Lecture Nine: Chemical Chaos

In the early 1950s Belousov discovered oscillations in what was later dubbed the BZ reaction (Belousov - Zabutinsky). The system is very large and complicated, so from the 1970s people started looking at simpler chemical oscillators. Lengyel and others proposed a model for a similar, but simpler reaction using chlorinedioxide, iodine, and malonic acid.

$$\mathrm{MA} + \mathrm{I}_2 \longrightarrow \mathrm{IMA} + \mathrm{I}^- + \mathrm{H}^+ \tag{1}$$

$$\mathrm{ClO}_2 + \mathrm{I}^- \longrightarrow \mathrm{ClO}_2^- + \frac{1}{2}\mathrm{I}_2 \tag{2}$$

$$\mathrm{ClO}_2^- + 4\mathrm{I}^- + 4\mathrm{H}^+ \longrightarrow \mathrm{Cl}^- + 2\mathrm{I}_2 + 2\mathrm{H}_2\mathrm{O}. \tag{3}$$

In differential equation terms this translates to,

$$\frac{d}{dt}\left[\mathrm{I}_2\right] = -\frac{k_{1a}\left[\mathrm{MA}\right]\left[\mathrm{I}_2\right]}{k_{1b} + \left[\mathrm{I}_2\right]} \tag{4}$$

$$\frac{d}{dt}\left[\mathrm{ClO}_2\right] = -k_2\left[\mathrm{ClO}_2\right]\left[\mathrm{I}^-\right] \tag{5}$$

$$\frac{d}{dt}\left[\mathrm{ClO}_2^-\right] = -k_{3a}\left[\mathrm{ClO}_2^-\right]\left[\mathrm{I}^-\right]\left[\mathrm{H}^+\right] - k_{3b}\left[\mathrm{ClO}_2^-\right]\left[\mathrm{I}_2\right]\frac{\left[\mathrm{I}_2^-\right]}{u + \left[\mathrm{I}^-\right]^2}. \tag{6}$$

This is still too complicated for analysis, but Lengyel and his collaborators observed that MA, I_2, and ClO_2 varry more slowly than I^- and ClO_2^-. After simplifications such as nondimensionalization we get,

$$\dot{x} = a - x - \frac{4xy}{1+x^2}, \dot{y} \qquad = bx\left(1 - \frac{y}{1+x^2}\right). \tag{7}$$

With the usual analysis we can find periodic solutions and Hopf bifurcations, which we discussed in class.

Also in the 1970s, people started studying the possibility of chaotic solutions for BZ or BZ-like reactions. Chemists took the BZ reaction and let new reactants keep flowing in and stirred them. In one such reaction, Roux and others noticed the time-series for Bromide seemed chaotic. Later they used a data-analysis technique called attractor reconstruction to construct the strange attractor from the time-series. While analysis is difficult the experiment is really cool!