

Introduction to oscillating chemical reactions: The Lotka-Volterra model.

References used:

- (1) Ron Poshusta, Wisconsin State University, <http://www.sci.wsu.edu/idea/OscilChem/index.htm>
- (2) P.W. Atkins, Physical Chemistry 5th edn., Oxford University Press, 1995.
- (3) Ira N. Levine, Physical Chemistry 4th edn., Tata McGraw Hill, 1995.

Modern chemists are aware that certain chemical reactions can oscillate in time or space. Prior to about 1920 most chemists believed that oscillations in closed homogeneous systems were impossible. The earliest scientific evidence that such reactions can oscillate was met with extreme scepticism. The most famous oscillating chemical reaction is the **Belousov-Zhabotinsky (BZ) reaction**. This is also the first chemical reaction to be found that exhibits spatial and temporal (= in time) oscillations. Theoretical models of oscillating reactions have been studied by chemists, physicists, and mathematicians. The simplest one may be the **Lotka-Volterra model**. Some other models are the **Brusselator** and the **Oregonator** (these are not included in the syllabus and hence not discussed. For discussions, see the cited references). The latter was designed to simulate the famous Belousov-Zabotinskii reaction (the BZ reaction for short). A recipe for the BZ reaction is given below:

Prepare a solution with the following concentrations of reactants. The reaction mixture should be stirred constantly with a magnetic stirring bar. These concentrations will give a system that oscillates (alternating blue and red flashes) with a period of about 30 sec and the oscillations will continue for 50 minutes or more. The reactants can be mixed in any order.

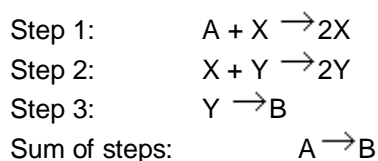
<u>Reactant</u>	<u>Concentration, M</u>
Ce(NH ₄) ₂ (NO ₃) ₅ (catalyst)	0.002
CH ₂ (COOH) ₂	0.275
KBrO ₃	0.0625
H ₂ SO ₄	1.5
Ferriin (indicator)	0.0006

[Why construct theoretical models of oscillating chemical reactions? A model for a chemical reaction consists of the following parts:

- A mechanism. This is a set of elementary chemical reactions to describe how reactants form intermediates, intermediates combine with one another and reactants, and ultimately products are produced.
- A set of Rate equations. These are differential equations corresponding to the reaction mechanism and giving the rates of change of all reactants, intermediates, and products.
- A set of Integrated rate equations. These show the concentrations as functions of time for reactants, intermediates, and products. They are obtained by integrating the rate (differential) equations.

The criterion for an acceptable theoretical model is that it agrees with experimental observations of measured time varying concentrations. When a theoretical chemist finds an acceptable model he says he "understands" the reaction.]

The Lotka-Volterra model of oscillating chemical reactions: This is the earliest proposed explanation for why a reaction may oscillate. In 1920 Lotka proposed the following reaction mechanism (with corresponding rate equations). Each reaction step refers to the MOLECULAR mechanism by which the reactant molecules combine to produce intermediates or products. For example, in step 1 a molecule of species A combines with a molecule of species X to yield two molecules of species X. This step depletes molecules A (and adds molecules X) at a rate proportional to the product of the concentrations of A and X. The overall chemical reaction is merely $A \rightarrow B$ with two transient intermediate compounds X and Y:

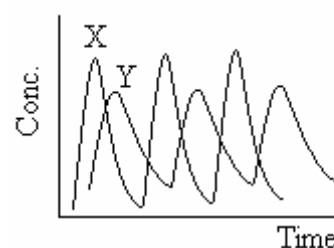


The effective rate laws for the reactant A, the product B, and the intermediates X and Y are found by summing the contributions from each step:

$$\begin{aligned}\frac{d[A]}{dt} &= -k_1[A][X] \\ \frac{d[X]}{dt} &= k_1[A][X] - k_2[X][Y] \\ \frac{d[Y]}{dt} &= k_2[X][Y] - k_3[Y] \\ \frac{d[B]}{dt} &= k_3[Y]\end{aligned}$$

Step 1 is **autocatalytic** because X accelerates its own production. Likewise step 2 is autocatalytic. To derive the mechanism, it is required to solve for [A], [X], [Y], and [B] as functions of time. Lotka obtained oscillating concentrations for both intermediates X and Y when the concentration of reactant A is constant (as, for example, A is continuously replaced from an external source as it is consumed in the reaction. Lotka's mechanism can be re-interpreted as a model for oscillating populations of predators and preys as was done by Volterra. In this, A represents the ecosystem in which prey X and predator Y live. Step 1 represents procreation: prey population increases at rate $k_1[A]$ (typical exponential growth). Then Y is the population of predators that consume the prey in order to sustain (and expand) their population. Step 2 represents this inclination of predators to reproduce in proportion to the availability of prey. Finally (step 3), predators die at a certain natural rate (also exponential) so that they are removed from the ecosystem.

[Example of ducks and wolves: Suppose that food grain is available in plenty to ducks. Since food is plentiful, the duck population multiplies fast (ducks produce more ducks = autocatalysis). Wolves prey on ducks. When ducks are available in plenty, the wolf population multiplies fast (wolves produce more wolves = autocatalysis). When the wolf population reaches a very large value, the ducks are eaten so fast that the duck population dwindles. When very few ducks remain, the wolf population dwindles due to starvation and death. When the number of wolves becomes small, the remaining ducks again get a chance to multiply. This process is repeated in a cyclic fashion, where there is a sudden increase in ducks followed by a sudden increase in wolves followed by a decrease in the number of ducks followed by a decrease in the number of wolves followed by a sudden increase in ducks ...]

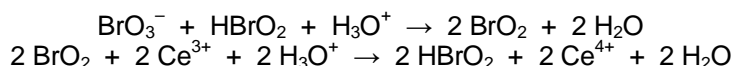


The periodic variation of the concentrations of intermediates X and Y in the Lotka-Volterra model. Note that the increase of Y slightly lags behind that of X.

Many examples of **autocatalytic chemical reactions** are available, a few of which are listed below:

- (1) When oxalic acid solution is titrated against permanganate, it is noted that decolourisation of the first drop is slow; subsequent drops react very fast. This is because the Mn^{2+} ions produced by the reaction of the first drop catalyses further reaction. ie. Mn^{2+} ions help to produce more Mn^{2+} ions.
- (2) Acid catalysed ester hydrolysis. Ester gives alcohol and acid on hydrolysis. Thus acid produces more acid. Therefore the rate of the reaction increases with time.
- (3) Biologically, ATP molecules supply the energy required for chemical reactions, and in the process they are converted to ADP. But ATP itself is synthesized from glucose, with the help of ATP. One glucose molecule produces two molecules of ATP. Thus ATP helps produce more ATP.

In the BZ reaction itself, the following equations represent a portion of the process taking place:



Note that the product BrO_2 in the first step is a reactant in the second step. Therefore production of BrO_2 in the first step increases the rate of the second step. Also note that the product $HBrO_2$ in the second step is a reactant in the first step. Therefore production of $HBrO_2$ in the second step increases the rate of the first step. These steps are therefore autocatalytic. But when the rate of the first step increases, more $HBrO_2$ is consumed and its concentration falls. This will decrease the production of BrO_2 which in turn decreases the rate of the second step. When the rate of the second step

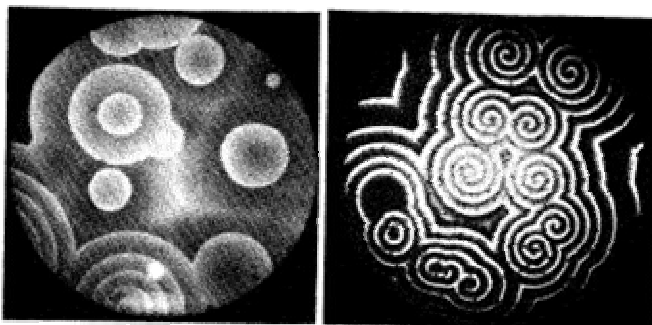
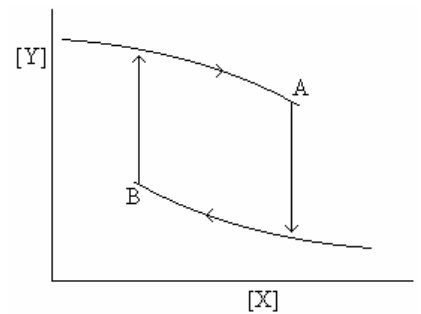
decreases, more of the available HBrO_2 reacts in the first step producing more BrO_2 which then increases the rate of the second step ... The reaction thus results in high concentrations of BrO_2 and HBrO_2 alternately producing a reaction oscillating in time, and the indicator flashes red and blue.

It may at first appear that oscillating chemical reactions violate the rules of thermodynamics since ΔG must decrease continuously in a reaction (cannot oscillate) and finally reach equilibrium. But note that an oscillating reaction is far from equilibrium. Just like an oscillating pendulum slowly loses energy and slows down, finally coming to rest at the equilibrium position, the oscillations of the reaction gradually die off and the reaction finally reaches equilibrium. (But while the pendulum passes through the equilibrium position as it oscillates, the chemical reaction does not pass through equilibrium as this is not permitted by the rules of thermodynamics.) Attempts have been made to discover the underlying causes of oscillations more deeply than simply recognizing the role of autocatalysis. It appears that three conditions must be fulfilled in order to obtain oscillations:

- (1) The reactions must be far from equilibrium.
- (2) The reactions must have autocatalytic steps.
- (3) The system must be able to exist in two steady states.

The third condition above is called **bistability**, a property well beyond the familiar equilibrium properties. It may be considered analogous to something like supercooling in which a liquid may be cooled well below its freezing point without solidifying. But the supercooled liquid may suddenly solidify. At a given temperature, the substance may exist either in the solid form, or in the liquid (supercooled) form. There are thus two **steady states**. The system may jump spontaneously from one steady state to the other.

Consider a reaction in which there are two intermediates X and Y. If the concentration of Y is at some high value in a reactor, and then X is added, the concentration of Y may decrease along the upper curve in the figure. If X is at some high value initially and then Y is added, reaction might result in a slow increase of Y as shown by the lower curve. However, in each case, a concentration may be reached (A or B) at which the process may jump from one curve to the other. The upper and lower curves represent two **steady states**. Now consider what happens when a third intermediate Z is present. Suppose Z can react with both X and Y. In the absence of Z, the flow of material may correspond to a state on the upper curve. However, as Z reacts with Y to produce X, the system moves along the curve to the right. When the system reaches the state A, a sudden transition occurs to the lower curve. Then since the concentration of X is now high, Z reacts with X producing more Y and the system moves along the lower curve to the left. When it reaches point B it jumps to the upper curve and the process repeats.



If the reaction mixture is not stirred, different areas in the mixture may have different concentrations of X and Y, producing oscillating patterns like waves (oscillations in space). It is currently believed that breathing, heart beat and other periodically varying biological functions are also controlled by oscillating chemical reactions.

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