First-order Kinetics

- A first order rate process is:

$$d[A]/dt = -k[A].$$

First-order Kinetics

- A first order rate process is:

$$d[A]/dt = -k[A].$$

- Separating the variables [A] and t we have:

$$\int_{[A]_0}^{[A](t)} \frac{d[A]'}{[A]'} = -k \int_0^t dt'$$

- The integrated form is

$$ln([A](t)) - ln([A]_o) = -kt$$

Integrated rate law

- We can write the integrated form as:

$$ln\left(\frac{[A](t)}{[A]_o}\right) = -kt$$

- Then we exponentiate both side to obtain:

$$[A](t) = [A]_o exp\{-kt\}$$

- This function is known as a single exponential.

Half life and natural lifetime

- The single exponential form, $[A]=[A]_0e^{-kt}$, can be characterized in terms of the natural lifetime, $\tau = 1/k$.
- An alternative useful time constant is the half life. We derive is as follows: $k\tau_{1/2} = -\ln([A]_0/2[A]_0) = -\ln(1/2)$
- Therefore, $\tau_{1/2} = \ln(2)/k$

Thinking about half life

- Half life is a useful way to talk about kinetic processes. Clearly, we can easily calculate the fraction, f, of material remaining after n half lives:

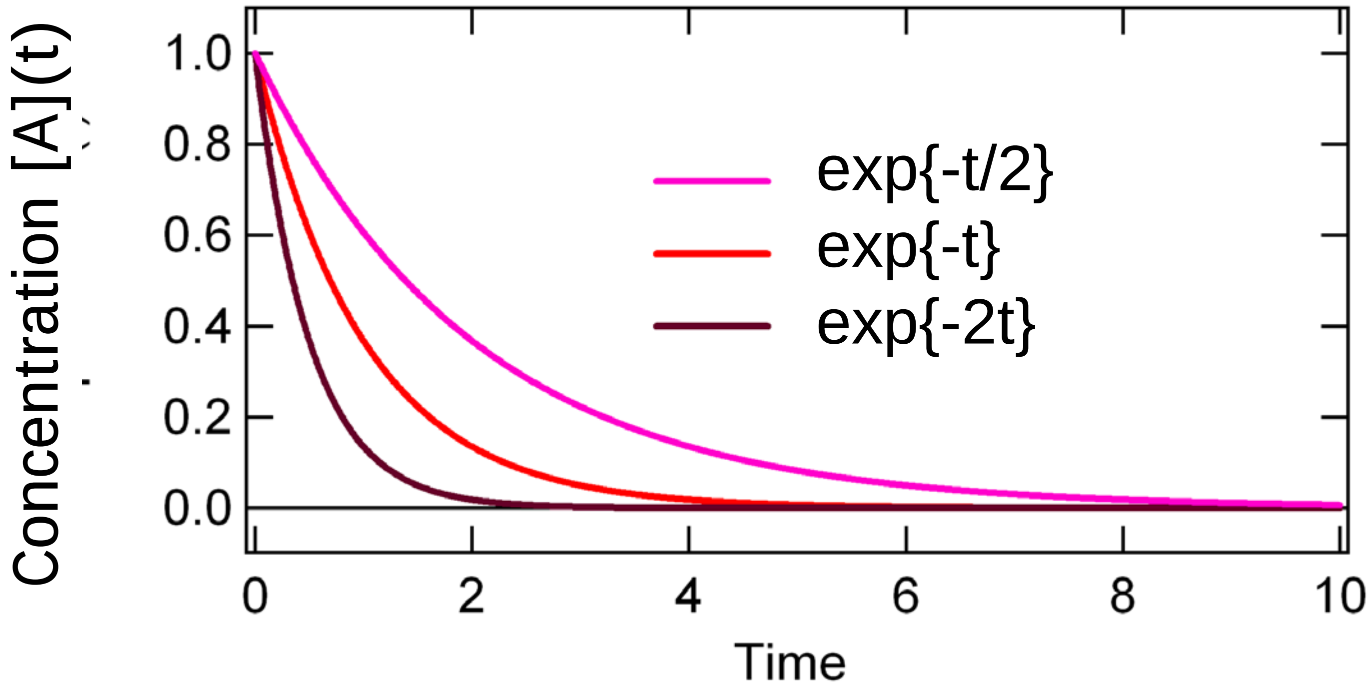
$$f = \left(\frac{1}{2}\right)^{n}$$

- If the question is how many half lives will pass before a given fraction remains, we can solve for n:

$$n = \frac{\ln(f)}{\ln\left(\frac{1}{2}\right)}$$

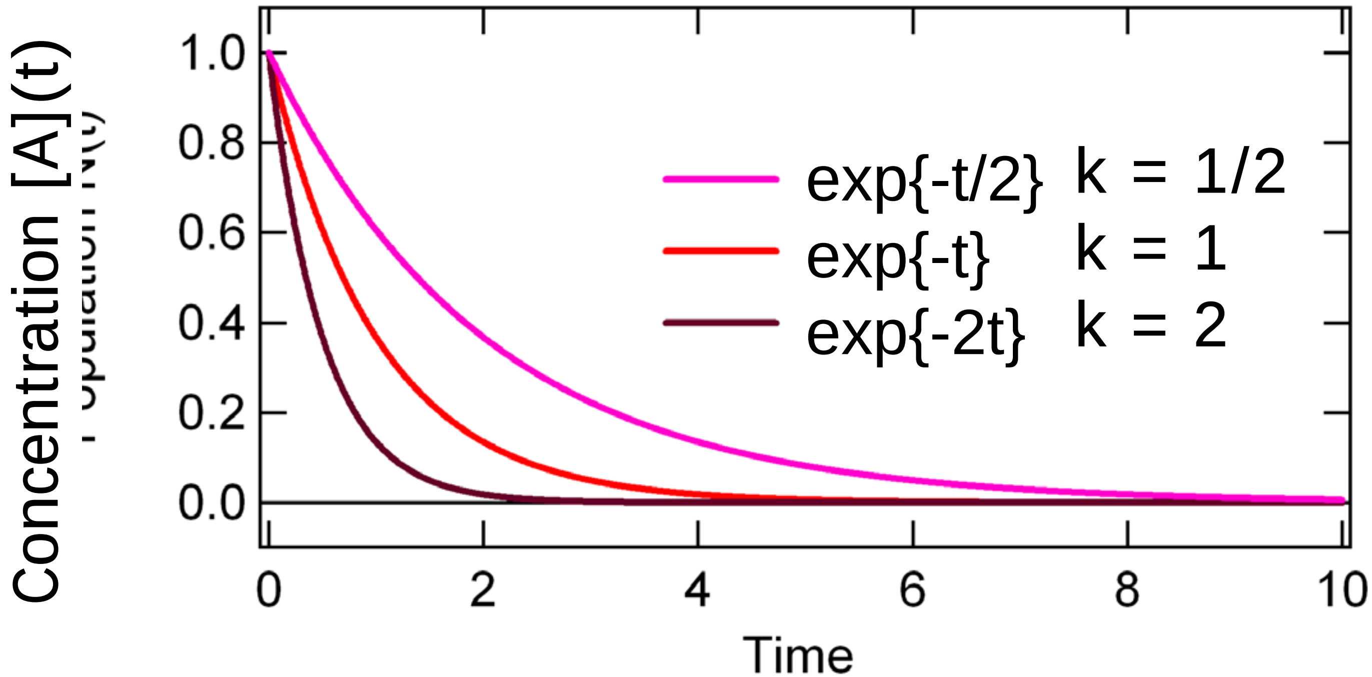
- Note: n does not have to be an integer.

Exponential kinetics



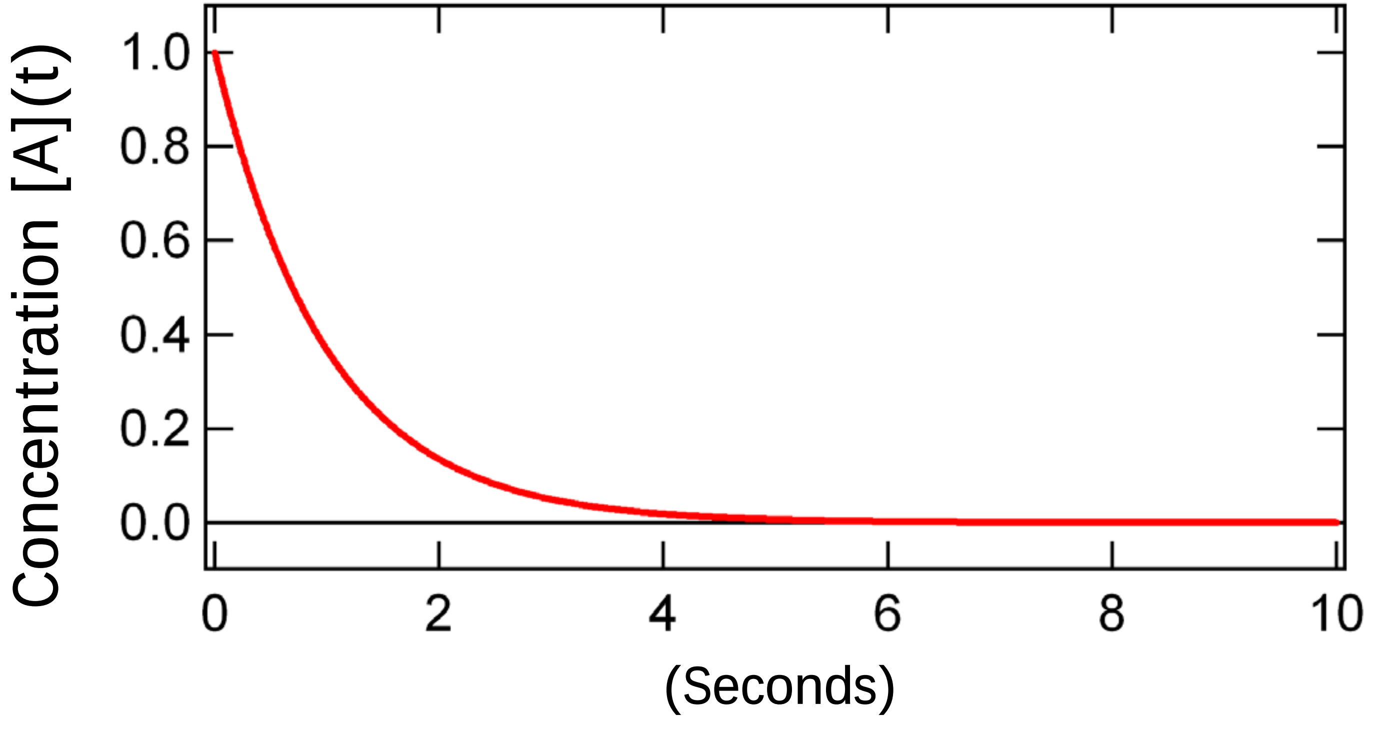
On the y-axis we can plot population or concentration. These are two ways of saying the same thing.

Exponential kinetics



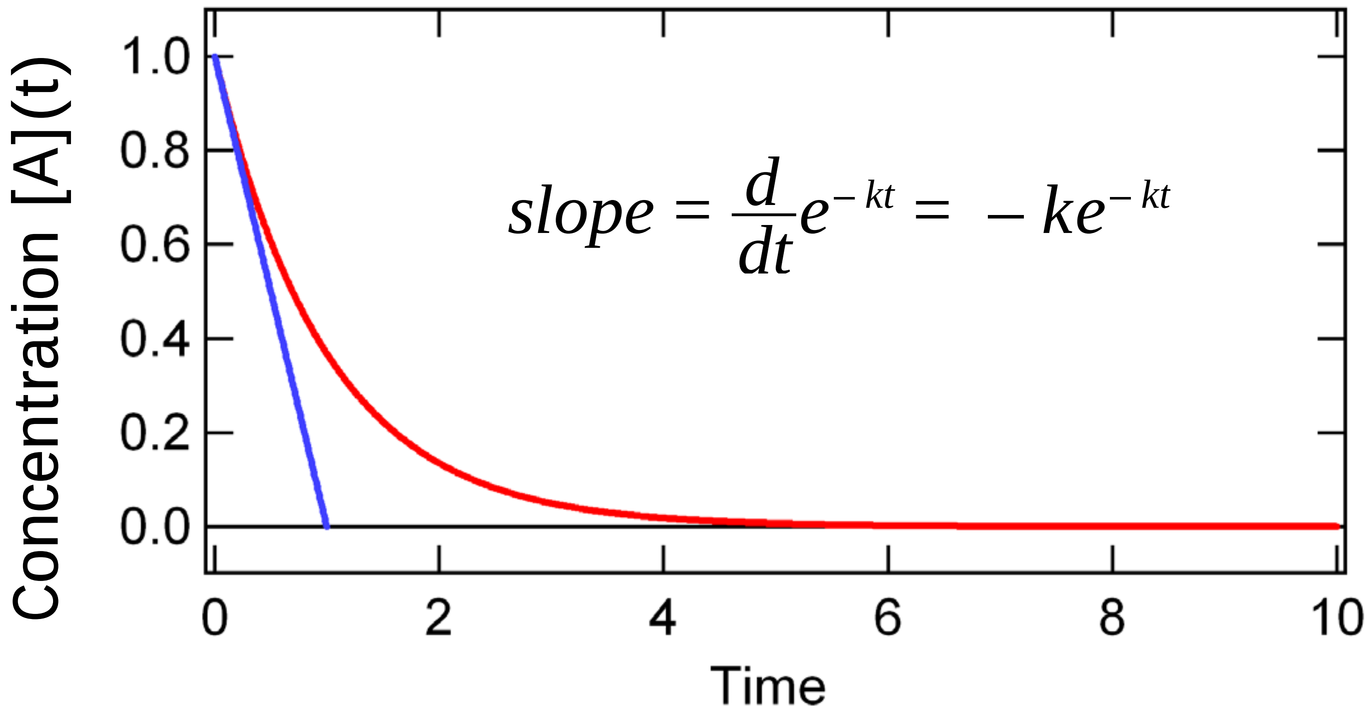
An exponential process has a 1/e time that corresponds to $\tau = 1/k$, where k is the rate constant. Three examples are shown to graphically illustrate the differences in k.

Exponential kinetics



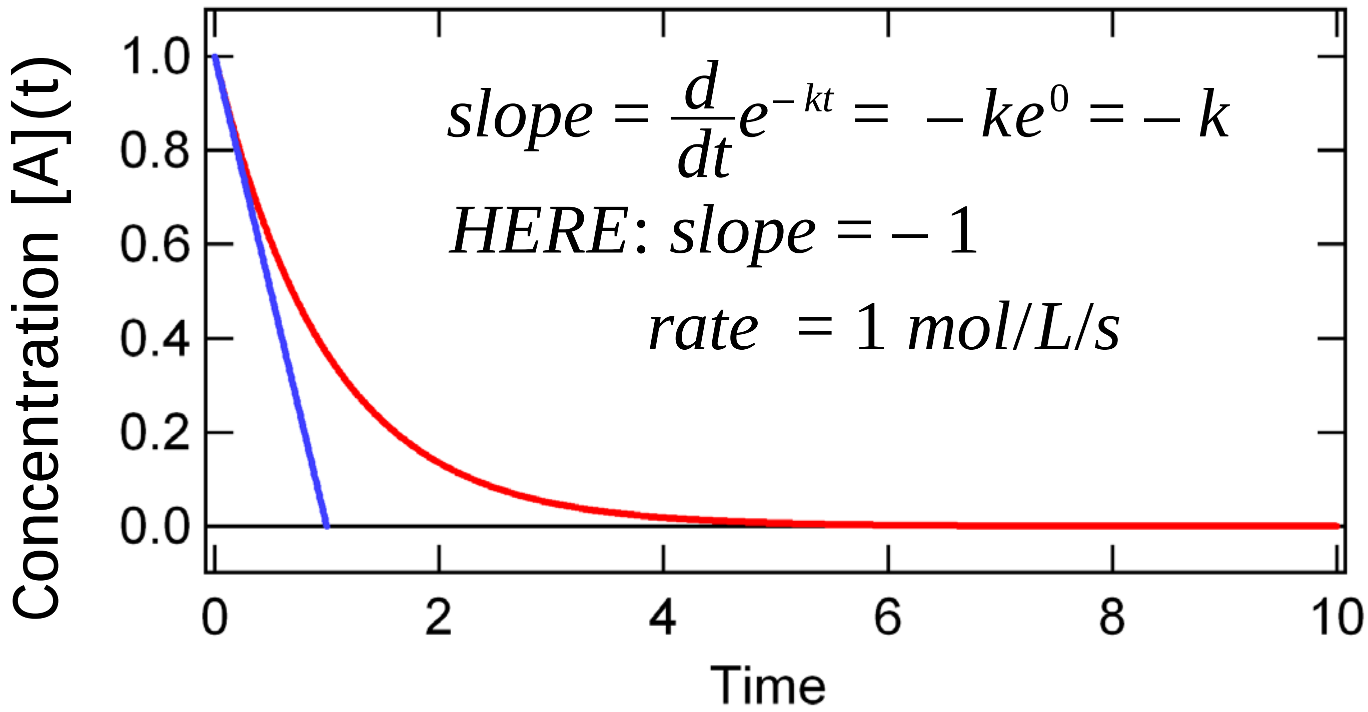
We focus on the exponential process with a rate constant of $k = 1\ s^{-1}$. We would say the natural lifetime is 1 second.

Exponential kinetics



The initial rate is the slope at time zero. This is given by the blue line in the figure. It is obtained from the derivative.

Exponential kinetics



The initial rate is the slope at time zero. This is given by the blue line in the figure. The derivative is the slope at t=0.

Summary of first-order processes

1. First-order processes have an exponential time course.
2. The rate constant k can be related to a 1/e time τ or a half-time $\tau_{1/2}$. $k = 1/\tau$, $k = \ln(2)/\tau_{1/2}$.
3. The units of the rate constant are s^{-1}.
4. The approach to equilibrium is the sum of forward and reverse rate constants.
5. The rate v is the instantaneous change (slope).