January 2011 RAE schedule and proposal format

January 10: post exam questions at 9am; question selection by noon of that day (email selection to Ms. Kathy Lopresti)

January 19: turn in exam (electronic copy only by noon); it is your responsibility to obtain validation of submitted exam from Ms. Lopresti

January 20-21: oral exams

January 25: exam results

Prepare write-up in form of proposal:

Page 1: Title page and Project summary; be sure to include university honor pledge

Pages 2-6: Project background information including literature search, problem motivation

Pages 7-10: Proposed research including plan of work, preliminary calculations

References: no page limit

Any written report not following the format above will be returned with a failing grade

The exam is an individual effort – do not discuss the exam or your solution with anyone. Please direct all questions to Professor Adomaitis

Question 1

In recent years, several companies (Ecogreen, Ecopurer, Stocretec etc..) have developed photocatalytic paints containing photoactive titania nanoparticles. These paints, it is claimed, can reduce the concentration of pollutants such as nitrogen oxides (NOx = NO and NO2) in the air. NOx compounds are precursors for the formation of ozone, and NOx can react in the atmosphere to form nitric acid, leading to acid rain. In order to consider pollution reducing paints in comparison to other pollution reduction strategies, it is necessary to have an understanding of the performance of the paint under realistic conditions of use. Ideally, one would like to know the amount of NOx removed from the air as a function of the cost of the paint, including the cost of applying the paint. It is important to ensure other gas phase compounds which may adversely affect air quality such as HONO (an important source of hydroxyl radical) are not formed in significant quantities. Another concern with these paints is that the photoactive nanoparticles will degrade the binder in the paint, leading to chalking, washing away of the active ingredients, and shortening the useful lifetime of the paint.

In your proposal, address the following:

1. What is the mechanism of NOx removal using titania nanoparticle based paints?
2. How should this paint be applied for optimimum effectiveness?
3. Are there potential adverse environmental effects associated with using photoactive paints on a large scale?
4. Develop an experimental plan for determining the useful lifetime of a photocatalytic paint product. Evaluate the utility of ASTM standard procedures for accelerated exposure testing and incorporate if appropriate.
5. Develop an experimental plan for quantifying the heterogeneous reaction kinetics associated with NOx removal that could be used to predict NOx removal rates under realistic conditions. How would you test your predictions? Develop an experimental plan for field testing of a photocatalytic paint.

Potentially useful references:

Allen NS et al., “Photocatalytic Coatings for Environmental Applications” Photochemistry and Photobiology, 81 (2005) 279–290

Laufs S. et al., “Conversion of nitrogen oxides on commercial photocatalytic dispersion paints” Atmospheric Environment 44 (2010) 2341-2349

Question 2

Modeling signal transduction networks in living cells
One of the methods by which living cells respond to stimuli is through signal transduction networks. These networks consist of a series of chemical reactions (Fig. 1), each of which involves the interconversion of a molecule (e.g. A) and its activated form (e.g. $A^{å}$). The rate constants of the *n*th step depend on the extent of the (*n*-1)th reaction. Thus such a network transfers information between a stimulus and a response without transferring material. An example of a stimulus-response pair is the binding of the hormone insulin to a cell (stimulus) and the reduction of blood glucose concentration (response), or an insect bite on a plant leaf (stimulus) and the secretion of compounds that defend the leaf cells from the bite (response).

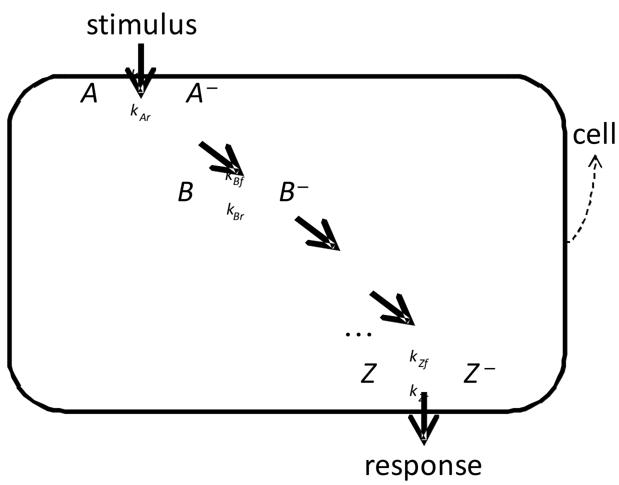

Figure 1. A signal transduction network (signal transduction) in a cell. The rate constants of the *n*th step depend on the extent of the (*n*-1)th reaction. Thus the network transfers information (depicted as solid single-sided arrows) between a stimulus and a response without transferring material.

The mathematical modeling of signal transduction networks involves several chemical engineering principles. While accurate mathematical models facilitate the prediction of a cell's response to a given stimulus or how deficient genes or proteins compromise a cell's response, such models are challenging to construct.
Suppose the objective of your Ph.D. work is to model a certain signal transduction network. You have performed several high-precision experiments using a time-variant stimulus and obtained time course profiles of several intermediates in this network, as depicted in Fig. 2.

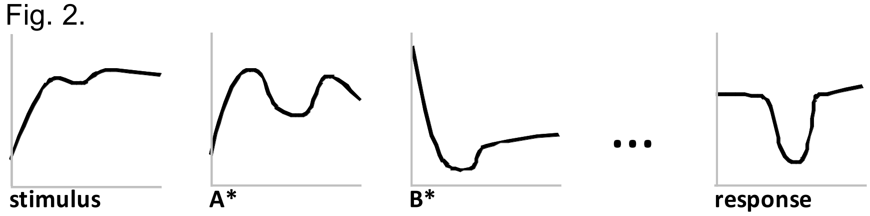

Figure 2. Experimental signal transduction data.

How would you go about modeling the network? Specifically:

a. **Model formulation.** What types of equations would you write? What assumptions (from a chemical engineering perspective) would you make in writing these equations? Before answering, it is suggested that you study at least one article that reports a signal transduction model. Good examples are models of the insulin signaling pathway (Sedaghat et al. 2002), the G protein signaling pathway (Bornheimer et al. 2004) or the NF-κB signaling pathway (Lipniacki et al. 2004).

b. **Solution and parameter estimation.** How would you solve the equations so that you can predict the dynamics of the pathway? Importantly, how would you use your experimental data to obtain the values of the myriad parameters (e.g. rate constants) in the model? For help, look up Chu et al. (2009) or any article that covers the use of optimization in parameter estimation.

c. **Modeling interesting dynamics.** Some signal transduction networks exhibit interesting dynamic features, such as the existence of feedback loops or conversion of a continuous input to a switch-like response. If such features are apparent in your experimental data, how would you adapt your model to mimic these dynamics? You are suggested to read (Giri et al. 2004) (example paper) or (Mangan and Alon 2003) (review).

References

Bornheimer, S.J., Maurya, M.R., Farquhar, M.G., Subramaniam, S., 2004. Computational modeling reveals how interplay between components of a GTPase-cycle module regulates signal transduction. *Proceedings of the National Academy of Sciences* **101,** 15899-15904.

Chu, Y., Huang, Z., Hahn, J., 2009. Improving prediction capabilities of complex dynamic models via parameter selection and estimation. *Chemical Engineering Science* **64,** 4178-4185.

Giri, L., Mutalik, V., Venkatesh, K., 2004. A steady state analysis indicates that negative feedback regulation of PTP1B by Akt elicits bistability in insulin-stimulated GLUT4 translocation. *Theoretical Biology and Medical Modelling* **1,** 2.

Lipniacki, T., Paszek, P., Brasier, A.R., Luxon, B., Kimmel, M., 2004. Mathematical model of NF-[kappa]B regulatory module. *Journal of Theoretical Biology* **228,** 195-215.

Mangan, S., Alon, U., 2003. Structure and function of the feed-forward loop network motif. *Proceedings of the National Academy of Sciences* **100,** 11980-11985.

Sedaghat, A.R., Sherman, A., Quon, M.J., 2002. A mathematical model of metabolic insulin signaling pathways. *American Journal of Physiology – Endocrinology and Metabolism* **283,** E1084-1101.

Question 3

Concentrating solar thermal energy systems currently are used to produce high-pressure steam to drive conventional steam turbines connected to electrical power generators. Alternatively, the solar energy can be used directly to drive chemical reactions that produce hydrogen as part of a thermochemical cycle. The basic concepts behind these cyclic systems are that

1. Concentrating solar energy collectors are used to create a sufficiently high temperature to force an equilibrium reaction in a direction opposite of what is observed at more moderate temperatures in the hot portion of a thermochemical cycle;
2. The concentrators also provide the energy needed to power the endothermic reactions that constitute the hot portion of the cycle.

Consider, for example, the ZnO/Zn cycle studied by Weimer and coworkers at the University of Colorado, NREL, and ETH Zurich (2009) ([1] and the references therein) in which water is split in a reaction with zinc in an exothermic reaction $\Delta Hr = -62$ kJ/mol at 700 K in the following oxidation reaction:

$Zn(s) + H_2O(g) \rightarrow ZnO(s) + H_2\ (g)$

and Zn is recovered in the high temperature (2400 K) endothermic reduction step ($\Delta Hr =$ 557 kJ/mol):

$2\ ZnO(s) \rightarrow 2\ Zn(g) + O_2\ (g)$

There are many practical considerations in making this process work. For this RAE problem, propose a research program combining reactor system modeling, prototype design, and experimental evaluation of the following elements of the overall thermochemical cycle. In your proposal, focus on the following four process elements

1) For the “off-sun” H_2 production reactor, describe alternative reactor designs, how the solid Zn would be fed to the reactor, and what the optimal form (e.g., Zn nanoparticles?) would be determined so as to minimize the formation of a passivating ZnO film on the reaction surface, reducing the rate of the oxidation reaction. Be specific in terms of the form of the reactor model you anticipate developing
2) Repeat the analysis above, but applied to the on-sun side of the reaction cycle. Additionally, describe the features unique to your reactor design that account for the solar heating. Assume this reactor operates near atmospheric pressure and about 2400 K.
3) Propose a separation process for the O_2 and Zn produced in the on-sun reactor. Note that the Zn product exists as a gas at the prescribed reactor conditions.
4) Identify opportunities for energy integration in the overall process.

Reference

[1] Weimer, A. W., C. Perkins, P. Lichty, H. Funke, J. Zartmen, C. Bingham, A. Lewandowski, S. Haussener, and A. Steinfeld, Development of a solar-thermal ZnO/Zn water-splitting thermochemical cycle, Final report DE-PS36-03GO93007, 2009.