

CHEM-UA 652: Thermodynamics and Kinetics

Notes for Lecture 22

I. THE COMPLEXITY OF MULTI-STEP CHEMICAL REACTIONS

It should be clear by now that chemical kinetics is governed by the mathematics of systems of differential equations. Thus far, we have only looked at reaction systems that give rise to purely *linear* differential equations, however, in many instances the rate equations are nonlinear. When the differential equations are nonlinear, the behavior is considerably more complex. In particular, nonlinear equations can lead to oscillatory solutions and can also exhibit the phenomenon of *chaos*. Chaotic systems are systems that are highly sensitive to small changes in the parameters of the equations or in the initial conditions. Basically, this means that the behavior of a chaotic system can be unpredictable, since such small changes can occur in the form of small errors in determining the parameters (rounding to the nearest 10th or 100th) or in specifying the initial conditions, and these small changes can cause the system to evolve in time in a very different way.

In order to illustrate the concept of chaos, consider a very typical and well known system, the Lorenz equations. These actually closely resemble the kinds of equations that arise in the study of nonlinear chemical kinetics. In this case, the differential equations are stated for three variables $x(t)$, $y(t)$, and $z(t)$:

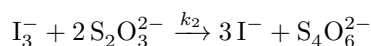
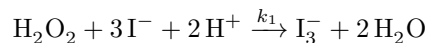
$$\begin{aligned}\frac{dx}{dt} &= \sigma(x - y) \\ \frac{dy}{dt} &= x(\rho - z) - y \\ \frac{dz}{dt} &= xy - \beta z\end{aligned}\tag{1}$$

where σ , ρ , and β are the parameters, and the equations have as initial conditions $x(0) = x_0$, $y(0) = y_0$, and $z(0) = z_0$. These equations cannot be solved analytically, but we can solve them very accurately using a computer program. The trajectory in x , y , and z space can be viewed dynamically on the following wikipedia page: http://en.wikipedia.org/wiki/Lorenz_system. If you follow the trajectory point $\mathbf{r}(t) = (x(t), y(t), z(t))$, you'll see that the motion is highly unpredictable, although it stays on a series of two rings, its motion from one ring to another appears to be random, even though the motion is entirely deterministic.

Keep the Lorenz system in mind as we now explore nonlinear chemical kinetics.

II. THE IODINE CLOCK REACTION

The iodine clock reaction is a popular chemistry experiment in which one can visualize how different rate constants in consecutive reactions affect the concentration of species during the reaction. Iodine anions (I^-) are colorless. When I^- is reacted with hydrogen peroxide and protons, triiodide is formed, which has a dark blue color. Consider the following series of irreversible reactions:



The rate laws for this system are

$$\begin{aligned}\frac{d[I_3^-]}{dt} &= k_1[I^-]^3 - k_2[I_3^-][S_2O_3^{2-}]^2 \\ \frac{d[I^-]}{dt} &= -k_1[I^-]^3 + 3k_2[I_3^-][S_2O_3^{2-}]^2 \\ \frac{d[S_2O_3^{2-}]}{dt} &= -k_2[I_3^-][S_2O_3^{2-}]^2\end{aligned}\quad (2)$$

In order to make the equations look a little simpler, let us introduce the variables:

$$x = [I^-], \quad y = [I_3^-], \quad z = [S_2O_3^{2-}]\quad (3)$$

In terms of these, the rate equations are

$$\begin{aligned}\frac{dx}{dt} &= -k_1x^3 + 3k_2yz^2 \\ \frac{dy}{dt} &= k_1x^3 - k_2yz^2 \\ \frac{dz}{dt} &= -k_2yz^2\end{aligned}\quad (4)$$

If we solve these numerically, we find the following time dependence of the three concentrations: This is a clear example of nonlinearity. Note how the concentration of I_3^- remains close to 0 for a period of time and then suddenly starts to increase. In a sense, think of the “straw that broke the camel’s back”. As we pile straws on the back of the camel, the camel remains upright until that last straw, which suddenly breaks the back of the camel, and the cammel suddenly falls to the ground. This is also an illustration of nonlinearity.

Despite the complexity of the rate equations, we can still analyze the approximately and predict the behavior seen in Fig. 1. In this reaction mechanism, $k_2 \gg k_1$. Given the rate law for I_3^- ,

$$\frac{d[I_3^-]}{dt} = k_1[I^-]^3 - k_2[I_3^-][S_2O_3^{2-}]^2\quad (5)$$

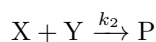
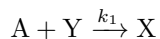
if we use the steady-state approximation, we can set the $\frac{d[I_3^-]}{dt}$ equal to 0, yielding

$$[I_3^-] = \frac{k_1}{k_2} \frac{[I^-]^3}{[S_2O_3^{2-}]^2}\quad (6)$$

Since $k_2 \gg k_1$, the concentration of $[I_3^-]$ is approximately 0 as long as there are $S_2O_3^{2-}$ ions present. As soon as all of the $S_2O_3^{2-}$ is consumed, the concentration of I_3^- can build up in the solution, changing the solution to a dark blue color. Figure 1 displays the concentration profiles for I^- , I_3^- , $S_2O_3^{2-}$. As can be seen from the figure, the concentration of I_3^- (dashed line) remains at approximately 0 mol/L until all of the $S_2O_3^{2-}$ (dotted line) has been depleted.

III. OSCILLATING REACTIONS

In all of the examples we have seen thus far, the concentration of intermediate species displays a single maximum during the course of the reaction. There is another class of reactions called *oscillating reactions* in which the concentration of intermediate species oscillates with time. Consider the following series of reactions



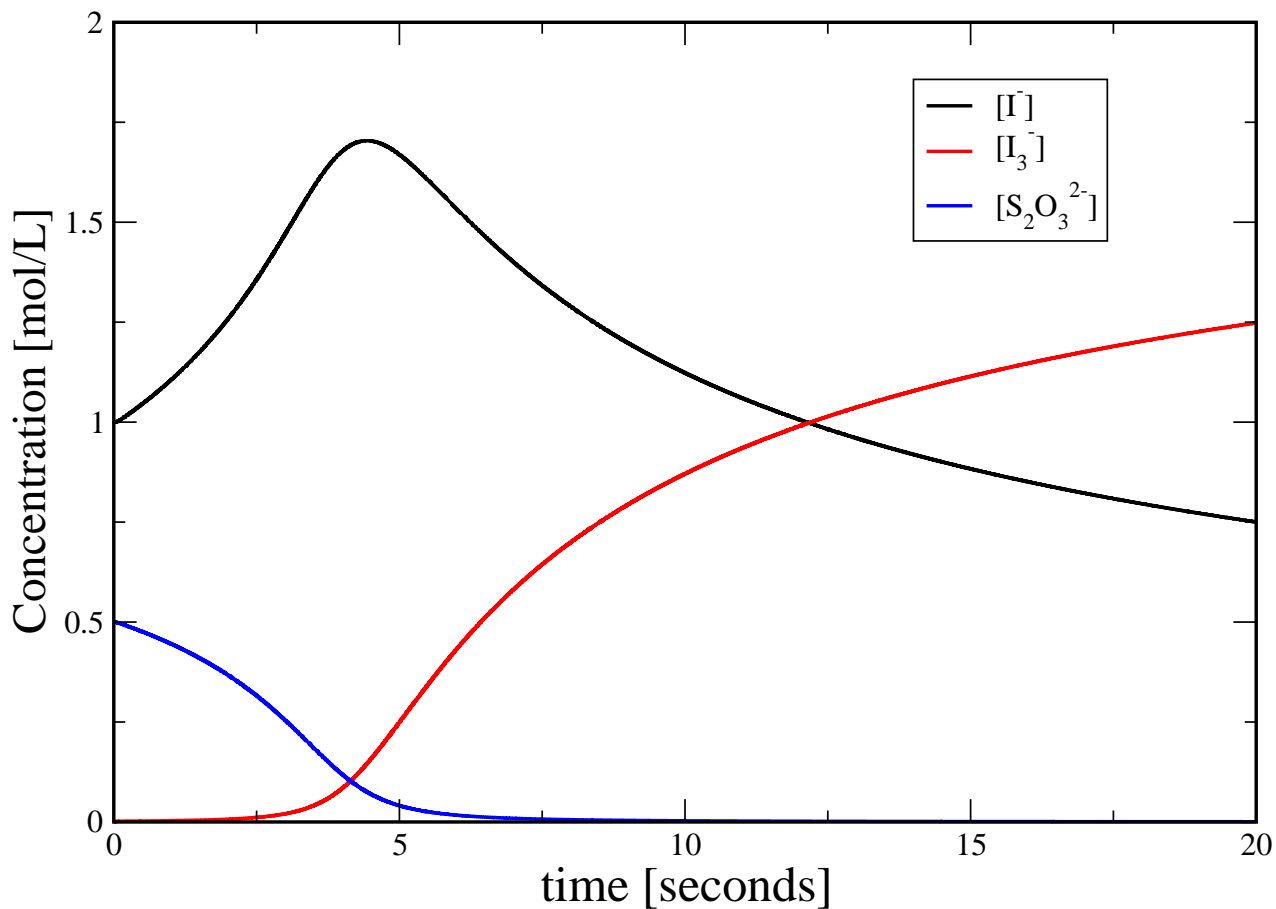
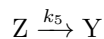
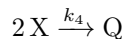
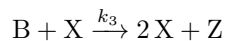


FIG. 1. Concentrations as functions of time of the three species in the iodine clock reaction.



In the above reaction mechanism, A and B are reactants; X, Y, and Z are intermediates; and P and Q are products. The third reaction in which B and X react to form X and Z is known as an "autocatalytic reaction" in which at least one of the reactants is also a product. Such reactions are a key feature of oscillating reactions, as will be discussed below. Let us assume that the concentrations of A and B are large, such that we can approximate them to be constant with time. The rate equation for species X can be written as

$$\frac{d[X]}{dt} = k_1[A][Y] - k_2[X][Y] + k_3[B][X] - 2k_4[X]^2 \quad (7)$$

Using the steady-state approximation, we can set $dX/dt = 0$ and rewrite Equation 7 as

$$(-2k_4)[X]^2 + (k_2[Y] - k_3[B])[X] + k_1[A][Y] = 0 \quad (8)$$

We can then use the quadratic formula to solve for X:

$$[X] = -\frac{(k_2[Y] - k_3[B]) \pm \sqrt{(k_2[Y] - k_3[B])^2 - 4(-2k_4)(k_1[A][Y])}}{2(-2k_4)} \quad (9)$$

Thus, there are two solutions for the concentration of X accessible to the reaction system. To examine solutions for [X], let us first assume that y is large. Under these conditions, the first two reactions in the reaction mechanism largely determine the concentration of [X]. We can thus approximate Equation 7 as

$$0 \approx k_1[A][Y] - k_2[X][Y] \quad (10)$$

Solving for [X] yields

$$[X] \approx \frac{k_1[A]}{k_2} \quad (11)$$

As the reaction continues, species Y is depleted and the assumption that [Y] is large becomes invalid. Instead the 3rd and 4th steps of the reaction mechanism determine the concentration of X. In this limit, we can approximate Equation 7 as

$$0 \approx k_3[B][X] - 2k_4[X]^2 \quad (12)$$

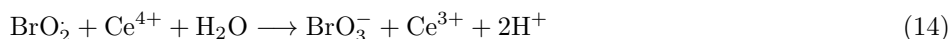
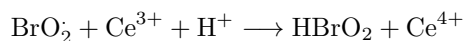
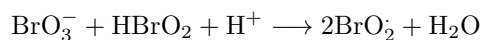
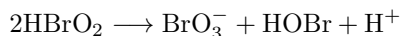
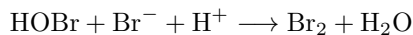
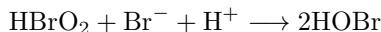
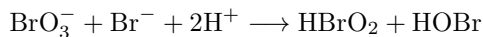
Solving for [X] yields

$$[X] \approx \frac{k_3[B]}{2k_4} \quad (13)$$

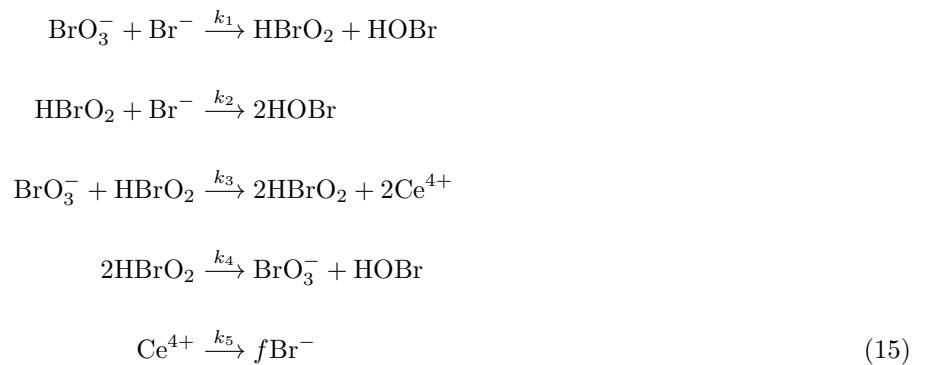
In the second mechanism, the autocatalytic reaction step leads to an increase in the concentration of X and Z, which in turn leads to an increase in the concentration of Y. The feedback loop between the production of species X and Y leads to oscillatory behavior in the system. This reaction mechanism is known as the Belousov-Zhabotinskii reaction first discovered in the 1950s.

- The autocatalytic reaction of X in which X reacts with B to form more X in reaction 3
- The regeneration of species Y in reaction 5
- The competition between reaction 2 and 3 for the consumption of X and the involvement of Y in reaction 2

The actual Belousov-Zhabotinskii reaction is complex, involving many individual steps, and involves the oscillation between the concentration of HBrO_2 and Br^- . The reaction equations are



The essential steps in this mechanism can be reduced to the following set of reactions. Note that we leave this unbalanced and only include the species whose concentrations as functions of time we seek.



Setting the variables as follows:

$$x = [\text{HBrO}_2], \quad y = [\text{Br}^-], \quad z = [\text{Ce}^{4+}] \tag{16}$$

We make the approximation that $[\text{BrO}_3^-]$ to be a constant a . In this case, the rate equations become

$$\begin{aligned}
 \frac{dx}{dt} &= k_1 a y - k_2 x y + k_3 a x - k_4 x^2 \\
 \frac{dy}{dt} &= -k_1 a y - k_2 x y + f k_5 z \\
 \frac{dz}{dt} &= 2k_3 a x - k_5 z
 \end{aligned} \tag{17}$$

Solving these equations numerically, we obtain the trajectory of two of the species show in the Fig. 2. On the other hand, we can drive this system to become chaotic by changing the parameters a little. When this is done, we find the follow plot of the concentration of x :

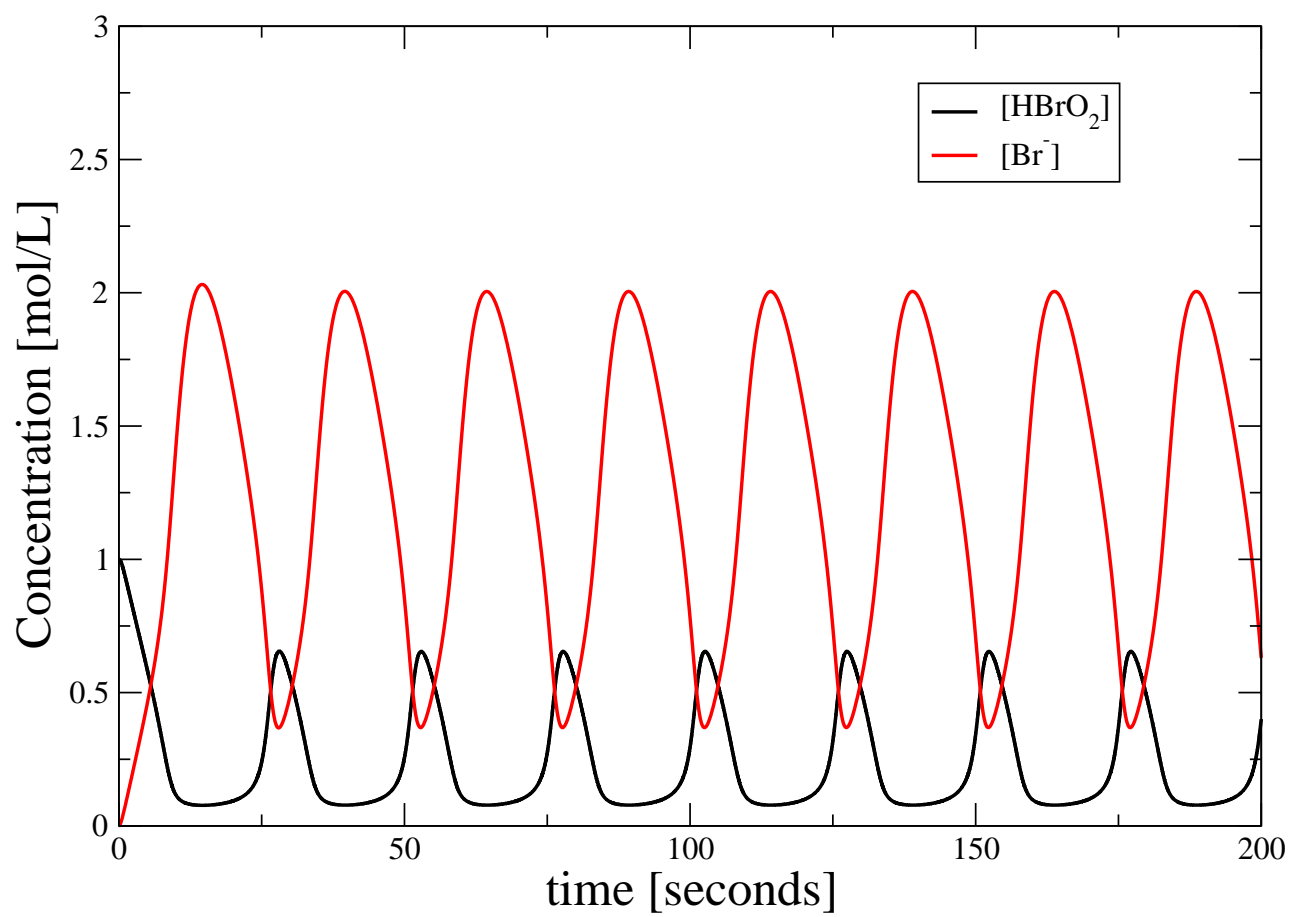


FIG. 2. Oscillating pattern of the concentrations in the Belousov-Zhabotinski reaction.

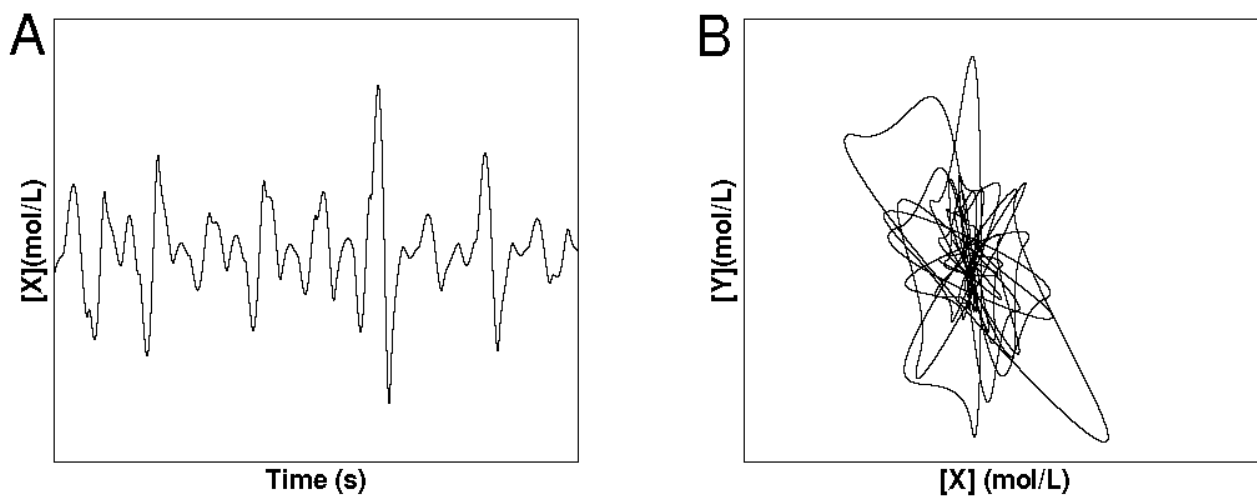


FIG. 3. Chaotic behavior in the Belousov-Zhabotinskii reaction.