**Second Homework**

**Question I:  Resonance fluorescence detector**. **(3 pts)**
Explain (with the help of one illustration) the principle behind, and the technical implementation of the resonance fluorescence detector.  Discuss the applicability, benefits and limitations of this detector.

**Question II:  Thermal Decomposition of HI (7 points)**

**Learning Objective: Different ways to look at the same data:**
　　　　There are several ways to establish the reaction order based on the kinetic data.  For example, the reaction order could be calculated from the rate versus concentration data without knowing the rate constant.  This analysis does not require integration of the differential rate law.  Alternatively, when the rate information is not directly available, the reaction order could be established by testing if a particular kinetic model produces consistent values for the rate constant. The latter calculation typically requires the use of the appropriate integrated rate equation.  If the reaction progress is monitored at one initial concentration as a function of time then linear or nonlinear fitting to concentration versus time data yields rate constants.  Frequently this is technically impossible.  Instead, kinetic data is obtained by carrying out multiple reactions (each with different initial concentration) and the extent of each reaction is determined after stopping each of the reactions.  In this scenario, the rate constant is typically determined for each initial concentration based o the integrated rate law solved for the rate constant.  The independence of rate constants from concentration or extent of the reaction indicates that a particular kinetic model is appropriate.

　　　　Analysis of experimental data is complicated because the data always has errors and one must decide if deviations from the data reflect the quality of the experiment or indicate that a model used for analysis is inadequate.  A number of statistical tests have been devised to measure the goodness of fit (see http://www.itl.nist.gov/div898/handbook/pmd/section4/pmd44.htm).  Regression analysis often provides a measure of statistical uncertainty for the regression parameters.  For example, if we believe that the data is free of systematic errors and the linear regression of $\log[dC/dt]$ versus $\log[C]$ provides a slope of 1.97 with a standard deviations of 0.05 one would conclude that the reaction is second-order and the small deviation from the expected value 2 is due to random noise in the data.  On the hand if the linear regression of data provides a slope of 1.82 with a standard deviation of 0.22 it may be difficult to tell if the data is bad or the model inappropriate without further analysis.  A valuable tool to assess the validity of the model is graphical analysis of residuals.  The residuals are the difference between the observed values and the values predicted by the model.  A good model will yield residuals that are randomly scattered above and below the zero at all values of the experimental variables.  A bad fit shows systematic variations of residuals with the values of experimental variables.  Typically, a plot of residuals versus the independent variable (e.g. the time or initial concentration) is analyzed to assess the goodness of fit.  Similar plots can be constructed with respect to dependent variables (remaining concentration, extent of the reaction) and may be useful for revealing the presence of systematic errors in the data.

**Background Information**

   Max Bodenstein and George Kistiakowsky studied the thermal dissociation of hydroiodic acid at higher temperatures in the last part of 19th century and early 20th century.  This reversible reaction appeared to follow second order kinetics and it was postulated that the reaction occurred by one-step bimolecular collision between two hydroiodic acid molecules.  Data by Bodenstein and later researchers (e.g. W. Craven, *J. Am. Chem. Soc.* 78, 3297 (1956)) also provided the temperature dependence for the equilibrium constant and the dissociation rate constant.  In particular, it was found that the reaction enthalpy is slightly temperature dependent and can be calculated at as

$$\Delta H^0 = 1468.1 + 3.1482\ T - 1.6266\ 10^{-3}\ T^2 + 1.982\ 10^{-7}\ T^3$$

In this equation, temperature is in kelvins and reaction enthalpy in cal/mol.  The activation energy of the dissociation reaction was found to be temperature dependent (Arrhenius plot is non-linear) but near 321.4 ºC the temperature dependence of rate can be described as

$$k(\text{degrees}-321.4) = k(321.4) * (1 + 0.061(\text{degrees}-321.4)).$$

Kistiakowsky carried out a series of rate measurements at various concentrations of HI in the absence of initial $H_2$ or $I_2$.  The PDF copy of his 1928 paper is posted, and is recommended reading not only for his lucid description of experiments ("*Numerous explosions which, of course, ruined the rather costly quartz vessels were the unpleasant result*") but also for a thorough analysis of sources of possible errors.  In short, the purified hydroiodic acid was sealed in the quartz vessels at low temperature, the reaction was initiated by immersing the vessels into a large thermostat filled with molten lead, and stopped after a certain time by cooling the vessel rapidly.  The concentrations of formed iodine and remaining HI were determined by titration and the fraction of decomposed HI was calculated as

$$x = \frac{[I_2]}{[I_2] + \frac{1}{2}[HI]}$$

This fraction was then converted into percentage of HI decomposed and is presented in Table III of his paper.  The relevant portion is reproduced below and is available electronically at http://www.chem.ucsb.edu/~kalju/chem111/private/Kistiakowsky.txt

| Temp, C | Time, s | A₀, mol/L | Decomp % |
|---------|---------|-----------|----------|
| 322.40  | 82800   | 0.02337   | 0.826    |
| 321.60  | 172800  | 0.03838   | 2.567    |
| 322.10  | 180000  | 0.04333   | 3.286    |
| 322.70  | 173100  | 0.04474   | 3.208    |
| 321.60  | 81000   | 0.1027    | 2.942    |
| 321.60  | 57560   | 0.1126    | 2.670    |
| 322.40  | 61320   | 0.1912    | 4.499    |
| 321.40  | 19200   | 0.3115    | 2.308    |
| 321.60  | 18000   | 0.3199    | 2.202    |
| 321.30  | 16800   | 0.3279    | 2.071    |
| 321.40  | 17400   | 0.3464    | 2.342    |
| 321.40  | 17700   | 0.4075    | 2.636    |

| | | | |
|---|---|---|---|
| 320.40 | 18000 | 0.4228 | 2.587 |
| 321.30 | 23400 | 0.4736 | 4.343 |
| 321.60 | 6000 | 0.9344 | 2.224 |
| 321.70 | 5400 | 0.9381 | 1.903 |
| 321.10 | 8160 | 1.1380 | 3.326 |
| 321.70 | 5400 | 1.2310 | 2.741 |

Note that the data is arranged in the order of increased initial concentration, and the reaction time was chosen such that it gives a similar low percentage of decomposition in each reaction. At concentrations above 1.2 M, the non-ideal gas behavior becomes important and this portion of data is omitted here. Also note that because of temperature changes in the thermostat, each reaction occurred at a slightly different temperature.

**Data Analysis**

Prof. Horia Metiu's textbook provides analysis of this data based on a more modern approach than Kistiakowsky's. First, by programming his own global optimization routine, Prof. Metiu was able to perform a global analysis of Kistiakowsky's data. Second, the fitting equation that Prof. Metiu derived with Mathematica is simpler than the equation used by Kistiakowsy (see Eq. 3 in the paper). Interestingly, the Prof. Metiu's analysis suggests that the decomposition of HI is not a direct bimolecular reaction while Kistiakowsky and his peers felt that the "rate of decomposition is bimolecular in the whole range of concentrations investigated".

In this homework you are asked to critically evaluate the data on your own and provide your opinion about whether this data is consistent with the decomposition being a direct bimolecular reaction or not. To get started, you may use the PDF copy of a *Mathematica* notebook at
http://www.chem.ucsb.edu/~kalju/chem111/private/Second_Order_AAPQ_Extent_v9.pdf that derives the equation linking the extent of this reaction with the time, equilibrium constant, and the rate constant $k_2$ for the reverse ($H_2 + I_2$) reaction. You are not expected to repeat Prof. Metiu's global analysis. Instead, start by following the path outlined in Exercise 6.6 of his text and carry out all corrections and statistical analyses to establish how well the reversible second-order kinetic model fits this data.

**Extra credit** (5 points)

Derive Equation 3 in Kistiakowsky's paper starting with either equation 6.50, 6.75, or 6.84 in Metiu's book. This extra credit will be added to your score after the grading curve is established to see if you qualify for a grade bump. Note that I have not done this part and cannot guarantee that *Mathematica* is able to work through the algebra. You are of course welcome to reverse-engineer back from Equation 3.

**Question III:  Business Decisions & Chemical Kinetics**

You have learned that "*In industrial synthesis one is interested in economically and quickly producing reasonable yields of sufficiently pure material.  Kinetics allows estimating the reaction yield as a function of time and initial reactant concentration.*"  The following two assignments illustrate what this means in practice.

Imagine that you work in a DNA synthesis facility and are in charge of a smooth operation of the DNA annealing reactor.  The reaction that occurs in this reactor is a simple bimolecular association of two complementary strands of single stranded DNA that anneal to form a DNA double helix.  The annealing is always carried out by mixing equimolar concentrations of two purified single-stranded oligonucleotides in a slightly viscous buffer solution at pH 7.  The reaction leading to dimeric DNA can be written as

$$ssDNA1 + ssDNA2 \rightleftarrows dsDNA$$

Your facility has a state-of-the art reactor with capacity of 1 mL and caters to individual customers who have unique requirements for the sequence (which determines the rate constants), the final amount, and urgency.  You must decide the appropriate annealing strategy for each order.

**Task 1**.  ( 5 points)
   Customer Bill has requested 20 µmoles of dsDNA that under standard annealing conditions forms with the rate constant of 0.08 $M^{-1}$ $min^{-1}$ and dissociates with the rate constant of 0.01 $min^{-1}$.  Bill is a busy and wealthy customer and he is willing to pay extra to have his synthesis finished fast. ***What is the minimal initial concentration of ssDNA that you should use to have Bill's order fulfilled in 1 hour?***  Assume that the product can be extracted from the reaction mixture with 100% yield and that the reaction setup, product extraction, and packaging takes 30 minutes together.

**Task 2.**  (5 points)
   Customer Monica has requested 110 µmoles of dsDNA that under standard annealing conditions forms with the rate constant of 0.04 $M^{-1}$ $min^{-1}$ and dissociates with the rate constant of 0.005 $min^{-1}$.  Monica is a price-conscientious customer who cannot afford to pay for more than 400 µmoles of ssDNA starting material. ***What is the minimal time required to fulfill Monica's order***?  Assume that the product can be extracted from the reaction mixture with 100% yield and that the reaction setup, product extraction, and packaging takes 30 minutes together.