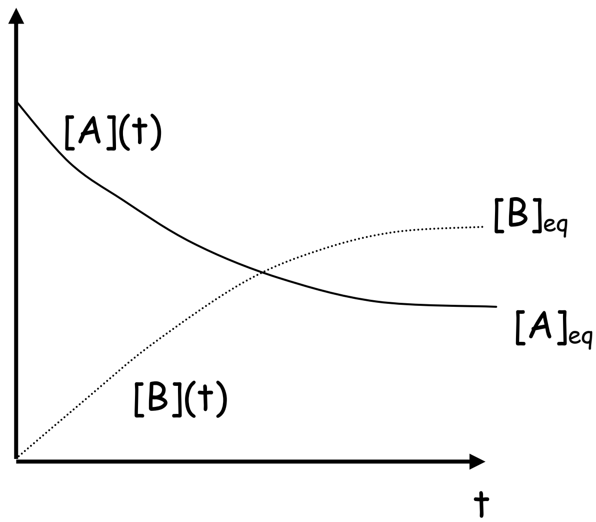
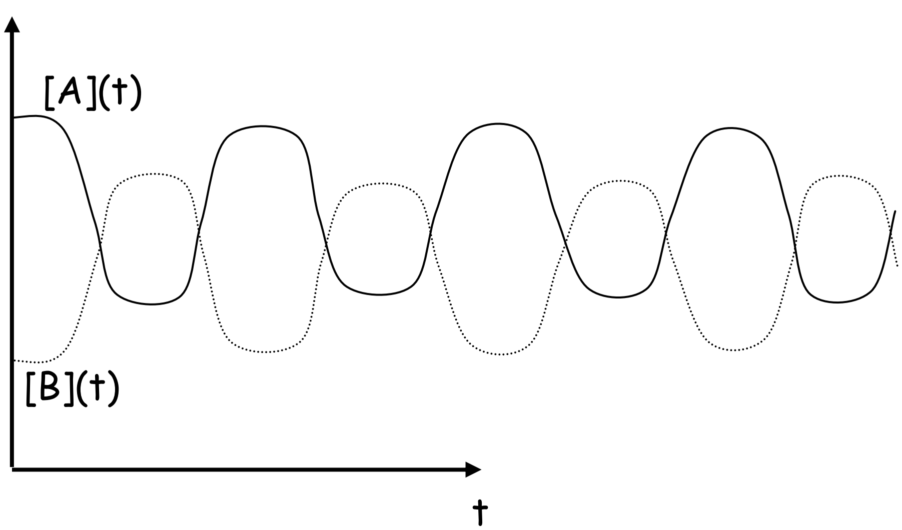
Chemical Oscillations

The reactions we have seen so far have approached equilibrium monotonically

e.g. $A \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} B$



But some reactions, when started far from equilibrium, oscillate like springs, or a weight on a rubber band,



Oscillations can result from feedback or autocatalysis:

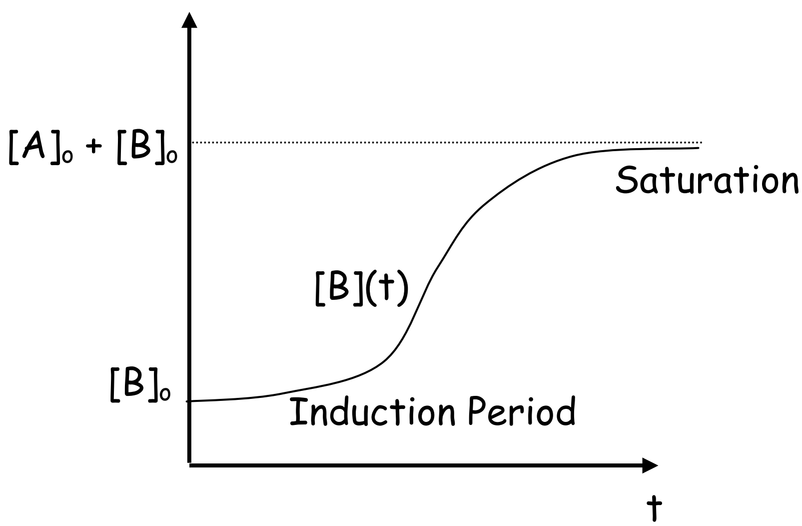
When a product is also one of the reactants

e.g. $A + B \xrightarrow{k_1} 2B$

$$-\frac{d[A]}{dt} = k[A][B] \qquad [B] = [A]_o + [B]_o - [A]$$

After integrating,

$$[B] = \frac{[A]_o + [B]_o}{1 + \left([A]_o / [B]_o\right) e^{-k([A]_o + [B]_o)t}}$$



S-shape is typical of an autocatalytic process.

Simplest mechanism for oscillatory chemical system: Lotka-Volterra or Predator-Prey mechanism

$$A + B \xrightarrow{k_1} 2B$$
$$B + C \xrightarrow{k_2} 2C$$

Autocatalytic steps (A is kept constant)

$$C \xrightarrow{k_3} \text{Products}$$

$$\frac{dB}{dt} = k_1 AB - k_2 BC$$
$$\frac{dC}{dt} = k_2 BC - k_3 C$$

Suppose steady state: $\frac{dB}{dt} = \frac{dC}{dt} = 0$

$$B_{SS} = \frac{k_3}{k_2} \qquad C_{SS} = \frac{k_1}{k_2} A$$

(A is kept Constant)

Now suppose the system is perturbed and a fluctuation in B and C occurs

$$B = B_{SS} + \delta B \qquad C = C_{SS} + \delta C$$

$$\frac{d(\delta B)}{dt} = -k_3 \delta C \qquad \frac{d(\delta C)}{dt} = k_1 A \delta B$$

These are Coupled Differential Equations.

The general solutions are:

$$\delta B(t) = \chi_+ e^{i\omega t} + \chi_- e^{-i\omega t} \qquad \delta C(t) = \zeta_+ e^{i\omega t} + \zeta_- e^{-i\omega t}$$

where $\omega = (k_1 k_3 A)^{1/2}$

Let $\delta B(t=0) = \delta B_0$ and $\delta C(t=0) = \delta C_0$

$$\Rightarrow \qquad \delta B(t) = \delta B_o \cos\omega t - \left(\frac{k_3}{k_1 A}\right)^{1/2} \delta C_o \sin\omega t$$

$$\Rightarrow \qquad \delta C(t) = \delta B_o \cos\omega t + \left(\frac{k_1 A}{k_3}\right)^{1/2} \delta B_o \sin\omega t$$