February 1, 2015

Dear EECE 503 students,

Here is my **weekly letter No. 4** reminding you to review, learn, arrange and summarize the material covered in class **during week 3 of lectures (January 27 and 29)**:

1. **Transition state theory (TST) and elementary gas phase reactions (Ch. Section 6.2; section 6.4.1 electrolyte effect, pressure effect, chain reactions).**

You need to know the three basic postulates of the transition state theory and that the rate of an elementary reaction is the product of the universal frequency and the concentration of the transition state (which is in equilibrium with reactants). The Gibbs free energy change involved in the estimate of this equilibrium constant contains reflects a non-charged entity. The rates of many seemingly elementary are really obtained from the principle of microscopic reversibility applied to unimolecular and bimolecular reactions. These are a particularly useful in deciphering the termination steps in chain reactions. The pressure effect and electrolyte effect (at dilute ionic strengths) can be assessed by TST (the second requires the application of Debbye-Huckel theory).

2. **Transition state theory (TST) - liquid phase reactions; solvent effects and electrostatic effects. Diffusion limited reactions. (Ch. 7N sections 7.4 pp 4-6; 7.5 pp7-13; 7.8).**

With the help of basic physics regarding forces on charged elementary entities in solution lead to the estimates of rates between ions and ions and molecules. The Gibbs free energy change for creation of the transition complex is no extended to include the addition work required to create a charge entity. Both the dual and single sphere model predicts the same relationship with regard to the dielectric constant of the liquid medium.

The realization that the formation of the transition state will in many systems much faster than the tow reactants coming in sufficient proximity to create a transition state led to the models for diffusion limited reactions. Remind yourself of the concepts of diffusion from your favorite text. In addition review to notes provided. It is your ability to properly use the resulting final formula for the diffusion limited liquid elementary reaction that counts.

3. **Compartmental models for single phase systems. Ch. 5 Sect. 5.4; pp 14-17.**

It is very important to master the basic component mass balance for a reacting species (or product species) and write its rate in terms of other stable components in the system. The rates whenever possible instead of being empirical are derived for a separate consideration of reaction mechanisms by using PSSA or RLSA to eliminate the concentrations of active intermediates. Another alternative is to solve a complete set of equations for both stable species and active intermediates.

4. **Applications to ozone interactions with pollutants. (Ch. 5; sect.5.5 pp18-34).**

The lecture by Joyce Yu and the text quoted above should be sufficient to master these sections. If there are questions, bring them up in writing please.