January 2009 RAE - Start time: 9:00 a.m., Monday, Jan. 12.

There are three problems shown below. Each student has to choose one and let Kathy Lopresti (lopresti@umd.edu) know by e-mail by **12:00 noon today.** You have until **Thursday, Jan. 22, at 12:00 noon,** to complete and submit a written report. The written report should be e-mailed to Kathy Lopresti and a hard copy delivered to her by the due time.

The requirements for the written report, as explained on the ChBE website (http://www.chbe.umd.edu/grad/phd-aptitude.html) are:
The solution to the exam problem is to be in the form of a document not exceeding 10 doublespace pages using a 12pt font. The 10 pages must include the title page, proposal body, and all figures; the number of pages used for references is unlimited.

The report **must** follow the following format:
1. It should include a single title page with a project summary.
2. It should include at most 5 pages dedicated to background information relevant to the particular RAE problem (including the figures of this section).
3. The remainder of the 10 page report must focus on proposed approach to solving the stated problem, any preliminary calculations or research results, the expected outcomes of the project, and a summary of the laboratory equipment and computational resources necessary to carry out the project.

The 10 page limit will be strictly enforced.

You are reminded that students are not allowed to consult with anyone during the RAE, including with faculty members. For procedural questions, you may contact members of the graduate committee (Drs. Adomaitis, Dimitrakopoulos, Ehrman, Raghavan, and CS Wang).

The oral exams will take place on **Friday January 23 between 8:30 am and 5 pm.** A schedule with the times of the exams will be prepared by January 21 and sent to you by email. Each student should plan on a brief (under 30 minutes) oral presentation. The presentation file can be brought to the examination room by the student on a memory stick. If this is not possible, please contact Kathy Lopresti prior to the examination time for alternate arrangements for transferring the file.

RAE Problem 1
Kinetic versus transport limited polymerization

Background

A conventional unseeded (i.e., no small particles added at the beginning) batch emulsion polymerization reaction can be divided into three intervals. Particle nucleation occurs during Interval I and is usually completed at low monomer conversion (2-10%) when most of the monomer is located in relatively large (1-10 micron) droplets. Particle nucleation is believed to take place when radicals formed in the aqueous phase grow via propagation and then enter into micelles or become large enough in the continuous phase to precipitate and form primary particles which may undergo limited flocculation until a stable particle population is obtained. Significant nucleation of particles from monomer droplets is discounted because of the small total surface area of the large droplets. Interval II involves polymerization within the monomer-swollen polymer particles with monomer supplied by diffusion from the droplets. Interval III begins when the droplets disappear--or at least reach a polymer fraction similar to that of the particles--and continues to the end of the reaction. Additional background on emulsion polymerization may be found in any text on introductory polymer science. A particularly good starting reference is

"The Elements of Polymer Science and Engineering," Alfred Rudin, Academic Press, 1982.
Note: this reference book will be available during the RAE, to check out for three hour periods. See Patricia Lorenzana to check out this book.

Interval II is of particular interest. Calculations 50 years ago showed that if the monomer is styrene (water solubility of 0.24 wt %), the system is reaction, rather than diffusion limited.

Problem Statement

Your company has an opportunity to market isodecyl acrylate (water solubility of 0.0026 wt %) at a good profit margin if it can be produced via emulsion polymerization. Your assignment is to determine if such a system is likely to be reaction or diffusion limited during Interval II, since this will determine the design and sizing of the polymerization reactor system.

1. Critically review the literature dealing with this question. You might start with the following references:

> Back, Alan J. and F. Joseph Schork, "Mass Transfer and Radical Flux Effects In Dispersed-Phase Polymerization of Isooctyl Acrylate," *J. Applied Polymer Science*, **102**, 5649-5666 (2006).
>
> Back, Alan J. and F. Joseph Schork, "Emulsion and Miniemulsion Polymerization of Isobornyl Acrylate," *J. Applied Polymer Science,* **103**, 819-833 (2007).

Chai, X-S, F. J. Schork, Anthony DeCinque and Karl Wilson, "The Measurement of the Solubilities of Vinylic Monomers in Water," *Industrial & Engineering Chemistry Research,* **44(14),** 5256-5258 (2005).

2. Propose a simple mathematical model for monomer transport during Interval II emulsion polymerization. Make some judgments about the relative magnitudes of the various mass transfer resistances in the system. Assuming monomer droplets of 10 micron diameter, polymer particles of 0.1 micron diameter, a ratio of 1000 particles for every droplet at the beginning of Interval II, and a desired rate of polymerization of 1 wt% of the total monomer per minute, determine if the system is likely to be mass transfer limited.

3. Propose a set of laboratory experiments to confirm or refute your conclusions in (2).

RAE problem 2
CO_2 removal by absorption and reaction

Background
Carbon dioxide is a gas that has been implicated in climate change. One of the many strategies proposed to reduce the concentration of carbon dioxide in the atmosphere is removal and sequestration. One approach to CO_2 removal is to use a combination of absorption from the gas into a solvent, and chemical reaction, making use of a weak base such as alkanolamine to react with bicarbonate ion, formed as CO_2 reacts with water. This can be done in a packed bed column, see for example reference 1. For this RAE, your assignment is to critically analyze the potential of this approach for CO_2 removal at the level of a power plant the size of the plant that provides electricity for our campus (~ 27 MW) (reference 2). In your solution, develop a proposal for evaluation of this combined absorption/reaction approach at this scale, addressing the following:

1. Describe qualitatively how chemical reactions in the system affect the energy and species balances during absorption in combination with chemical reaction.
2. Set up material and energy balances for a differential segment of a packed bed column absorber/reactor, and describe any assumptions you make.
3. Describe how you could establish the mass transfer coefficients for this system by either laboratory experiments, correlations from the literature, or both. What other parameters in your model must be either measured or determined from first principles? For each, propose how you would obtain them.
4. Downstream of this absorber/reactor, what could be done with the absorber/reactor output stream in terms of permanent sequestration of carbon? Discuss the other steps involved.
5. The campus power plant runs on a mixture of oil and natural gas (reference 2). The regional average CO_2 emissions for natural gas fuel are about 1.2 pounds per kWh (reference 3). Assuming for simplicity that our campus plant operates entirely on natural gas, what are the most significant obstacles to CO_2 removal by absorption at this scale?

References:

1. Gabrielsen J., Michelsen M.L., Stenby E.H., and Kontogeorgis G.M., "Modeling of CO_2 absorber using an AMP solution, " AIChE Journal, 52, 3443-3451 (2006).
2. http://esm.versar.com/pprp/factbook/generation.htm
3. http://www.eia.doe.gov/cneaf/electricity/page/co2_report/co2report.html#table_4

RAE Problem 3
Selective precipitation for protein separation

The separation of proteins can be an arduous task that typically involves a trial-and-error process to determine optimal conditions for separation. Selective precipitation[1] is one of the many methods to separate proteins, in which precipitation of a less soluble protein occurs before any solidification of proteins that are more soluble. One of the key issues in this method is determining the optimal conditions for selective precipitation and until recently mainly involved trial-and-error changes in solution characteristics, e.g., salt concentration, salt type, pH, etc. Since protein crystallization and consequently precipitation depends on protein-protein interactions, optimal conditions of solidification have been suggested to occur when the osmotic second virial coefficient (a measure of such interactions) are within a certain range.[2] The use of measured osmotic second virial coefficients has been moderately successful in determining optimal conditions of binary protein separation.[3] For this RAE, please consider the following:

1) Review current techniques used to separate proteins in solution. This should include the method discussed above and at least two other approaches. Clearly state the advantages and disadvantages of each technology, e.g., do these methods work on only certain protein mixtures?

2) An accurate measure of the osmotic self (B_{ii}) and cross (B_{ij}) virial coefficients are required to determine optimal conditions of protein separations. Describe how B_{ii} and B_{ij} are used to predict optimal separation conditions including a sample calculation for a system of your choice. Discuss what experimental or theoretical method you would use to determine B_{ii}/B_{ij}. What are the assumptions in your chosen method and are there any limitations?

3) Consider that you are interested in extending this method to a ternary mixture of proteins in solution. Design a set of experiments to test the effectiveness of using B_{ii}/B_{ij} to determine optimal conditions for separation. What type of proteins should you study so that this method will be successful (give some examples)? Is it possible to separate all three proteins or just one from two? Ultimately, one would like to devise a set of criteria on the measured or calculated B_{ii}/B_{ij} for separation, how would you test the accuracy of such criteria?

(1) Dixon, M.; Webb, E. C. Enzyme Fractionation by Salting-Out: A Theoretical Note. *Adv. Protein Chem.* **1961**, *16*, 197.

(2) George, A.; Wilson, W. W. Predicting Protein Crystallization from a Dilute Solution Property. *Acta Crystallogr., Sect. D: Biol. Crystallogr.* **1994**, *50*, 361.

(3) Cheng, Y.-C.; Bianco, C.L.; Sandler, S.I., Lenhoff, A.M. Salting-Out of Lysozyme and Ovalbumin from Mixtures: Predicting Precipitation Performance from Protein-Protein Interactions. *Ind. Eng. Chem. Res.* 2008, **47**, 5203.