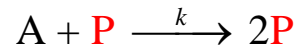


Autocatalysis



$$\text{rate} = -\frac{da}{dt} = \frac{dx}{dt} \quad [A] = a_0 - x, \quad [P] = p_0 + x$$

$$\frac{dx}{dt} = k(a_0 - x)(p_0 + x)$$

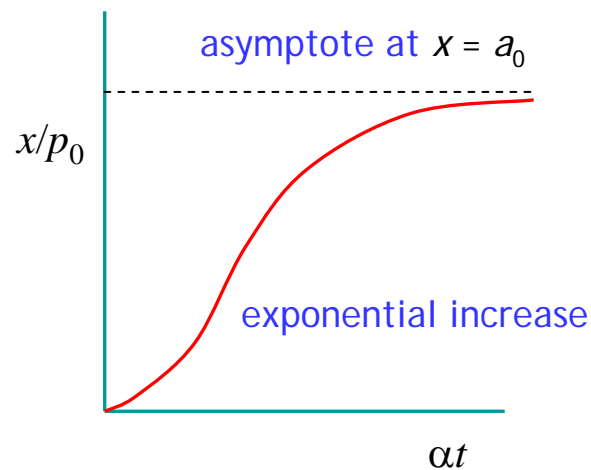
$$kt = \frac{1}{(a_0 + p_0)} \ln \left\{ \frac{a_0}{(a_0 - x)} \frac{(p_0 + x)}{p_0} \right\}$$

Substitute $\alpha = (a_0 + p_0)k$, $\beta = p_0/a_0$

$$\alpha t = \ln \frac{(1 + x/p_0)}{(1 - \beta x/p_0)}$$

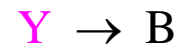
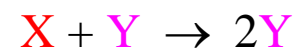
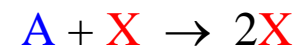
$$x/p_0 = \frac{e^{\alpha t} - 1}{1 + \beta e^{\alpha t}}$$

$$\begin{aligned} kt &= \int_0^x \left\{ \frac{dx}{(a_0 - x)(p_0 + x)} \right\} \\ &= \frac{1}{(a_0 + p_0)} \int_0^x \left\{ \frac{1}{(a_0 - x)} + \frac{1}{(p_0 + x)} \right\} dx \\ &= \frac{1}{(a_0 + p_0)} \left[-\ln(a_0 - x) + \ln(p_0 + x) \right]_0^x \end{aligned}$$



The Simplest Oscillating Reaction Model

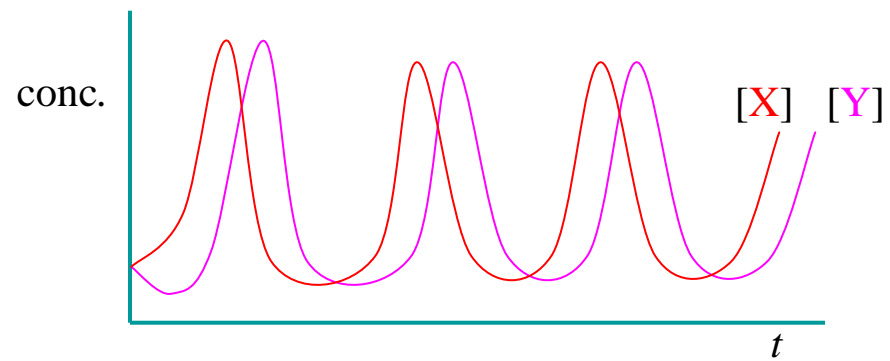
The Lotka-Volterra Mechanism



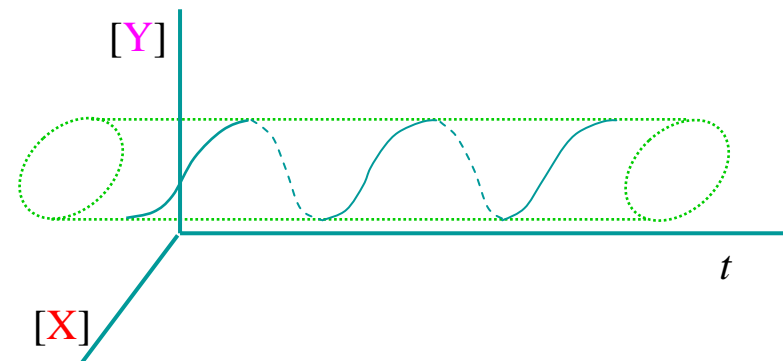
negative feedback
prevents runaway
acceleration

[A] is held constant (replenished).

[X] and [Y] oscillate.

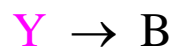
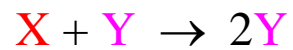


Two-component oscillations
look like a helix in three-
dimensional space.



A Swinging Chemical System

Consider the Lotka-Volterra Mechanism. [X] and [Y] have a steady state at



$$\frac{dx}{dt} = k_1 a_0 x - k_2 xy$$

$$\frac{dy}{dt} = k_2 xy - k_3 y$$

$$\begin{aligned} k_1 a_0 x_{ss} - k_2 x_{ss} y_{ss} &= 0 \\ k_2 x_{ss} y_{ss} - k_3 y_{ss} &= 0 \end{aligned} \Rightarrow \begin{aligned} y_{ss} &= a_0 k_1 / k_2 \\ x_{ss} &= k_3 / k_2 \end{aligned}$$

Make a small displacement from the S-S: (x_{ss}, y_{ss}) to $(x_{ss} + s, y_{ss} + z)$ where $s, z \ll x_{ss}, y_{ss}$

$$\frac{dx}{dt} = k_1 a_0 (x_{ss} + s) - k_2 (x_{ss} + s)(y_{ss} + z) = (k_1 a_0 - k_2 y_{ss} - k_2 z)(x_{ss} + s) = -k_2 x_{ss} z - k_2 s z = \frac{ds}{dt}$$

$$\frac{dy}{dt} = k_2 (x_{ss} + s)(y_{ss} + z) - k_3 (y_{ss} + z) = (k_2 x_{ss} + k_2 s - k_3)(y_{ss} + z) = k_2 y_{ss} s + k_2 s z = \frac{dz}{dt}$$

$$\left. \begin{aligned} \frac{ds}{dt} &= -k_2 x_{ss} z - k_2 s z \approx -k_2 x_{ss} z \\ \frac{dz}{dt} &= k_2 y_{ss} s + k_2 s z \approx k_2 y_{ss} s \end{aligned} \right\} \begin{aligned} \frac{d^2 s}{dt^2} &= -k_2 x_{ss} \frac{dz}{dt} = -k_2^2 x_{ss} y_{ss} s = -a_0 k_1 k_3 s \end{aligned}$$

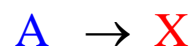
⇒ An oscillation: $s(t) = A e^{i\omega t} + B e^{-i\omega t}$, $\omega = (a_0 k_1 k_3)^{1/2}$

$$e^{i\omega t} = \cos(\omega t) + i \sin(\omega t)$$

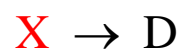
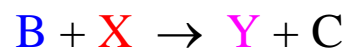
$$e^{-i\omega t} = \cos(\omega t) - i \sin(\omega t)$$

Other Simple Oscillating Reaction Models

Brusselator

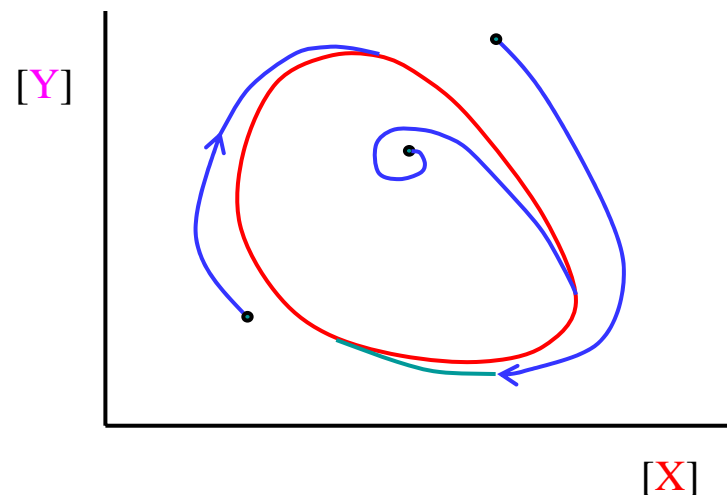


Prigogine *et al*



[A] and [B] are held constant.

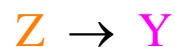
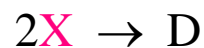
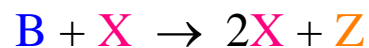
[X] and [Y] settle down to a **limit cycle**:



Oregonator



Noyes *et al*



The B-Z reaction is of this general form, with



but **many** steps and species.

Belousov Zhabotinskii Reaction – Schematic

Cerium catalyzed oxidation of malonic acid by bromate in sulphuric acid

Belousov, 1959

Spatial periodic variations of intermediate concentrations

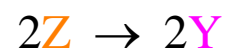
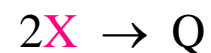
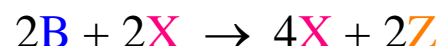
Zhabotinskii, 1967

Mechanism I



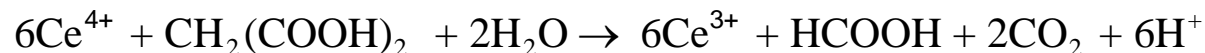
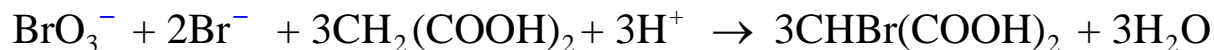
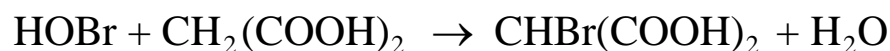
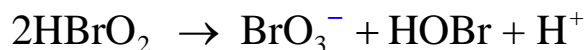
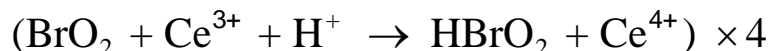
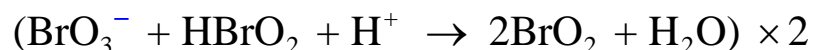
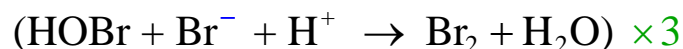
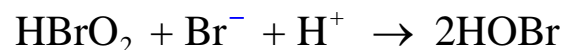
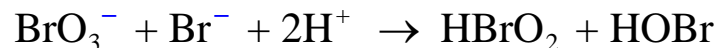
X is in steady-state but Y is consumed until [Y] falls below a critical value where X now reacts mostly with B.

Mechanism II



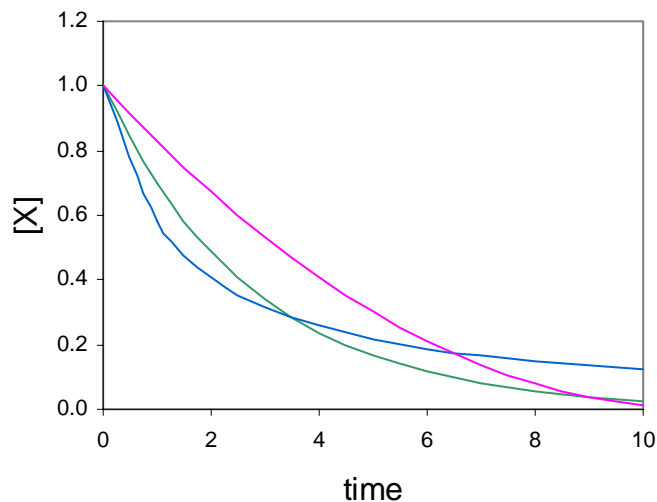
[X] rises until its production is balanced by its second-order decay to Q, reaching a new steady-state of X. The production of Z leads to more Y and mechanism I takes over again.

Belousov Zhabotinskii Reaction – Chemistry



Nonlinearity and Feedback

decay vs time



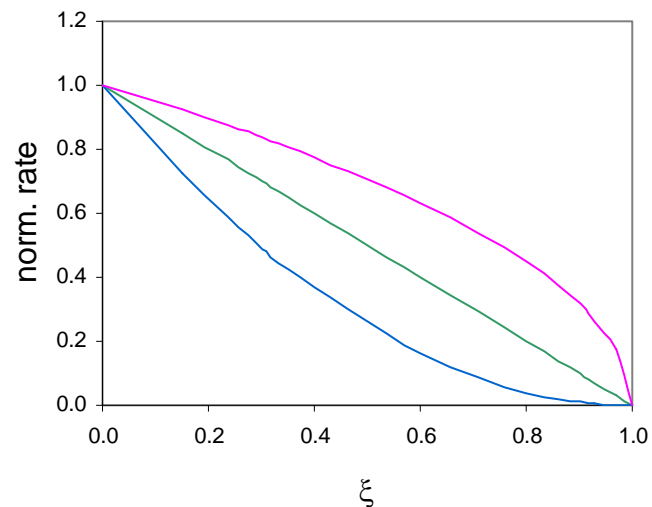
order

1st

2nd

half

rate vs advancement



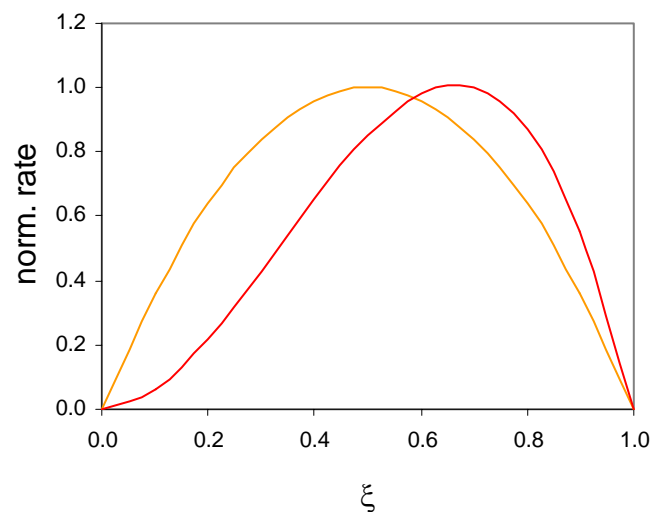
First-order kinetics are **linear**; all others are **nonlinear**.

The maximum rate occurs at $t = 0$.

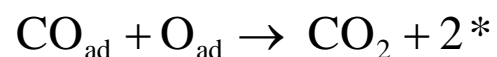
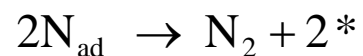
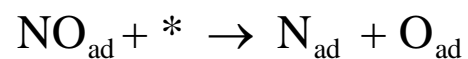
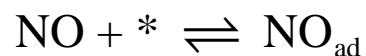
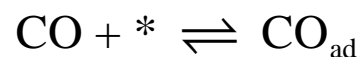
Feedback occurs when the products influence the rate.



$$\xi = \frac{[X]_0 - [X]}{[X]_0}$$

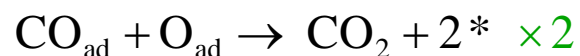
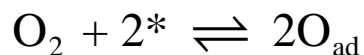
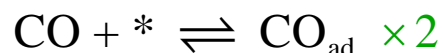


The NO + CO Reaction



Dissociation of NO is slow and requires an extra vacant site (*). The elimination of gaseous N₂ and CO₂ from the surface is autocatalytic since the extra vacant sites accelerate the dissociation of NO.

Catalytic Oxidation of Carbon Monoxide

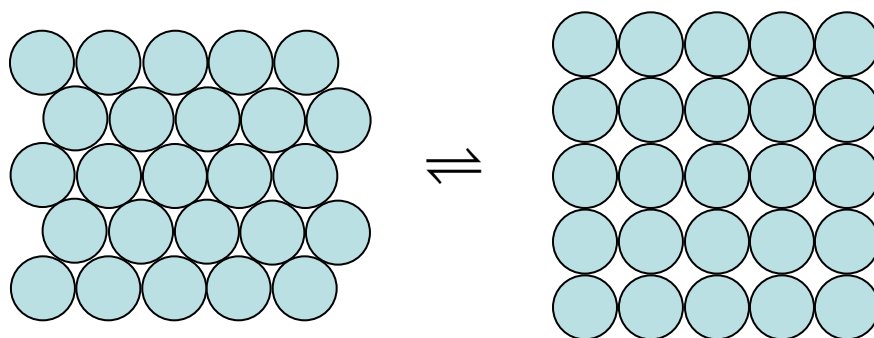


* = vacant site on Pt surface



Oscillatory behaviour occurs because there are two types of surface site, which have different sticking coefficients for O_2 and CO .

Only CO sticks to the hex surface.



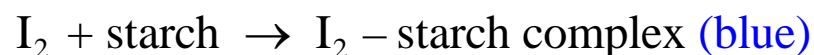
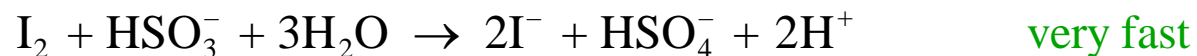
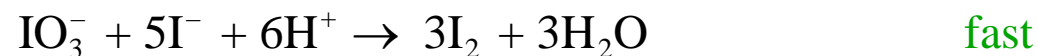
O_2 sticks well to the square lattice.

At a critical coverage of CO , a phase transition occurs.

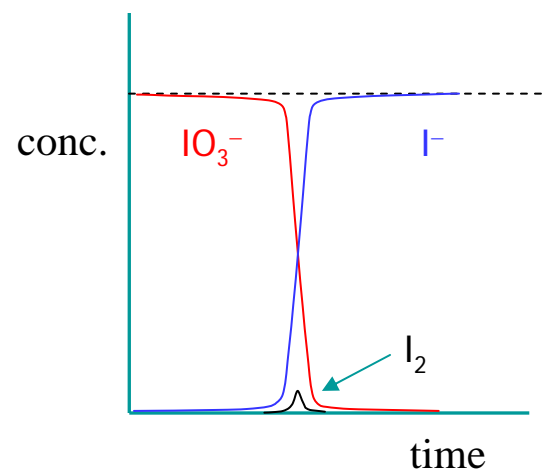
O consumes CO until the surface switches back to hex.

The Landolt Clock Reaction

e.g. 0.02 M KIO_3 + 0.02 M NaHSO_3 + a few drops of 1% starch solution



The reaction is extremely slow at the start because the auto-catalyst $[\text{I}^-]$ is so small. $[\text{I}_2]$ is also very low until the bisulphite is used up. Only then does the blue complex form.



Fronts, Targets, Spirals and Scrolls

Local initiation of a clock reaction results in a chemical **wavefront**.

The wave is a combined reaction-diffusion process. Such waves travel at constant velocity through the reaction mixture...

but often at speeds **much faster than diffusion** of the reactive species!

Reaction-diffusion processes underlie many biological signalling mechanisms.

Point source initiation of an oscillating reaction produces a series of concentric rings, i.e. a target pattern.

If the target wave pattern is broken by some asymmetry (a defect on a crystal surface), the two ends curl up to form a pair of counter-rotating **spirals**.

Extension of spirals into three dimensions results in **scroll** waves or more complicated patterns.

Scroll waves in the muscular wall of the heart can lead to fibrillation (chaotic contractions → **death**).

Calcium waves on the surface of a fertilized egg are the precursor to cell division → **life!**