March 2007 RAE - Start time: 9:00 a.m., Thursday, March 15.

There are three problems shown below, each on a separate page. Each student has to choose one and let Kathy Lopresti (lopresti@umd.edu) know by e-mail by **1 p.m. today.** You have until **Friday, March 23, at 4 p.m.,** 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 double-space 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.

Prof. Zafiriou will be available to answer questions. You are reminded that students are not allowed to consult with anyone during the RAE, including with faculty members.

The oral exams will take place on **Monday, March 26**. 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 transfering the file.

A schedule with the exact times and room numbers for each student is given below. If unforeseen factors necessitate any changes, you will be informed by e-mail.

Schedule for March 26, 2007, oral Research Aptitude Examinations.

George, Elijah; Time: 1:00 p.m. - 2:30 p.m.; Room: 2113 (conference room)
Walker, Justin; Time: 10:00 a.m. - 11:30 a.m.; Room: 2113 (conference room)

Problem 1

New chemistries have been developed in recent years to provide the benefits of living polymerization (anionic or cationic) to polymerizations done via free radical chemistry. These "living radical" or "controlled radical" polymerizations allow the production of block copolymers under much less stringent conditions that ionic polymerization. There are three chemistries for controlled radical polymerization: nitroxide mediated polymerization (NMP), atom transfer radical polymerization (ATRP) and reversible addition fragmentation transfer (RAFT) polymerization.

It is desired to carry out the RAFT polymerization of acrylic acid in an inverse emulsion. That is, the acrylic acid will be dissolved in water, and then the water will be dispersed into a water-in-oil emulsion where the continuous phase is cyclohexane. The acrylic acid will be polymerized using the RAFT chemistry within the submicron water droplets. Discuss the important considerations in the choice of an initiator and the choice of a RAFT agent for this system. Describe the experiments necessary to provide proof-of-concept for the system you have chosen. Describe the analytical tools to be used, and discuss how the data will prove that the polymerization has: (i) taken place, and (ii) has taken place under controlled conditions.

Problem 2

One of the important properties of a fluid is its viscosity. A simple, Newtonian fluid like water or honey has a constant viscosity (independent of the shear rate). To measure the viscosity of such a fluid, one normally uses a rheometer or viscometer. However, such instruments usually require at least about 0.5 mL of the sample. Currently, there is a need to measure the viscosity of many important biological fluids that are available only in very small quantities (e.g., a few microliters). How can one measure the viscosity of such small fluid samples?

(a) Review some of the methods that are currently used for measuring fluid viscosities using very small (μL) volumes.

(b) Propose a new approach to performing such a measurement. (It can be a variation of an existing approach, but you should clearly specify what is different.)

(c) Many fluids are non-Newtonian, i.e, their viscosity varies with shear rate. Can your method be adapted to work for such non-Newtonian fluids?

Problem 3

In Hong and Komiyama (J. Am. Ceram. Soc. 74(7) pp.1597-1604 (1991)), the production of CuO and CuO2 films by chemical vapor deposition along the walls of a tubular reactor system was examined. An interesting finding of this study was that under some circumstances an abrupt change in film morphology occurred along the tube length - that the film changed from a smooth dense film to a porous film partway down the tube. This effect was attributed to the onset of a gas phase nucleation reaction producing particles which subsequently deposited onto the substrate surface.

For this RAE problem, consider re-designing the reactor system so that it takes on a more conventional CVD reactor design: that the reactants mix in a showerhead device and the resulting reacting mixture flows over a wafer placed perpendicularly to the gas flow. Develop a plan for creating a mathematical model of the gas velocity and chemical species composition fields (assume isothermal operation) and the particle nucleation, transport, and deposition. Be sure to include a deposition mechanism for the smooth films, also. Finally, describe the numerical approach needed to determine the distance between the showerhead and substrate to guarantee a uniformly porous film.