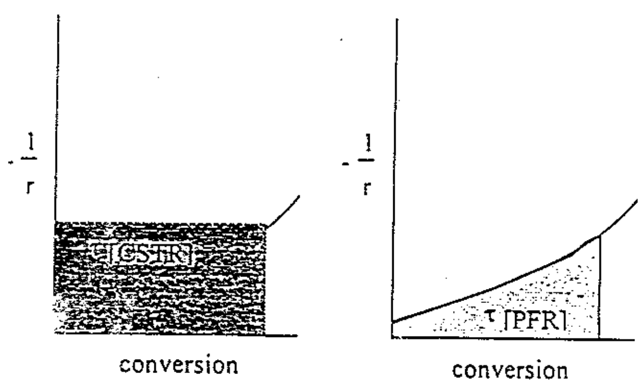
1. Environmental/Safety/Health concerns (ESH) of materials, reactants, products
2. Exothermic Reaction
3. Rate/Speed of Reaction
4. Rate of heat transfer through the casing
5. Cost

Since this was the Thermo/Kinetics section and not the Process Design part, of course we were interested in points 2-4. I drew a proposed design on the board (a casing and an inner container--break open the inner container to allow the reactants to come into contact and start the exothermic reaction)--I noted that it would basically be a batch reaction. I also mentioned that we wanted a slow rate so that the pack would last longer--to which Reimer made me do an energy balance. He made me look at the accumulation term ($mC_p\, dT/dt$). He later led me to reason out that the reaction typically is carried out very fast but the reactants and pack materials have a high heat capacity so they can last for about 30 minutes long.

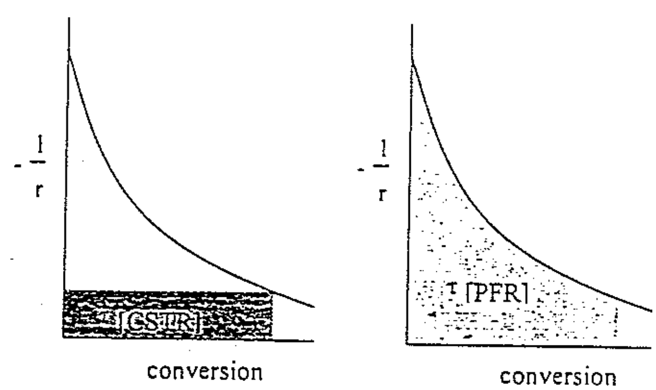
We then changed directions and he told me to consider a reaction of $A + B \rightarrow C$. We want to make large amounts of our product C. List the three main types of reactors and tell me which one would be best.

Of the three reactors (Batch, CSTR, PFR), I eliminated batch first because a flow process would probably be better for producing large amounts of our product. I then mentioned that in most cases, the PFR would be a better choice since it typically gives us a higher conversion than a CSTR (see situation A below) for the same residence time. However, there are cases where situation B applies. We need to look at the graph of -1/r vs. conversion.

Situation A




Situation B




This is also a good time to mention that studying why CSTRs had multiple steady states was very useful. Anyway, Reimer then asked me where does this analysis came from? I answered that they were from the reactor design equations, which are from the mass balance over the reactor. What's a *design equation*? Show me/Derive the design equations for the CSTR case. Pretty much the rest was basic material--we didn't have much time before we had to switch to thermo, however.

Schaffer

Schaffer's questions on Thermo were pretty basic. They included what's the First Law of Thermodynamics? What does it tell us? He made me express it in words and also mathematically. He made me define each term and also asked me about the difference in sign convention between physicists and chemical engineers (chemical

# PROCESS and DESIGN

## Prausnitz and Cairns

Describe your senior design project. I designed a methanol production plant. Basically I felt that I could have talked about it for as long as I wanted but I got nervous after having talked for so long without any comments from them so I stopped and let them rip into my design. You should know what your product is used for. They asked what methanol was used for and I said "for making formaldehyde." Then they asked what formaldehyde was used for and I said for "biology lab experiments" and they LAUGHED at me. Apparently, you should know that formaldehyde is used for polymers.

How do you make nickel? Cairns will most likely ask you about making metals like Ni, Na, Cu, Mg, Al, etc. Unfortunately I didn't study nickel but they led (dragged) me through the process. You should have a general understanding of general and organic chemistry or their attempts at helping you won't help very much. I had to figure out where we find copper in nature, the chemical formula, and how to convert it into the salt used in an electrochemical cell. Cairns kept sighing and Prausnitz kept yawning so I felt like they were disappointed with my performance. Somehow I passed.

## Prausnitz and Cairns

1. What was your senior design project?

I just drew the process flowsheet and described the streams. They didn't care that much about my design project.

2. Let's say we want to separate low concentration organics from water. How would you do that?

Liquid-liquid extraction, but you would introduce another organic compound into water.

Activated carbon.

   a. How would you set up the activated carbon system?

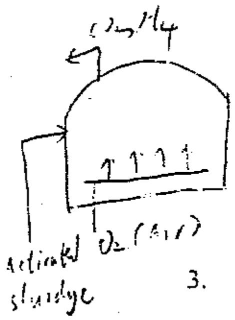
   Need to run two systems in parallel, so steam can be run through one activated carbon tank to reactivate the carbon.

   b. What do you do with the concentrated organic solution (from running steam through a tank)?

   aerobic microorganism decompose the raw material

   You could burn it for fuel, or you could use bacteria to decompose the organics.

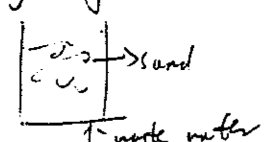
   solid may be burned, or get fert




   c. Draw the bacteria wastewater treatment reactor. What else do you need?

   Oxygen in excess. This led to a whole series of questions asking me to regurgitate how to make all these different compounds.

   reactor, may be fluidized bed.




3. How do you make oxygen? Draw flowsheet.

4. What do you do with the nitrogen?

Haber process. I had to draw the Haber process, but I couldn't remember what to do besides throttle it. They did help me through it.

If too high in organic, anaerobic fermentation

5. How do you make hydrogen?

6. How do you make silicon?

I knew Cairns would ask something like this, but I had focused more on zinc, lithium, and real metals. All I could remember was that silicon comes from $SiO_2$, which comes from sand, and then you need to reduce it with carbon. But Cairns led me through the problem.

## Lynn and Wallman

### Lynn

**So, tell me about your senior design project...**

My project was the synthesis of MTBE (Methyl t-Butyl Ether) from n-butane. I drew a flowsheet up, and he asked me some basic questions about how I handled/separated byproducts and also about the reactive distillation column.

Moving on with MTBE, he asked me if I had ever heard about the MTBE problem that was recently in the news. I told him that I had--MTBE was a fuel additive (oxygenator) that helps the combustion process of gasoline so that it is cleaner-burning. Unfortunately, while it has done wonders for the air pollution in California, it is being found in the water.

**Why is it being found in the groundwater, and why isn't gasoline?** Well, I reasoned that it was probably due to leaks in the underground storage tanks at gasoline stations. Since MTBE is fairly soluble in water (and hard to separate out from water), I said that it was probably because of the mass transfer characteristics of the MTBE and gasoline. Basically, the MTBE would easily be carried off by water flow in the soil, which would lead to MTBE getting in the groundwater.

**Can you think of some other substance that could be used to oxygenate fuel?** I couldn't, so he said that ethanol is used today. He asked if I thought that it would be a problem, and I said probably not (to which Wallman and Lynn shared some joke about "some people probably wouldn't mind having some ethanol in their water"--ha ha).

### Wallman

By then, thankfully, we had to move on to controls. Wallman asked me to draw up a flash drum. He asked some general questions--basically getting at the fact that I'd have to have a pump and a throttling valve in the picture, too. The controls questions were basic (**what variables do you think I would have to control?**). I said temperature, pressure, and the liquid level. He made me draw a feedback controller for controlling the inlet feed temperature.

The flash drum had k components in the feed. I had to do some degree of freedom analysis to justify the fact that I could control/specify the system (think about overall mass balance, component mass balance, energy balance, etc.)

## Blanch and Vorhis

### Vorhis

You are at a refinery where the gasoline/C4 splitter overhead drum is having level control problems. The drum is nearly empty, the vent valve off the drum is wide open, and the tower pressure is rising. What do you do to keep the safety valve on the tower from releasing? (This is probably not a question that Vorhis would ask unless you have some industrial experience. He gave some additional details along the way, which allowed me to get to the right answer: you have to increase the reboiler duty. This is counter-intuitive, because you might think that vaporizing more liquid in the tower would raise the tower pressure even further. However, since the tower is taking a propane/butane stream overhead, if the reboiler duty is insufficient, mostly propane will go overhead. The propane could not condense at the conditions he gave, so reflux to the tower was limited as the overhead drum went dry. Increasing the duty to the reboiler will send more butane and heavier components overhead, which will condense, lower the vapor pressure in the drum, and provide additional reflux/cooling to the tower.)

### Blanch

Design a tower to absorb dilute HCl from an air stream. (The main thing he wanted to hear was perform an energy balance and make sure you use enough water to control the exothermic absorption without boiling off the water.)

## Lynn and Wallman

### Lynn

Lynn started off asking the usual – senior design project. I did the design of a Dinitrotoluene plant and there wasn't much to say. He asked me about process chemistry, extent of reaction, reactants needed and in what quantities, and some process control. At one point I screwed up and said my organics were soluble in water, but they didn't fail me!

Wallman asked me about the control strategy for a flash vaporization chamber. He wanted to know what the relative T and P's were inside and outside of the vessel, where to place controllers and why, and type of controllers (feed back). He helped me whenever I got stuck and always gave useful hints. He also wanted to know how I would solve for the compositions of the outlet streams.

So overall, they were pretty fair with me, but I think that Lynn takes into account if you are confident or not at the board. Wallman seemed to be more helpful.