UNIVERSITY OF
ROCHESTER

DEPARTMENT OF CHEMISTRY
PChem II W. Udo Schröder

Due: **Next** Workshop

Physical Chemistry II

Exercises Set 3

Conceptional Review

A. Discuss some features of Logistic-Map (LM) dynamics: Why does the character of the iterations change so strongly with the magnitude of the gain/amplification parameter μ? Explain the plot of asymptotic intensity I_n vs. μ. What does "bifurcation" or multiple bifurcation mean? What are their relation to "periodic points," points of period n?

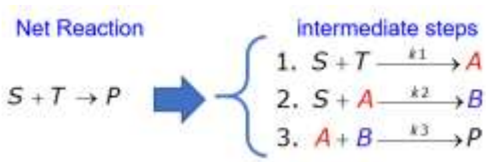
B. What is a heuristic meaning of the Lyapunov exponent λ? What is the character of LM iterations for λ=**0**?

C. Why would one expect the autocatalytic reaction $A + B \rightleftarrows B + B$ behave non linearly with respect to the concentrations of the reagents? What do the different lengths of the arrows imply?

D. Review the method of partial fraction decomposition for ratios of functions.

1. Kinetics of Coupled Chemical Reactions

Consider the set of coupled reactions discussed in class.



a. Why are they called autocatalytic?

b. What conditions determine maximum product output?

Referring to the results derived in class for stationary concentrations [A] and [B], what is the most effective of the above three reactions in "rate limiting" the sum reaction?

2. Rate and Yield of an Autocatalytic Reaction

Consider the autocatalytic reaction $A + B \rightarrow B + B$ occurring in a reaction vessel with reaction rate constant ***k***. Assume $C_A(t=0) = A_0$, $C_B(t=0) = B_0$ for the start concentrations at time zero.

a) Write down the differential rate law for $C_B(t)$.

b) Derive the solution $C_B(t)$ of that rate equation. (Hint: In the integration, use the method of partial fractions.)

c) What initial condition in A_0, B_0 provides the highest product yield?

3. Cooperative Phenomena in Complex Chemical Reactions

Consider the auto-catalytic reaction (Lotka-Volterra reaction) $A \rightarrow P$, which can be decomposed into a number of elementary steps,

$$A + x \xrightarrow{k_1} 2x \quad rate\ k_1 = 2.4$$
$$x + y \xrightarrow{k_2} 2y \quad rate\ k_2 = 4.2$$
$$y \xrightarrow{k_3} P \quad rate\ k_3 = 5.1$$

which, in an actual reactor, occur simultaneously. Here, the input reagent A is kept at a constant, but arbitrary concentration C_A=[A]=const. Catalysts are provided with initial concentrations $x_0 = 1.5$, $y_0 = 1.0$.

a) Write down and discuss the 3 corresponding rate equations for the associated elementary reactions. These equations define the evolution of the trajectories {$x(t)$, $y(t)$}. What is the role of the reagents x and y?

b) Determine the stationary concentrations X and Y for the intermediate products x and y as functions of the rate constants k_i and the concentration of the input reagent A.

c) Consider small (first-order) variations of the system about the stationary concentrations, $x(t) = X + \delta x(t)$ $\quad y(t) = X + \delta y(t)$
and derive the equations of motion for $\delta x\,(t)$ and $\delta y\,(t)$. Neglect higher-order variations.

d) Show that the concentrations δx and δy undergo periodic oscillations. Determine the dependence of the frequency of these oscillations on rate constants k_i and concentration of A.

4. Excel Coding Project: Coupled Chemical Reactions (AC)

Modify a provided MS-Excel code to model the time evolution of the set of coupled reactions (Lotka-Volterra Rxns)

$$A + x \xrightarrow{k_1} 2x \quad rate\ k_1 = 2.4$$
$$x + y \xrightarrow{k_2} 2y \quad rate\ k_2 = 4.2$$
$$y \xrightarrow{k_3} P \quad rate\ k_3 = 5.1$$

Use the rate equations derived in Exercise 3 above. Perform model calculations for different concentrations of the reagent (for example A = *0.01, 0.05, 1.0,* etc.).