Festival of the Mind 2014

Chaotic Chemical Waves: Oscillations and waves in chemical systems

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Some history – The BZ reaction

In 1951, Belousov, a Russian scientist, was trying to create an inorganic version of the Krebs citric acid cycle when he came across oscillations. He was unable to publish his “supposed discovery”.

Zhabotinsky took up his work and finally it was published in 1965 – the reaction is now known as the BZ reaction.

[Chemical oscillations in the BZ reaction](https://www.youtube.com/watch?v=tg9SRstGos4)
How to make Oscillations

Mix together:

1. an organic species like malonic acid: (similar to citric acid found in fruit): CH$_2$(COOH)$_2$

2. An inorganic species with bromine in it (smells like swimming baths) and acid: BrO$_3^-$ and H$^+$

3. A metal catalyst like the iron complex ferroin (similar to the iron complex that makes your blood red)

The reaction will change colour from red to blue and back for hours
From oscillations to Chemical waves and spirals

When the BZ reaction mixture is poured into a petri-dish, the oscillations start from points and propagate outwards, forming target waves and spirals.

This is driven by diffusion of the chemicals in the solution, like when a drop of ink is added to water.
Scientists studied the BZ reaction to help understand how chemical signals propagate in living systems.

The picture shows chemical waves in a living organism. Slime mould sends out waves of cAMP when cells are starving, causing them to aggregate and form a slug which seeks out a new source of food.
What causes the oscillations?

The overall reaction makes carbon dioxide, but this takes place by many steps.

The steps can be grouped into three main processes with two key intermediate species formed and removed during the oscillations:

- Br⁻ - bromide ion - *inhibitor*
- HBrO₂ – hypobromous acid – *autocatalyst*
Key processes - FKN mechanism

Process (A) Removal of inhibitor
reactions remove bromide, the iron complex is red, when the bromide reaches a critical value then.....

Process (B) Autocatalysis
.....a reaction makes its own catalyst so it gets faster and faster and the iron complex changes colour from red to blue then...

Process (C) Production of inhibitor
.....reactions make bromide, the iron complex goes slowly back to red
The key reaction steps are included in the FKN mechanism (named after its discoverers Field, Koros and Noyes):

(1) \[ A + Y \rightarrow X + P \]
(2) \[ X + Y \rightarrow 2P \]
(3) \[ A + X \rightarrow 2X + 2Z \]
(4) \[ 2X \rightarrow A + P \]
(5) \[ B + Z \rightarrow \frac{1}{2} f Y \]

We can write down an equation for each species that tells you how fast it is formed and consumed.

The equations are solved using a computer that predicts how the concentrations vary in time and space…
Making spirals – experiment

To make a spiral usually you have to break a target wave by, for example, dragging a pipette through it.

When the iron catalyst for the BZ reaction is put on a membrane (like in the movie on the right) there are patches with slightly different concentrations that cause waves to break and form spirals.
Making spirals - simulations

We can simulate spirals on a computer by solving the equations for the FKN mechanism and adding some terms for diffusion, as shown in the movie on the right.

Spirals form because of the local differences in initial concentrations.
Spirals occur naturally in heart and nerve tissue, cellular organisms, chemical reactions in petri dishes, catalytic surfaces, flames and galaxies.
Electrochemical waves in cardiac cells cause the heart to contract. When these waves break, this corresponds to a heart attack!

The movie on the right shows what happens as the waves break up forming spirals and chaos.

http://thevirtualheart.org/FentonCherry/wedo.html
First simulations of autocatalysis

Alan Turing was a British Mathematician famous for cracking the Enigma code in World War 2 and as a founder of computational theory

He also performed some of the very first computer simulations of chemical reactions

Manchester University's Mark I
http://en.wikipedia.org/wiki/Manchester_Mark_1
Turing showed how autocatalytic chemical reactions and diffusion in cells could explain how patterns form in nature.

THE CHEMICAL BASIS OF MORPHOGENESIS*

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It is suggested that a system of chemical substances, called morphogens, reacting together and diffusing through a tissue, is adequate to account for the main phenomena of morphogenesis. Such a system, although it may originally be quite homogeneous, may later develop a pattern or structure due to an instability of the homogeneous equilibrium, which is triggered off by random disturbances. Such reaction–diffusion systems are considered in some detail in the case of an

Fig. 3. Concentrations of Y in the development of the first specimen (taken from Table 1): (-------) original homogeneous equilibrium; (//////) incipient pattern; (---) final equilibrium.
Turing patterns

It was proposed that Turing patterns may account for the patterns on animal skin

Many years later, they were found in chemical reactions in experiments in the lab

Castets et al. 1990
Ouyang et al. 1991
Find out more:

These three books are a great start if you want to find out more:

Beginners

ISBN: 978-0198502432

...short with added maths

ISBN: 978-0198558446

...thorough

ISBN: 978-0195096705