Autocatalysis

$$\mathrm{A} + \mathrm{P} \xrightarrow{k} 2\mathrm{P}$$

$$\text{rate} = -\frac{\mathrm{d}a}{\mathrm{d}t} = \frac{\mathrm{d}x}{\mathrm{d}t} \qquad [\mathrm{A}] = a_0 - x, \;\; [\mathrm{P}] = p_0 + x$$

$$\frac{\mathrm{d}x}{\mathrm{d}t} = k\left(a_0 - x\right)\left(p_0 + x\right)$$

$$kt = \int_0^x \left\{ \frac{\mathrm{d}x}{\left(a_0 - x\right)\left(p_0 + x\right)} \right\}$$

$$= \frac{1}{\left(a_0 + p_0\right)} \int_0^x \left\{ \frac{1}{\left(a_0 - x\right)} + \frac{1}{\left(p_0 + x\right)} \right\} \mathrm{d}x$$

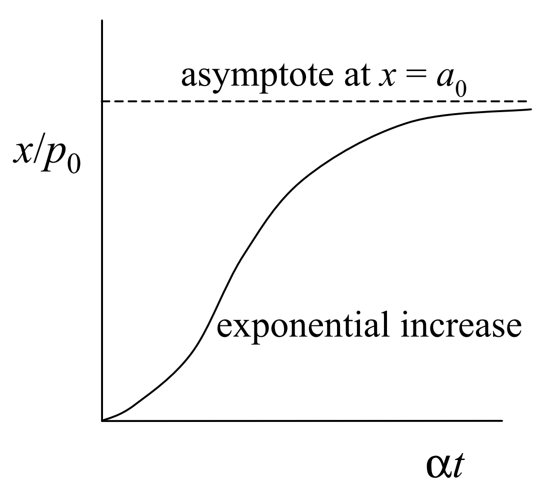
$$= \frac{1}{\left(a_0 + p_0\right)} \left[-\ln\left(a_0 - x\right) + \ln\left(p_0 + x\right) \right]_0^x$$

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

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

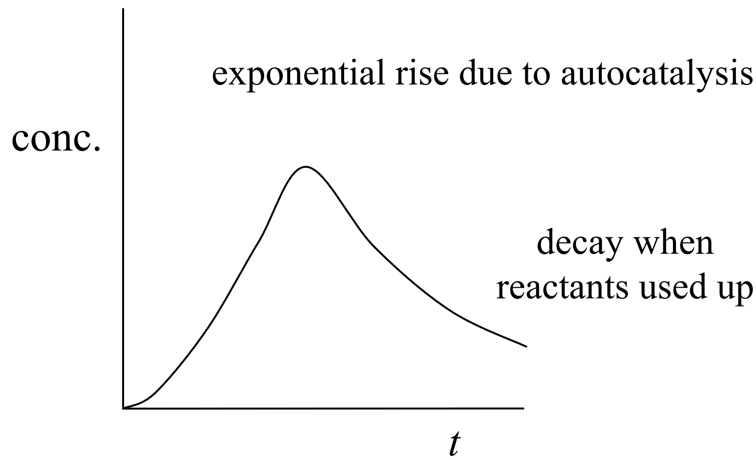
$$\alpha t = \ln \frac{\left(1 + x / p_0\right)}{\left(1 - \beta x / p_0\right)}$$

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

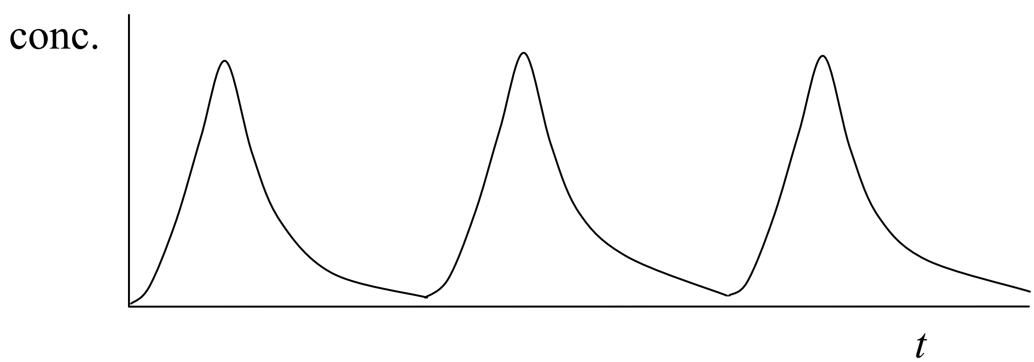


Oscillations in Gas Phase Kinetics

Consider the concentration profile of an intermediate in the $H_2 + O_2$ reaction.



What if more reactant is supplied?



Examples:

Flaring of phosphorus in a loosely stoppered flask
(Robert Boyle, 17th century)

Cool flames = limited combustion of hydrocarbons due to "long-lived" intermediates which damp the explosion.

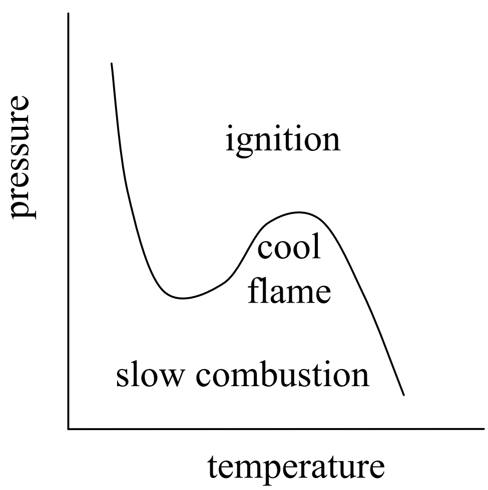
Pre-ignition (autoignition) producing "knock" in auto engines.

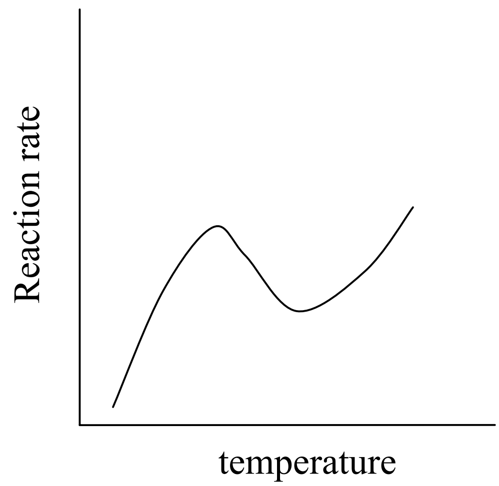
Cool Flame Oscillations

Hydrocarbon fuels spontaneously ignite in the presence of O_2 at $T > 400\text{-}500$ K.

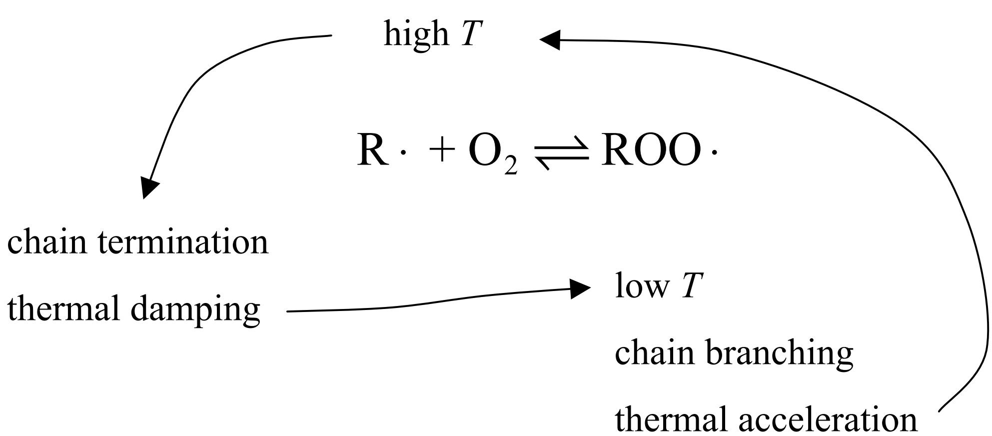
"True" ignition gives CO, CO_2, H_2O and T increases ~ 1000 K.

"Cool" flames produce ROH, RCHO, RCOOH and ΔT ~ 100 K





Oscillations occur because of both chemical *and* thermal feedback.



Oscillating Reactions

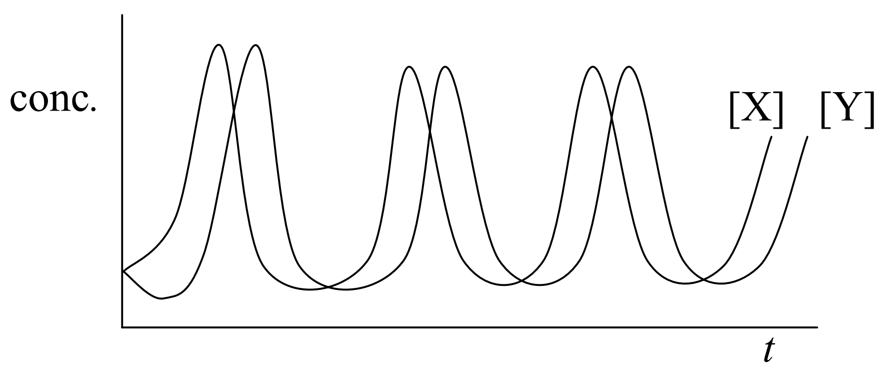
Lotka-Volterra Mechanism

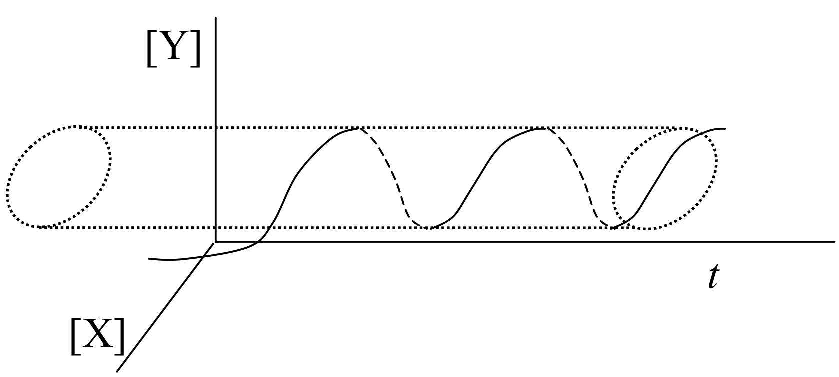
$$A + X \rightarrow 2X$$

$$X + Y \rightarrow 2Y$$

$$Y \rightarrow B$$

[A] is held constant (replenished). [X] and [Y] oscillate.





Such a model can be applied to population biology,

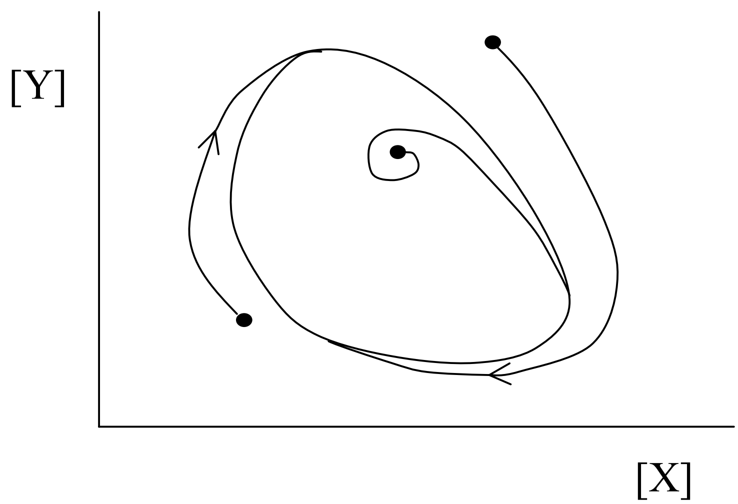
e.g. A = grain; X = geese; Y = wolves; B = dead wolves!

Oscillating Reactions

Brusselator Mechanism (Prigogine *et al.*)

$$A \rightarrow X$$
$$2X + Y \rightarrow 3X$$
$$B + X \rightarrow Y + C$$
$$X \rightarrow D$$

[A] and [B] are constant. [X] and [Y] settle down to a limit cycle:



Oregonator Mechanism (Noyes *et al.*)

$$A + Y \rightarrow X$$
$$X + Y \rightarrow C$$
$$B + X \rightarrow 2X + Z$$
$$2X \rightarrow D$$
$$Z \rightarrow Y$$

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

$X = HBrO_2$

$Y = Br^-$

$Z = 2Ce^{4+}$