Steady-state approximation

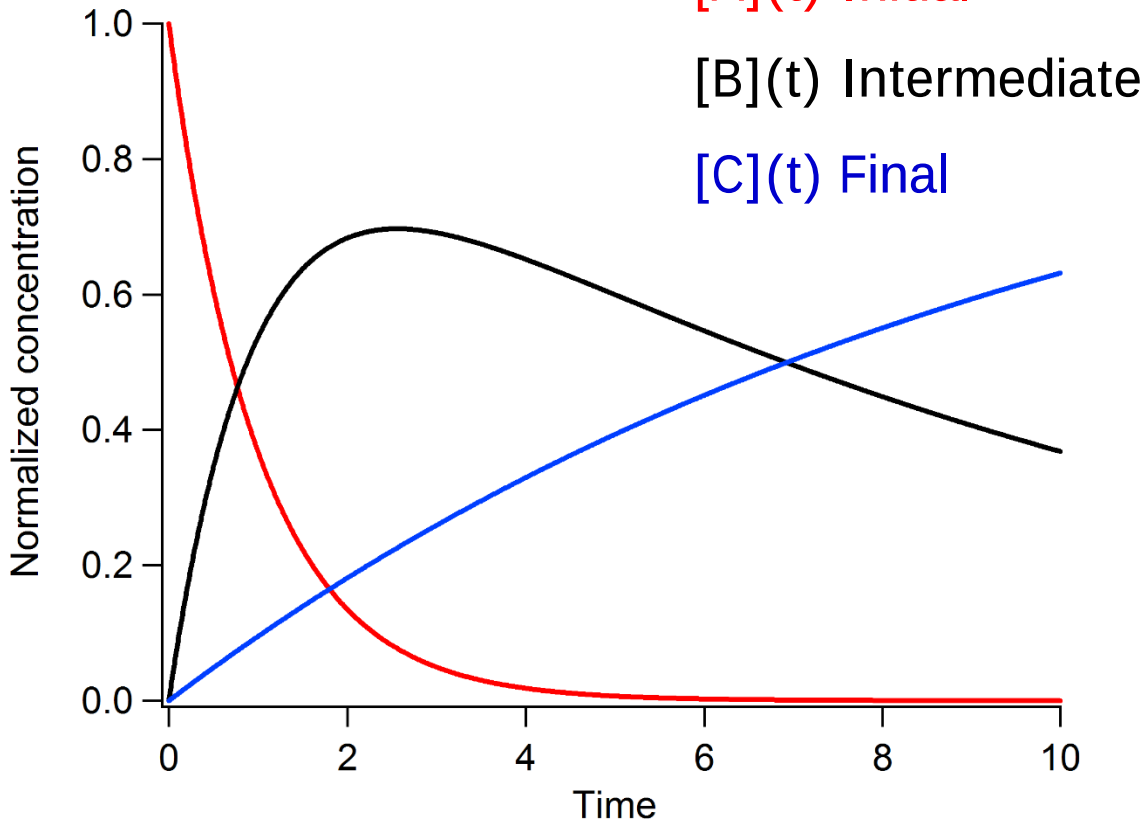
- Equations representing kinetic networks of more than three states are not soluble analytically.
- One means of pushing the techniques as far as possible using analytical solutions is to set the derivatives of intemediates equal to zero:

$$d[\text{Intermediate}]/dt = 0$$

- To see when one can use this approximation we consider the effect of increasing the second rate constant relative to the first.

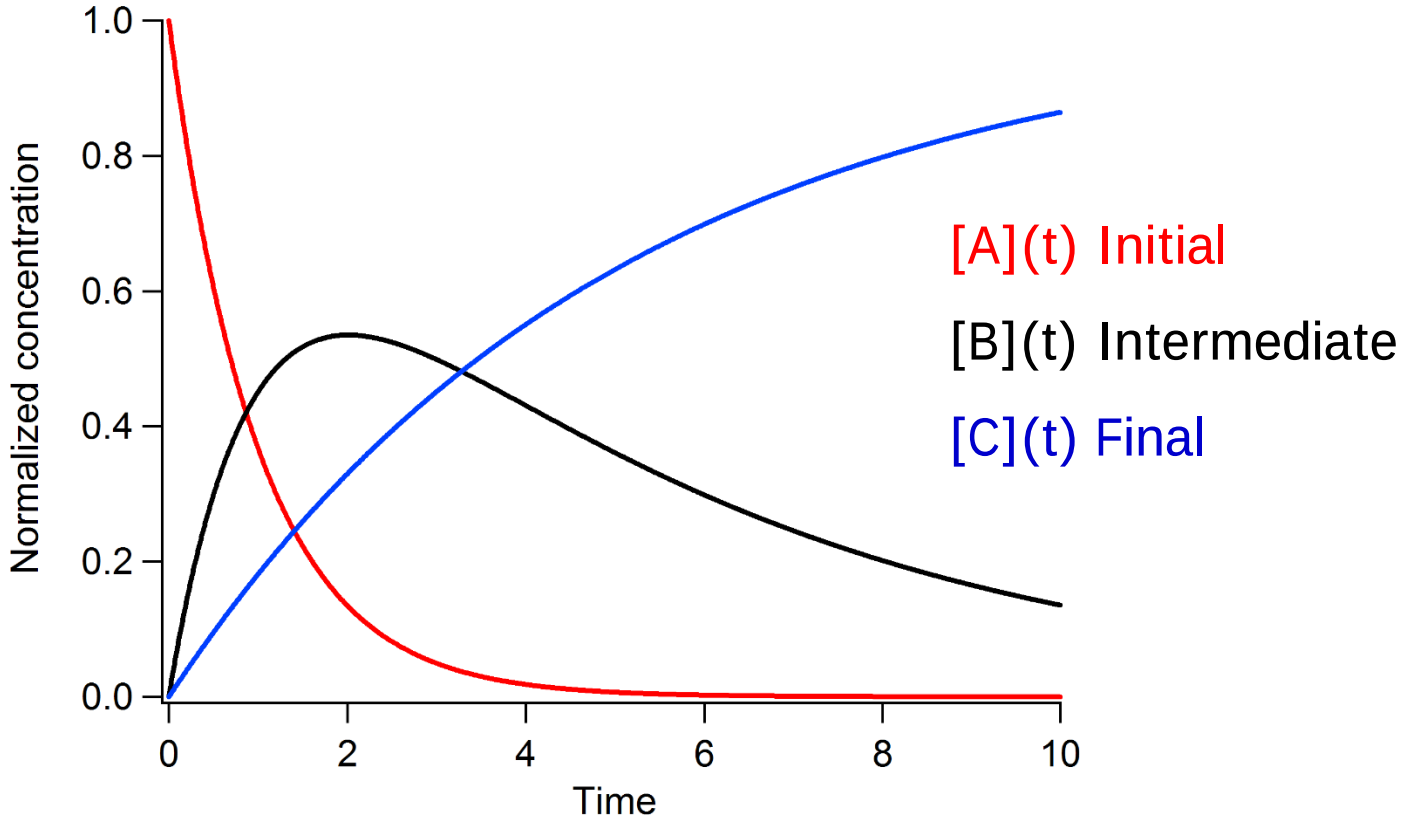
Steady-state approximation

- We start with $k_1 = 10\ k_2$.



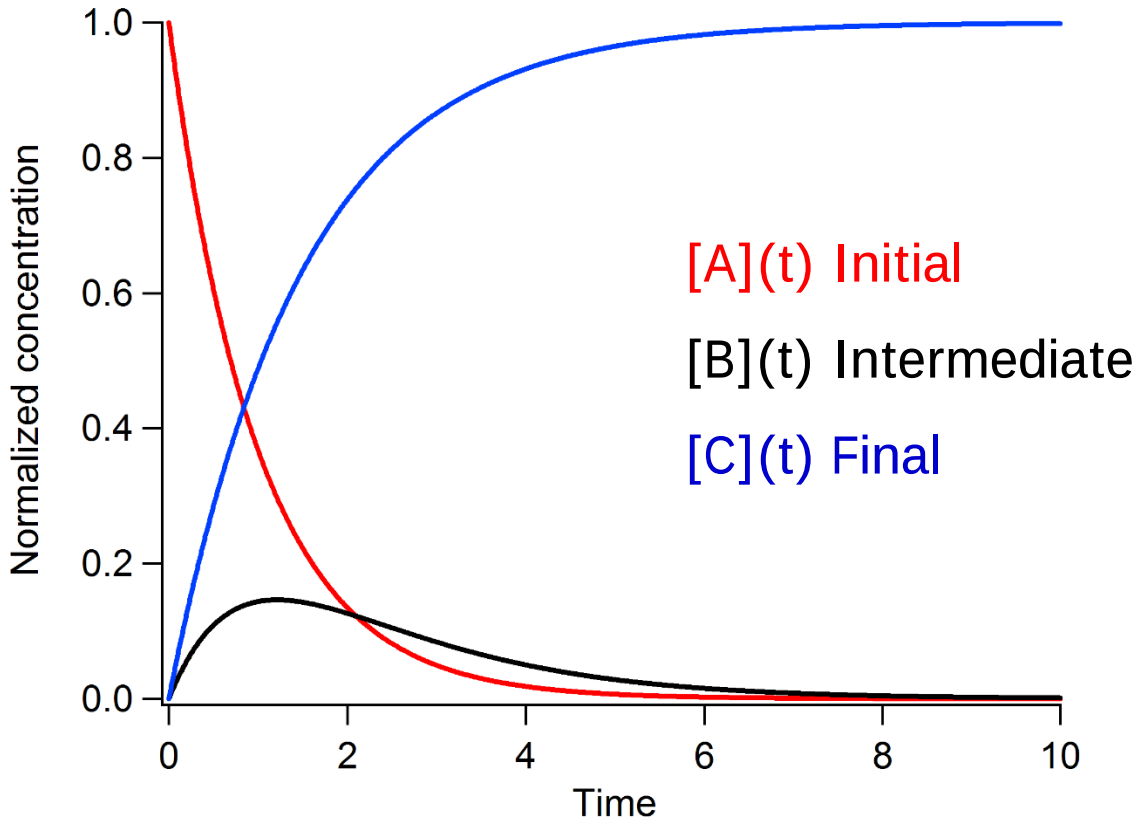
Steady-state approximation

- And then $k_1 = 5\ k_2$.



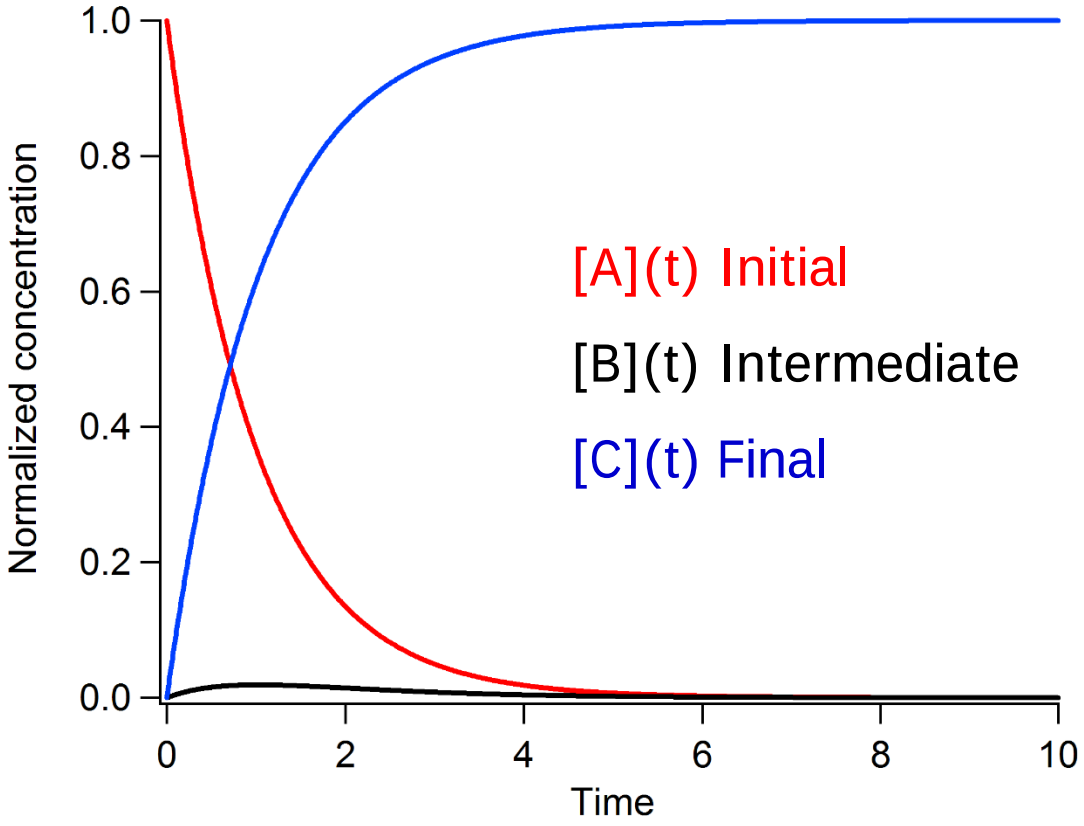
Steady-state approximation

- And then $k_1 = 1.5\ k_2$.



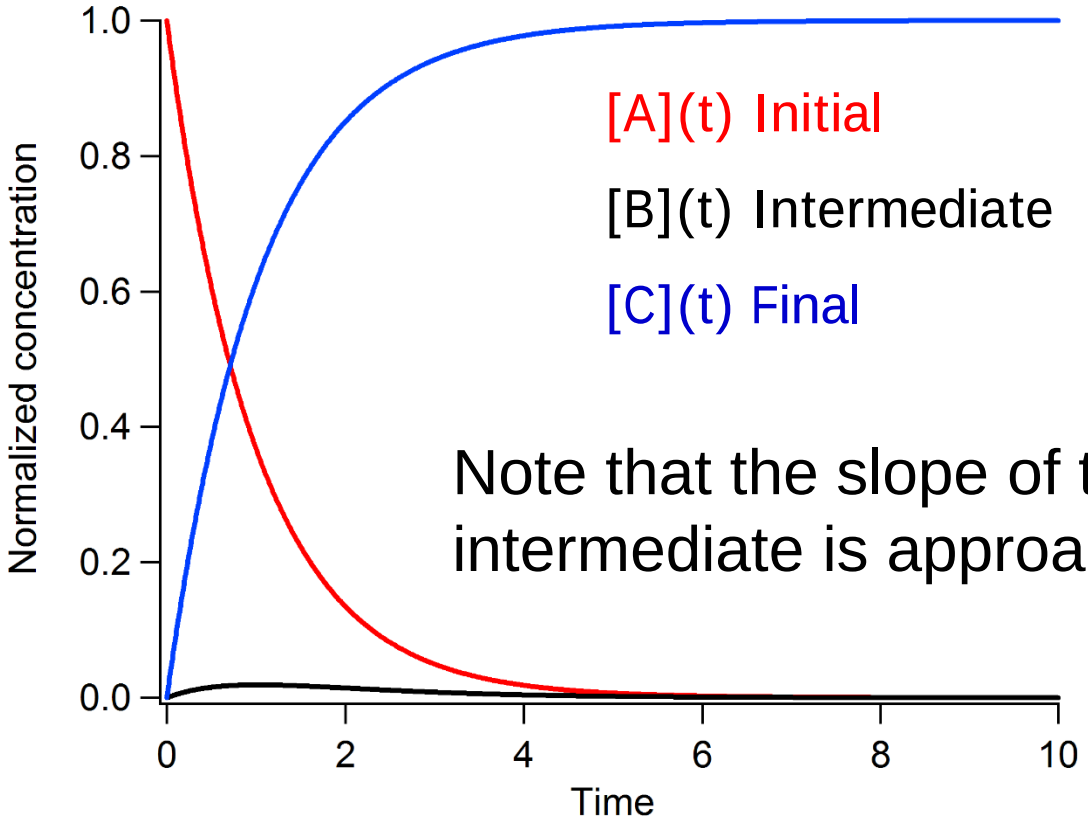
Steady-state approximation

- And finally $k_1 = 1.1\ k_2$.



Steady-state approximation

- And finally $k_1 = 1.1\ k_2$.



Note that the slope of the intermediate is approaching zero.

Application of the steady-state approximation

- The steady state approximation can be applied to the consecutive reaction scheme

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C.$$

if the concentration of B is fairly constant.

- The result of setting d[B]/dt = 0 is:

$$k_1[A] - k_2[B] = 0$$ and

d[C]/dt = k_1[A]. Since d[A]/dt = - k_1[A] we see that d[C]/dt = - d[A]/dt and [C]=(1 - exp{-k_1t})

Biexponential kinetics result when the steady-state approximation fails

- We cannot apply the steady state approximation if the concentration of B changes significantly during the process

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C.$$

- In this case we must solve the rate equations
- In general, for N processes the result will be kinetics with N exponential time constants.

  Here N = 2 so $[B](t) = \Phi_1 e^{-k_1 t} + \Phi_2 e^{-k_2 t}$