Oscillating Chemical Reactions

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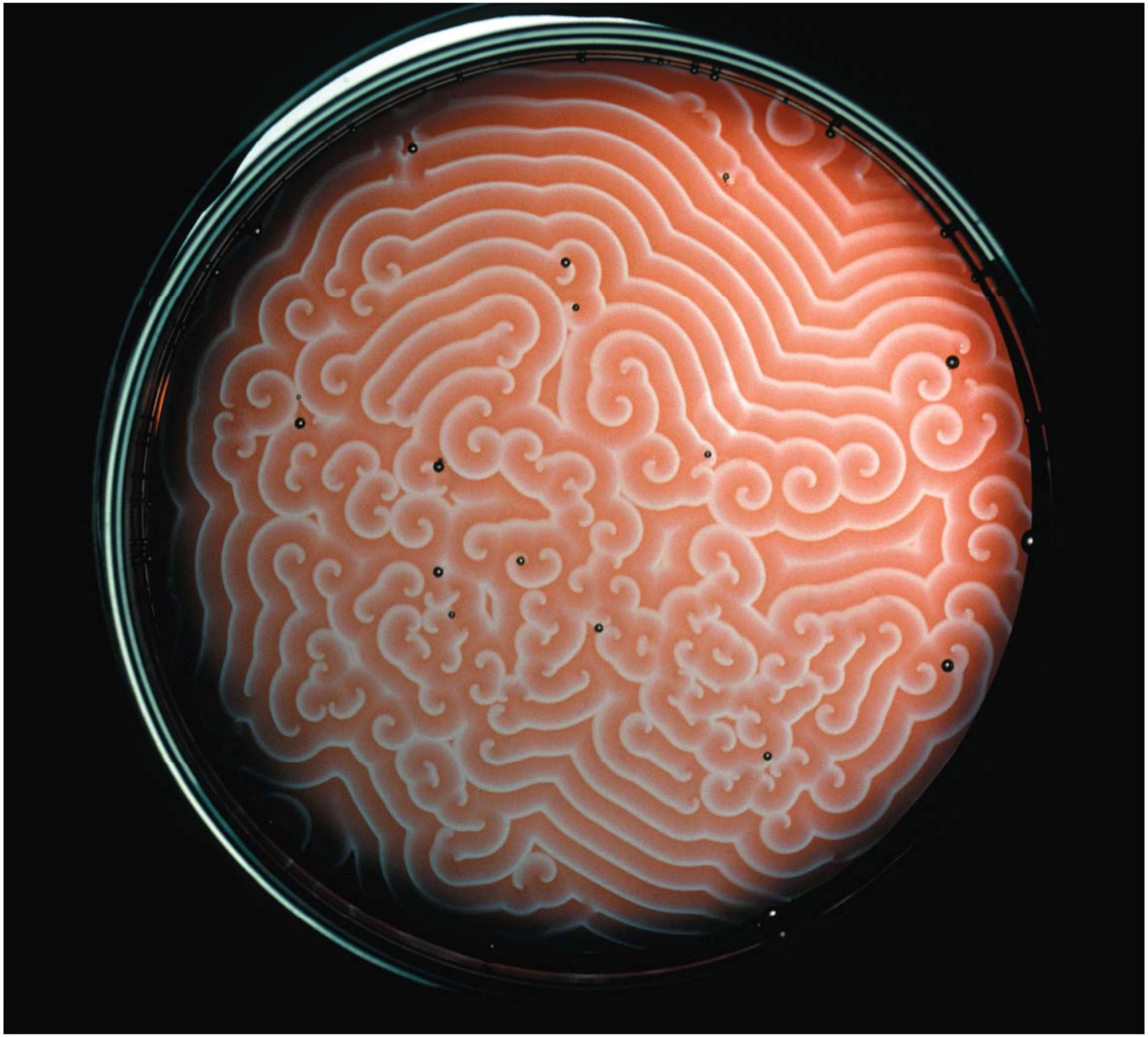


Kinetics

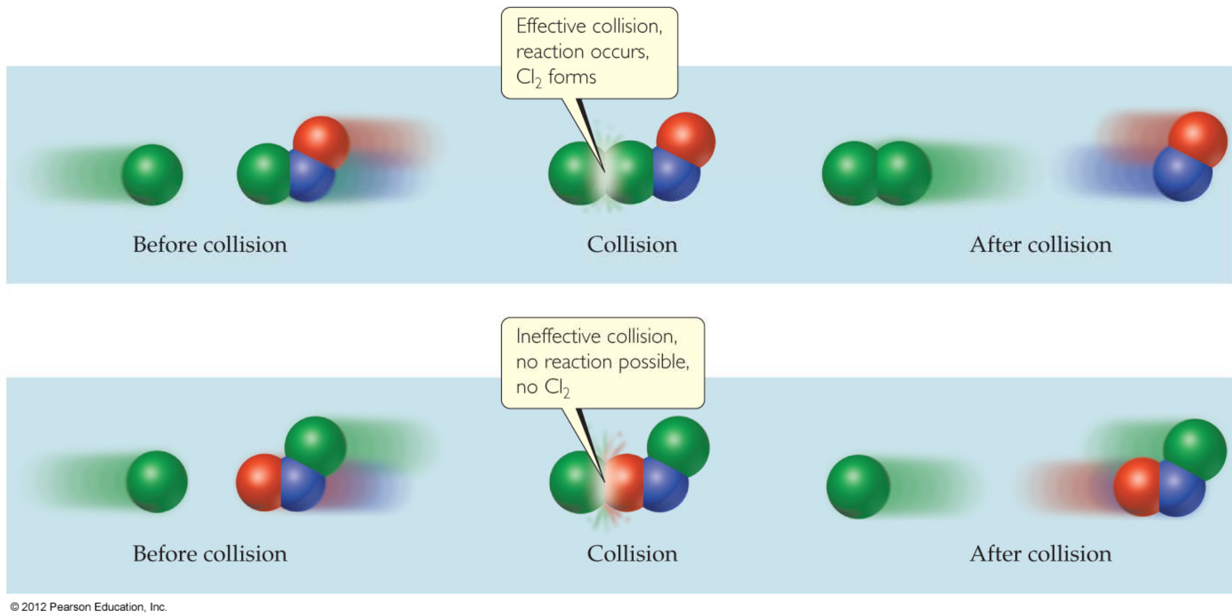
- In kinetics we study the rate at which a chemical process occurs.
- Besides information about the speed at which reactions occur, kinetics also sheds light on the **reaction mechanism** (exactly *how* the reaction occurs).

Reaction Mechanisms

The sequence of events that describes the actual process by which reactants become products is called the **reaction mechanism**.

The Collision Model

Molecules must collide with the correct **orientation** and with enough **energy** to cause bond breakage and formation.



Reaction Mechanisms

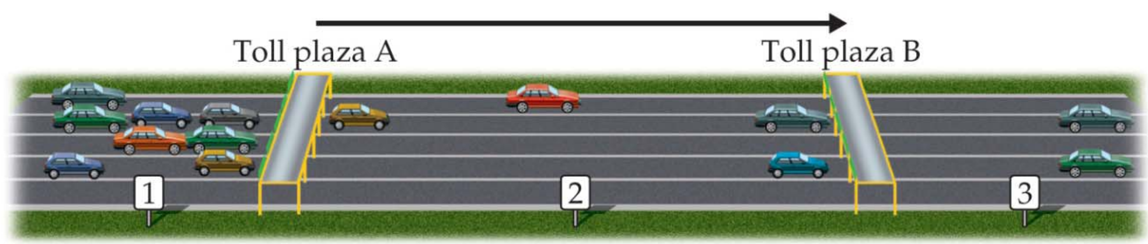
TABLE 14.3 • Elementary Reactions and Their Rate Laws

Molecularity	Elementary Reaction	Rate Law
*Uni*molecular	$A \longrightarrow$ products	Rate $= k[A]$
*Bi*molecular	$A + A \longrightarrow$ products	Rate $= k[A]^2$
*Bi*molecular	$A + B \longrightarrow$ products	Rate $= k[A][B]$
*Ter*molecular	$A + A + A \longrightarrow$ products	Rate $= k[A]^3$
*Ter*molecular	$A + A + B \longrightarrow$ products	Rate $= k[A]^2[B]$
*Ter*molecular	$A + B + C \longrightarrow$ products	Rate $= k[A][B][C]$

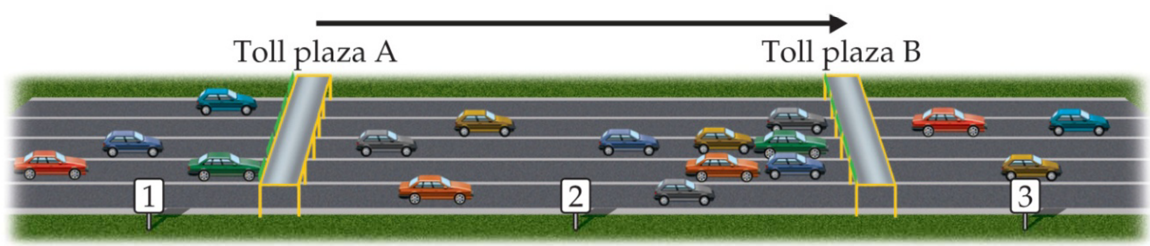
The **molecularity** of a process tells how many molecules are involved in the process.

Multistep Mechanisms

- In a multistep process, one of the steps will be slower than all others.
- The overall reaction cannot occur faster than this slowest, **rate-determining step**.



(a) Cars slowed at toll plaza A, rate-determining step is passage through A



(b) Cars slowed at toll plaza B, rate-determining step is passage through B

Oscillating Chemical Reactions

Generally, in our experience, chemical reactions only overall go in one direction. Chemical reaction don't generally reverse course, or reverse course multiple times

Discussion based on B. Z. Shakhashiri, Chemical Demontrations: A Handbook for Teachers in Chemistry, Vol. 2, University of Wisconsin Press, 1985.

Oscillating Chemical Reactions

- The oscillations in an oscillating chemical reaction are driven by a decrease in free energy of the mixture, as is the driving force in any spontaneous chemical reaction.
- Most reactions just do not oscillate.

Oscillating Chemical Reactions

- Oversimplifying somewhat, all the molecules in an oscillating reaction change their chemical identity simultaneously, at regular time intervals
- If the molecules are different colors, then a change of colors follows the rhythm of an oscillating reaction
- A new order seems to appears; coherence – a "communication" among molecules

Far from Equilibrium System

- Spontaneous appearance of order
- "unstable" state – certain fluctuations, instead of regressing, amplify and invade the system
- Catalytic loops
- Relationship to life?

Prigogine & Stengers, *Order Out of Chaos*, Bantom Books, 1984

Three Common Features of Oscillating Reactions

1) The chemical mixture is far from equilibrium while the oscillations occur; an energy-releasing reaction occurs that drives the oscillations.
2) The energy-releasing reaction can follow at least two pathways, and the reaction switches from one pathway to another.
3) One of the pathways produces an intermediate, while another pathway consumes it. The concentration of the intermediate is the "trigger" for switching from one pathway to another.

The Pathways

- When the intermediate's concentration is low, the reaction follows the intermediate producing pathway, leading to a relatively high concentration of the intermediate
- When the intermediate's concentration is high, the reaction switches to the consuming pathway, and the concentration of the intermediate decreases.
- Eventually the reaction reverts back to the producing pathway. The reaction then repeatedly switches from one pathway to another.

Simple Mechanisms for Sustained Oscillations

- Step 1: $A + X \rightarrow 2X$
- Step 2: $X + Y \rightarrow 2Y$
- Step 3: $Y \rightarrow Q$
- Intermediates are X and Y
- Steps 1 and 2 are autocatalytic – their rates increase as the concentrations of the products increase (feedback)
- Sustained when using a large excess of A so [A]~constant

Belousov-Zhabotinsky Reactions

- Carboxylic acids with common structure
  R-C(O)-CH2-C(O)-OH
- Potassium bromate
- Manganese(II) or cerium(IV) catalyst

- Proposed mechanism much more complicated (about 30 species detected)

Zaikin & Zhabotinsky *Nature* **225**, 535 (1970)
Field, Koros, & Noyes *J. Am. Chem. Soc.* **94**, 8649 (1972)

Manganese-catalyzes Bromate-Malonic Acid Reaction

- My choice as very easy to assemble and works
- Just be careful to not contaminate with chloride ions
- See handout for procedure
- Cycles between colorless and the orange color of bromine

Basic Reactions

- Bromide ions are produced by

$BrO_3^-(aq) + 5\ H^+(aq) + 4\ Mn(II)(aq) \rightarrow$

$HOBr(aq) + 4\ Mn(III)(aq) + 2\ H_2O(l)$

- Bromomalonic acid is formed by

$CH_2(CO_2H)_2(aq) + HOBr(aq) \rightarrow$

$BrCH(CO_2H)_2(aq) + H_2O(l)$

- The bromomalonic acid is oxidized by Mn(III) releasing bromide

$BrCH(CO_2H)_2(aq) + 4\ Mn(III)(aq) + 2\ H_2O(l) \rightarrow$

$Br^-(aq) + HCO_2H(aq) + 2\ CO_2(g) + 4\ Mn(II)(aq) + 5\ H^+$

Overall Reaction

- $BrO_3^-(aq) + CH_2(CO_2H)_2(aq) \rightarrow$
  $H_2O(l) + HCO_2H(aq) + 2\ CO_2(g)$