The two graphs at the right show the time dependence of the concentrations of two species in a reaction. We can look at the top one and immediately classify the behavior as zeroth order kinetics, but the bottom defies our usual classification schemes. How do such exotic behaviors arise? Are they rarities or commonplace? Many biological processes are clearly oscillatory, and at the most fundamental level are run by chemical reactions that therefore must oscillate as well. Larger reaction systems, such as the atmosphere, can also exhibit complex behavior, for example, the seasonal development of a "hole" in the tropospheric ozone layer over the poles. More systems probably exhibit these complex behaviors than do not. A half-century ago, researchers were not convinced that chemical reactions could exhibit oscillatory or other complex behaviors. The assumption was that the concentrations of species either decayed or increased monotonically, except for intermediates, which reached a maximum sometime during the reaction, then decayed to zero. In the 1950s, two Russian chemists discovered a reaction which clearly cycled from reactant to products multiple times before finally reaching equilibrium. The Belousov-Zhabotinsky reaction is spectacular to watch, flashing various colors, and has a complex autocatalytic mechanism. These reactions, while fascinating in and of themselves, opened the door to the exploration of "exotic kinetics," reactions that exhibit oscillatory or even chaotic patterns. Alan Turing, a computer scientist, proposed that such reactions could be used to produce regular patterns, suggesting that these sorts of reactions could give rise to biomorphogenesis – such as the stripes on a zebra.

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Exotic Kinetics

Random notes about chaos theory

Chaotic behavior, though apparently random, is generally deterministic. That is, the system follows a set of rules. Even very simple rules can give rise to complex behaviors.

Attractors are points, sets or curves toward which a system evolves (or is “attracted”) regardless of starting conditions. Strange attractors are never actually reached.

A phase portrait is constructed by representing each parameter (such as the concentration of a species) on a separate axis. Each point in phase space corresponds to the values of each of the parameters at some “moment.” A closed curve in phase space is a limit cycle and represents an oscillating systems.

Bifurcation results when a small change in a parameter controlling the system (such as a rate constant) results in very different evolution of the system.

Chaos is a name for any order that produces confusion in our minds.

George Santayana


Steady State Instability and Oscillation in Simplified Models of Tropospheric Chemistry

Mark R. Tinsley and Richard J. Field*

Questions and Problems

The questions and problems below are based on the paper cited. They are meant to encourage you to read the paper critically, you may need to consult other articles in the literature to answer these question. If you were the editor of the journal, what questions might you have for the authors?

1. What is the Belousove-Zhabotinksy reaction? What is autocatalysis?
2. What are some of the sources of VOCs in the atmosphere? What are possible sinks?
3. What is a dynamical system? What does “steady-state instability” mean? How is this different from oscillation?
4. How is the troposphere defined? What altitude range does it occupy? What are typical pressures and temperatures?
5. What do the authors consider their most significant finding?
6. The authors give rate constants for model M1, but don’t specify the temperature at which the rate constants were determined. Should they? Can you find the temperature?
7. Using the mechanism designated M1, apply the steady state approximation to ozone and solve for an expression for the concentration of ozone. Estimate (to an order of magnitude) the steady state concentration of ozone expected for this model when the concentrations of NO and NO2 are on the order of $10^{9.5}$ and that of HO$_2$ is $O(10^7)$. How does this compare to what model M1 produces.
8. The authors suggest that the oscillatory behavior
shown in Figure 1 is a switching between two steady state situations, one characterized by high concentrations of NO\textsubscript{x} and one by lower concentrations. Roughly what is the concentration of all the NO\textsubscript{x} species in the two states predicted by the four different models? How are the phases of the fluctuations in HO\textsubscript{x} and NO\textsubscript{x} related in each case? What are the key differences in the behaviors of the models?

9. The graphs in Figure 1 are too crude for the following to give you truly meaningful results, but this excercise will nonetheless give you a sense of what you might discover by constructing phase portraits from concentration versus time data. Use Figure 1c and sketch the phase behavior of HO\textsubscript{x} and NO\textsubscript{x}. What do you notice? Do your results support the authors’ contentions about the relationship between the two sets of species?

Joseph Francisco

Professor of Chemistry
Purdue University

Prof. Francisco received his Ph.D. in 1983 from MIT, then spent time as a post-doctoral fellow at Cambridge. His research focuses on the kinetics of reactions important in the upper atmosphere. Prof. Francisco’s group blends high resolution laser spectroscopy and sophisticated electronic structure theory to tease out the connections between reaction rates and chemical structure in free radical chemistries. His research has been key to showing that some alternative refrigerants, such as HFC’s may not pose the same hazards to the ozone layer as CFCs.
Alan Turing is perhaps best known for his work on codes in World War II, particularly with the Enigma machines. He is also often called the father of computer science. Turing also had a long standing interest in chemistry, and was a long distance running of near Olympic caliber.

### Further Reading

- Barbara J. Finlayson-Pitts and James N. Pitts, *Chemistry of the Upper and Lower Atmosphere*, Academic Press, 2000. A very detailed look at the chemistry of the atmosphere and the experimental methods used to study it. The introduction and sections on policy are very accessible to the beginning physical chemistry student. If you find the rest intriguing, contact UCIrvine for information about going to grad school there!
- B.Z. Shakhashiri, *Chemical Demonstrations: A Handbook for Teachers of Chemistry, Volume 2*, Wisconsin, US, The University of Wisconsin Press, 1985, pp. 248-256. Want to see an oscillating reaction in actions? This source has directions for running the Belousov-Zhabotinsky reaction. Alternatively, a good film of a demonstration is at Oxford's site: [http://www.chem.ox.ac.uk/vrchemistry/FilmStudio/oscillating/HTML/page03.htm](http://www.chem.ox.ac.uk/vrchemistry/FilmStudio/oscillating/HTML/page03.htm)
- Check this site for an introduction to chaos theory: [http://hypertextbook.com/chaos/](http://hypertextbook.com/chaos/)