

Unit 2 – Day 2

Kinetics

Integrated Rate Laws



Previously

Rates of chemical reactions

- Concentration
- Reactions rates
- Spectrometry

Rates as a function of time

- Instantaneous rate of reaction

Rate laws

- Reaction order
- Rate laws
- Rate constant

Lecture topics – integrated rate laws

Integrated Rate Laws

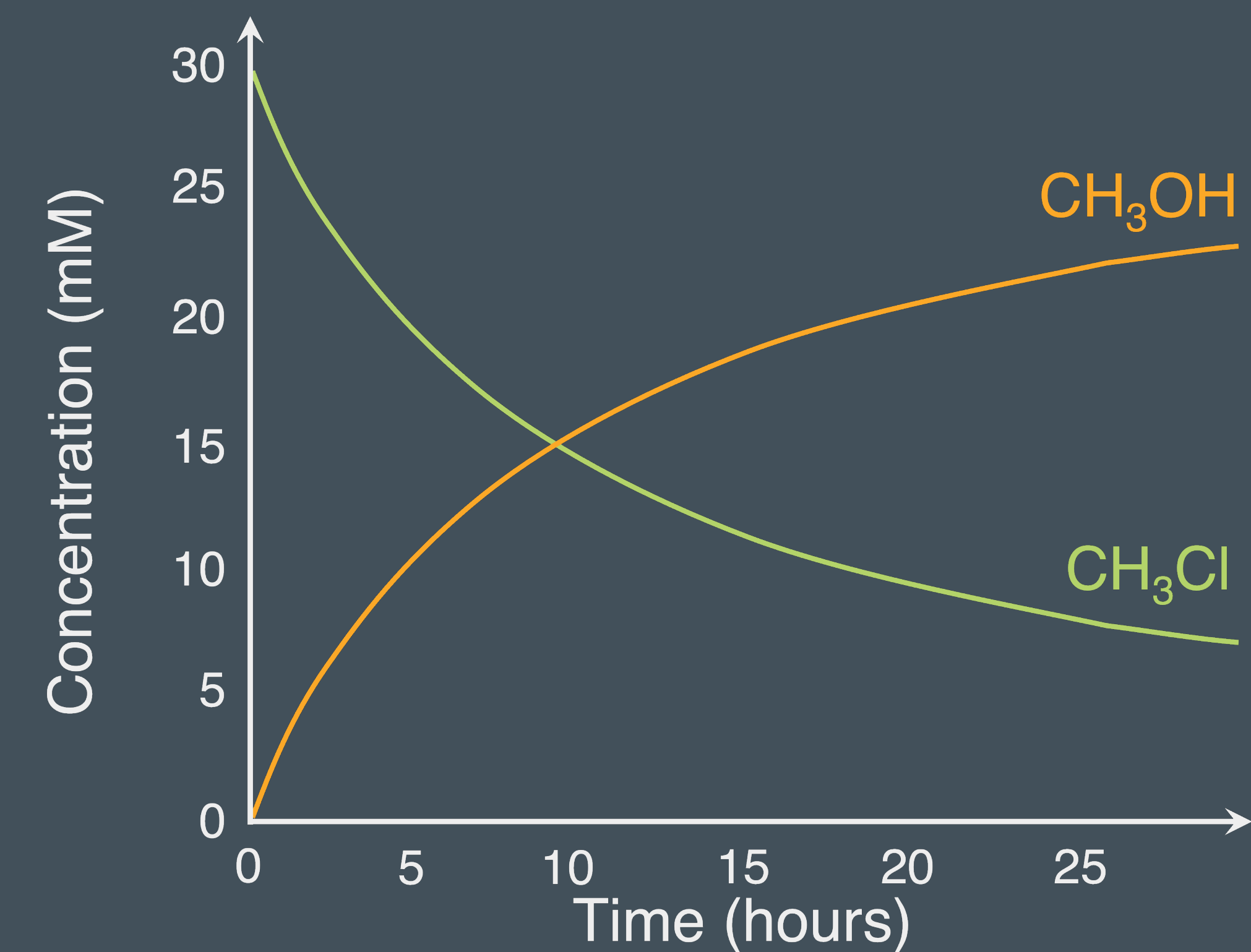
- First Order Integrated Rate Laws

Half Life

- Half-Lives of First-Order Reactions

Second Order Rate Laws

- Second Order Integrated Rate Laws



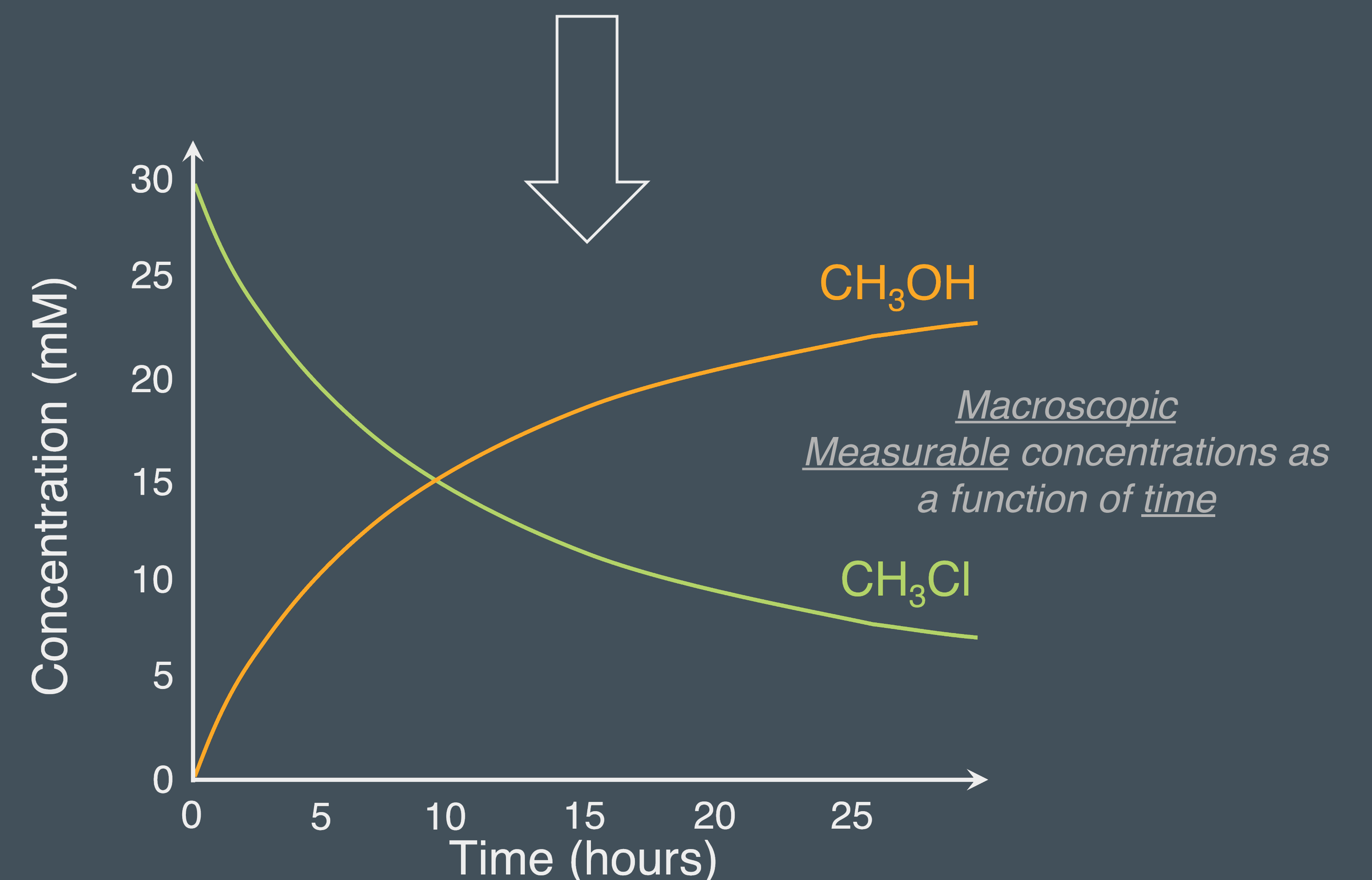
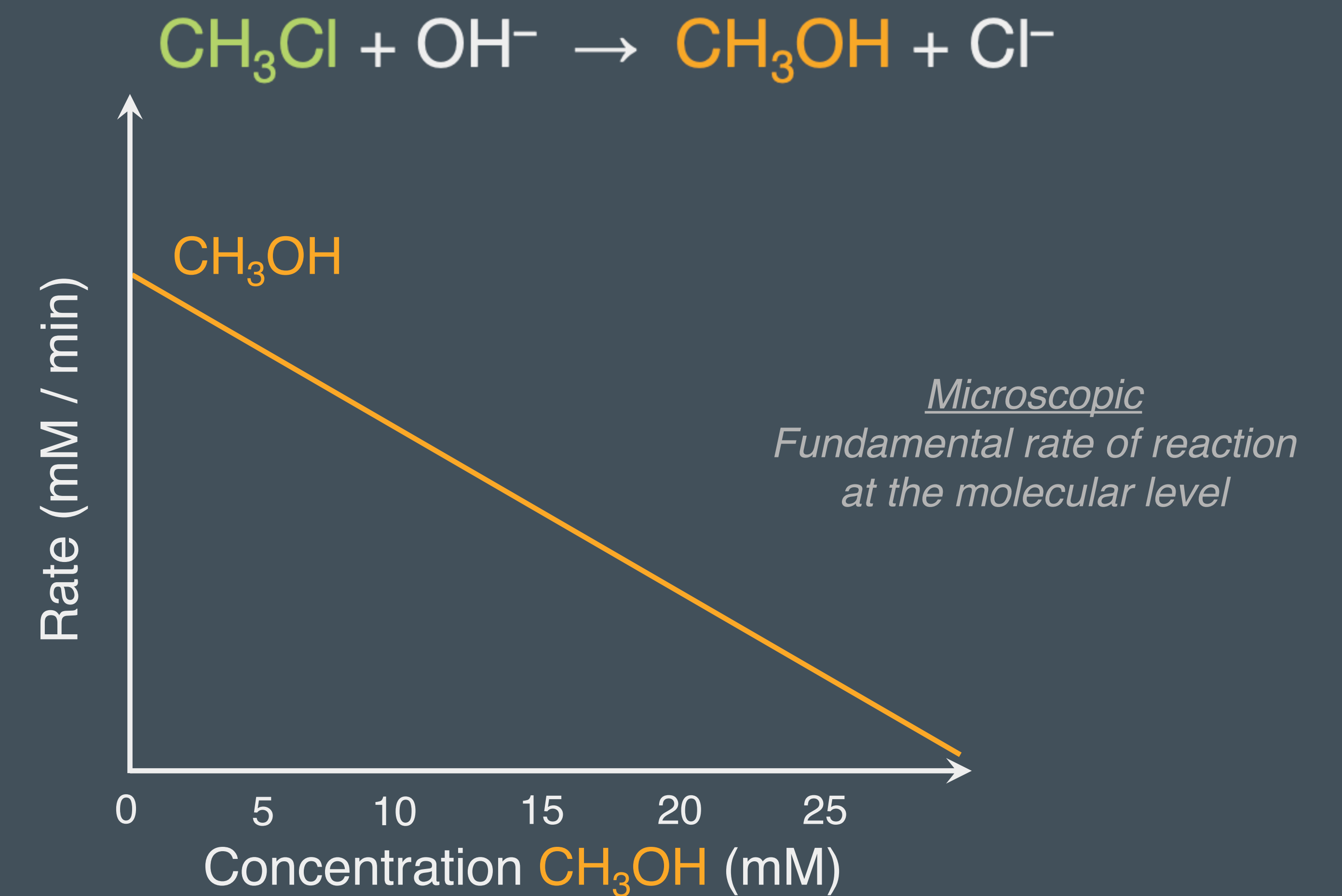
Review: rate laws

DEF **Rate law**: relates the rate of reaction to the concentration of the species participating. A generic rate law is

$rate = k[A]^x[B]^y$ where A and B are reactants and k is the rate constant.

Rate laws tell us the instantaneous reaction rate given the current concentrations.

However, rate laws can't tell us what the concentrations will be at a given time.

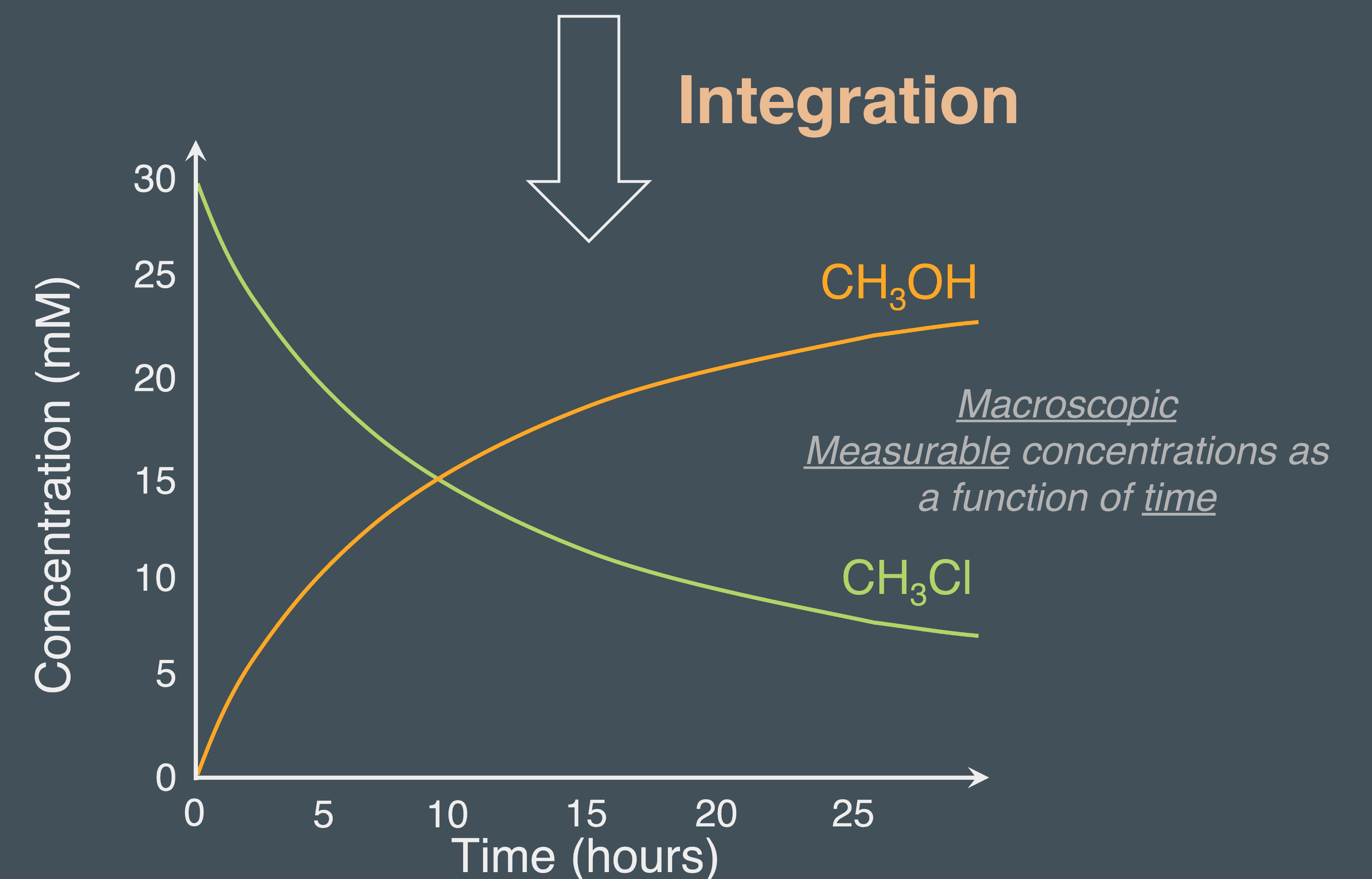
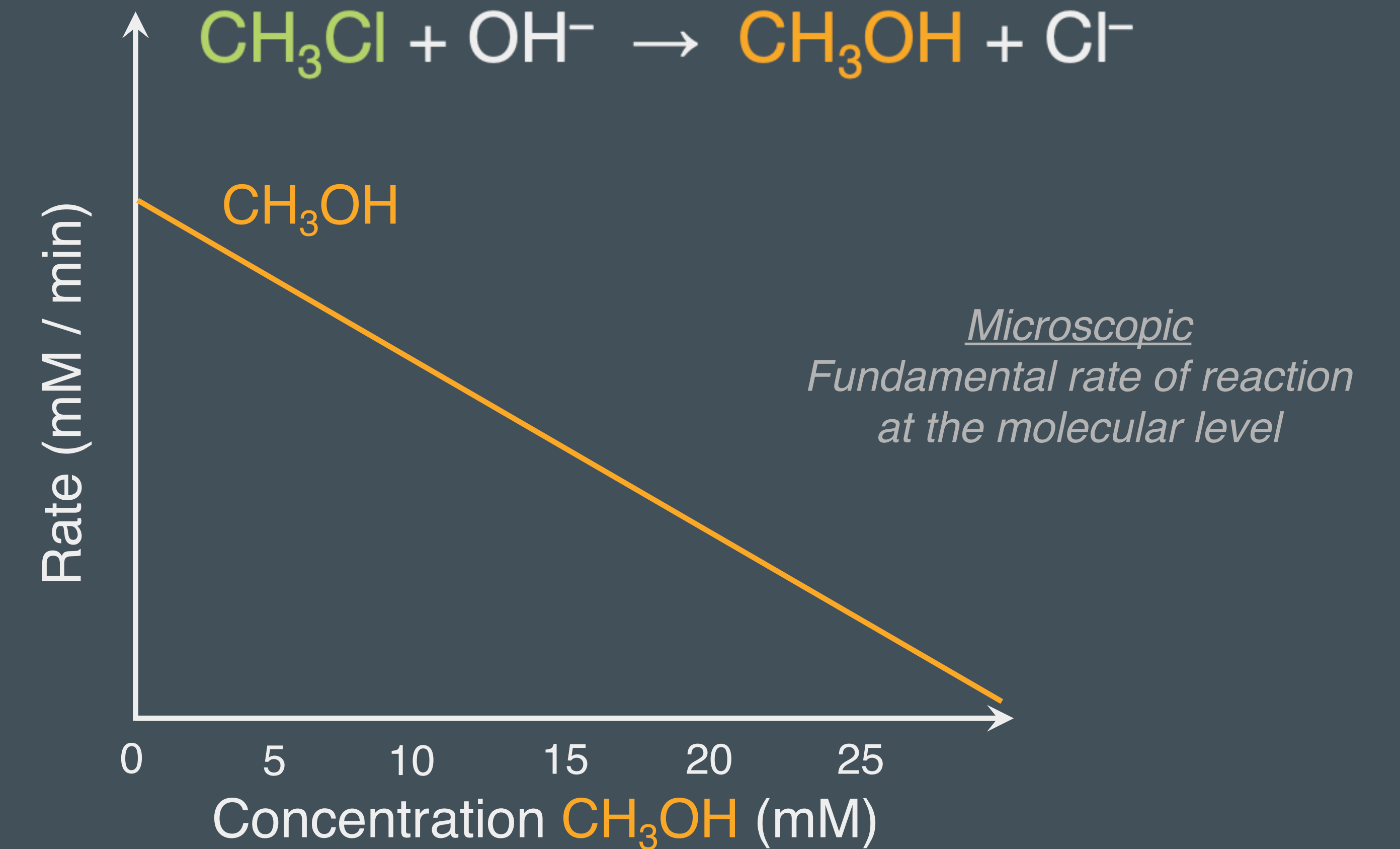


Integrated Rate Laws

Integrated rate laws show concentration as a function of time.

This allows us to calculate how much reactant is left after a certain amount of time has passed, or how much time is required for a certain amount of reactant to react.

When working with integrated rate laws, we will monitor only one reactant concentration at a time, reactant **A**.

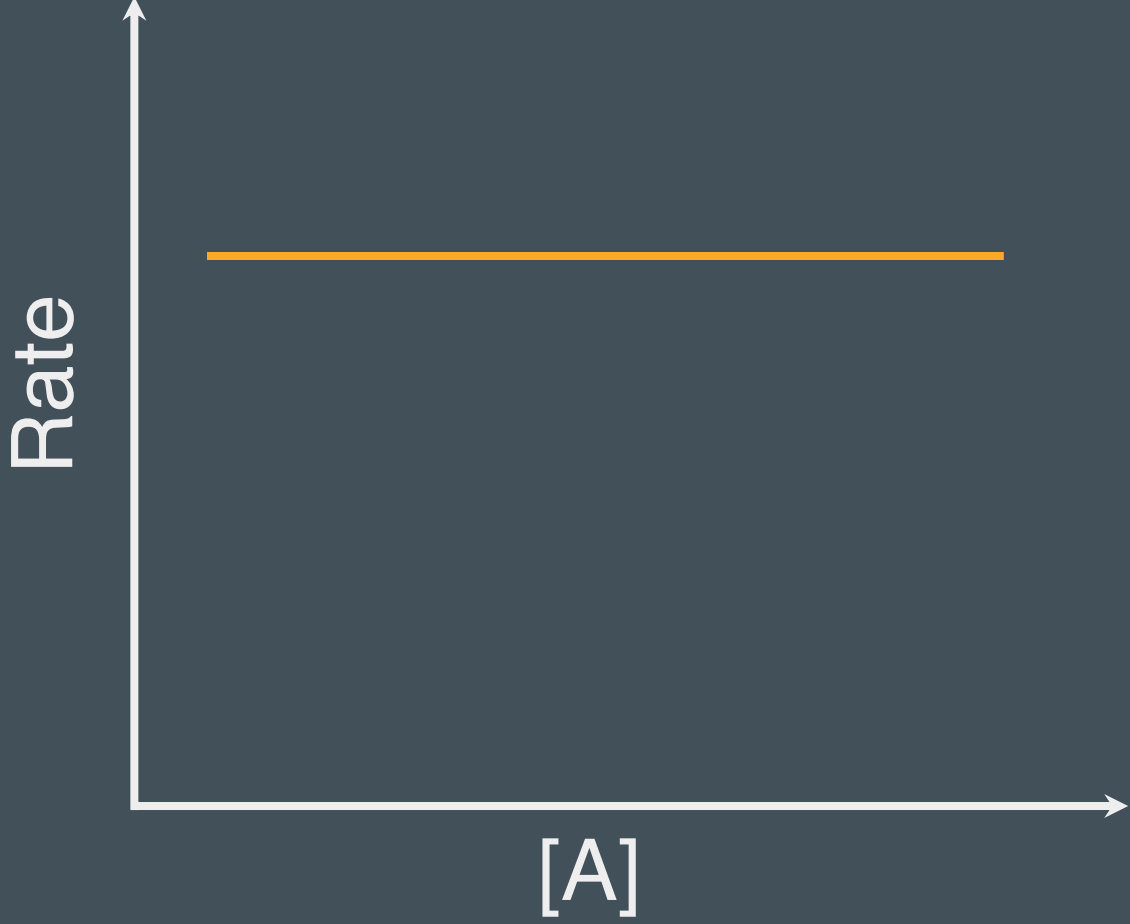
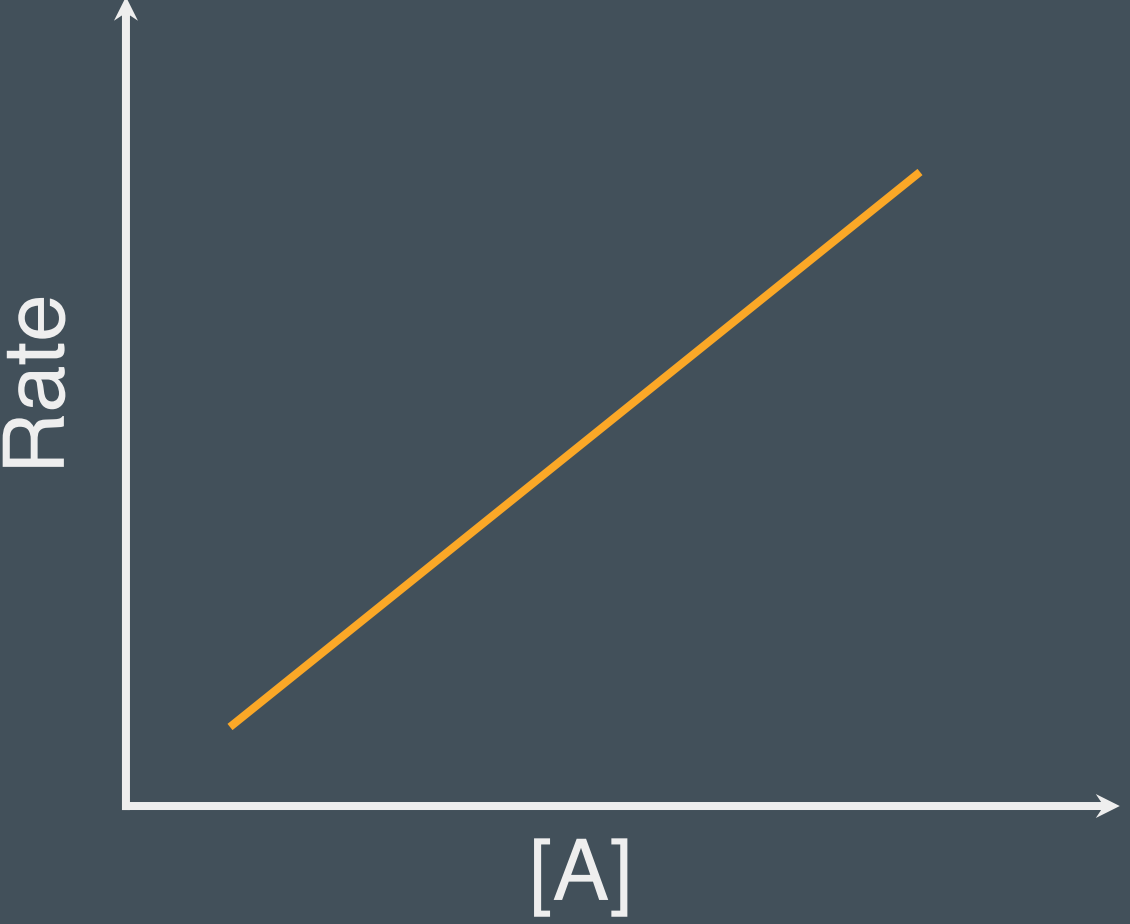
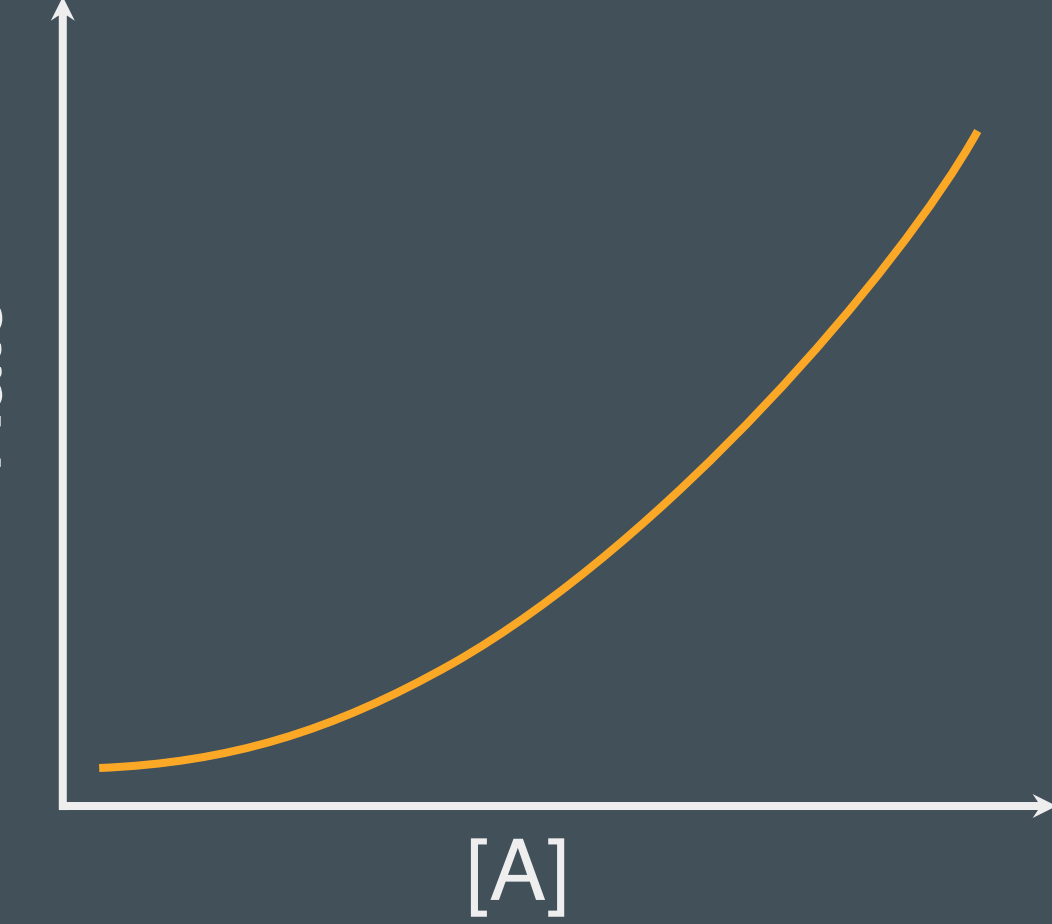
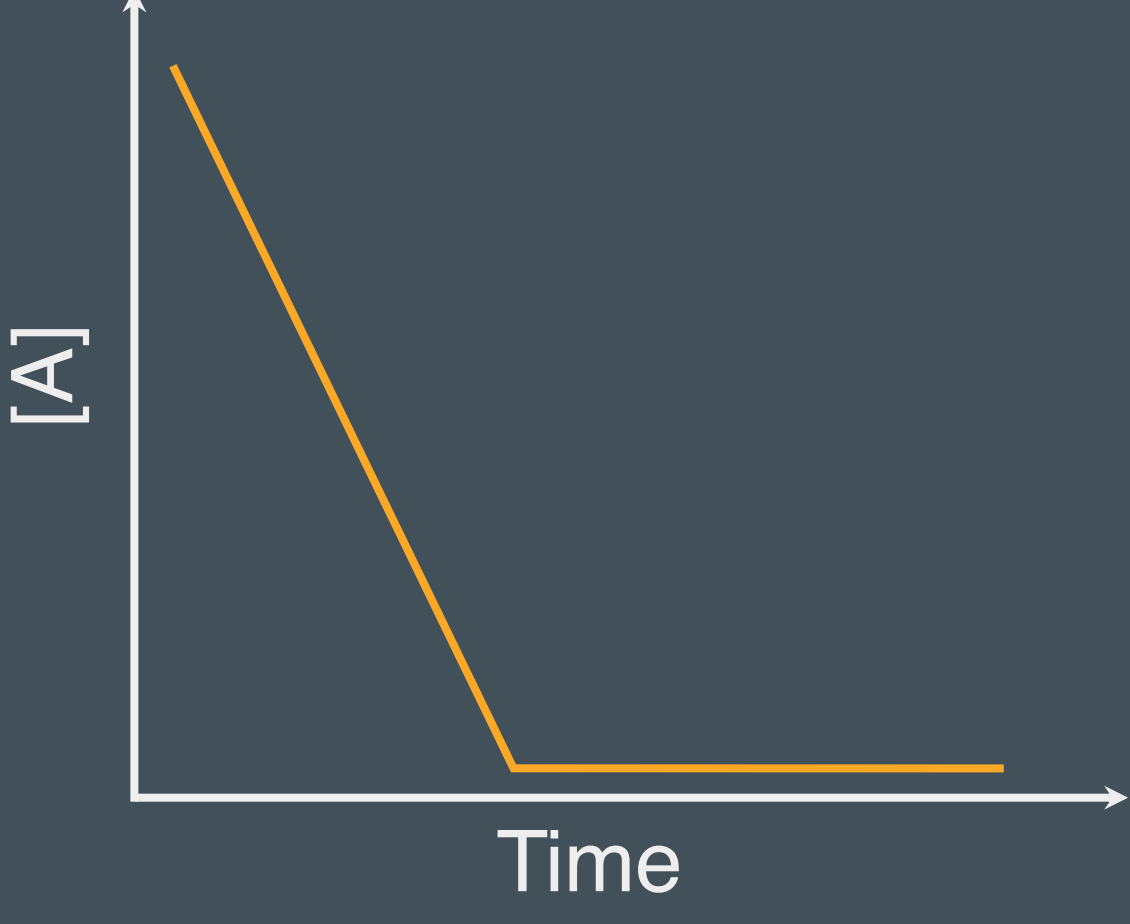
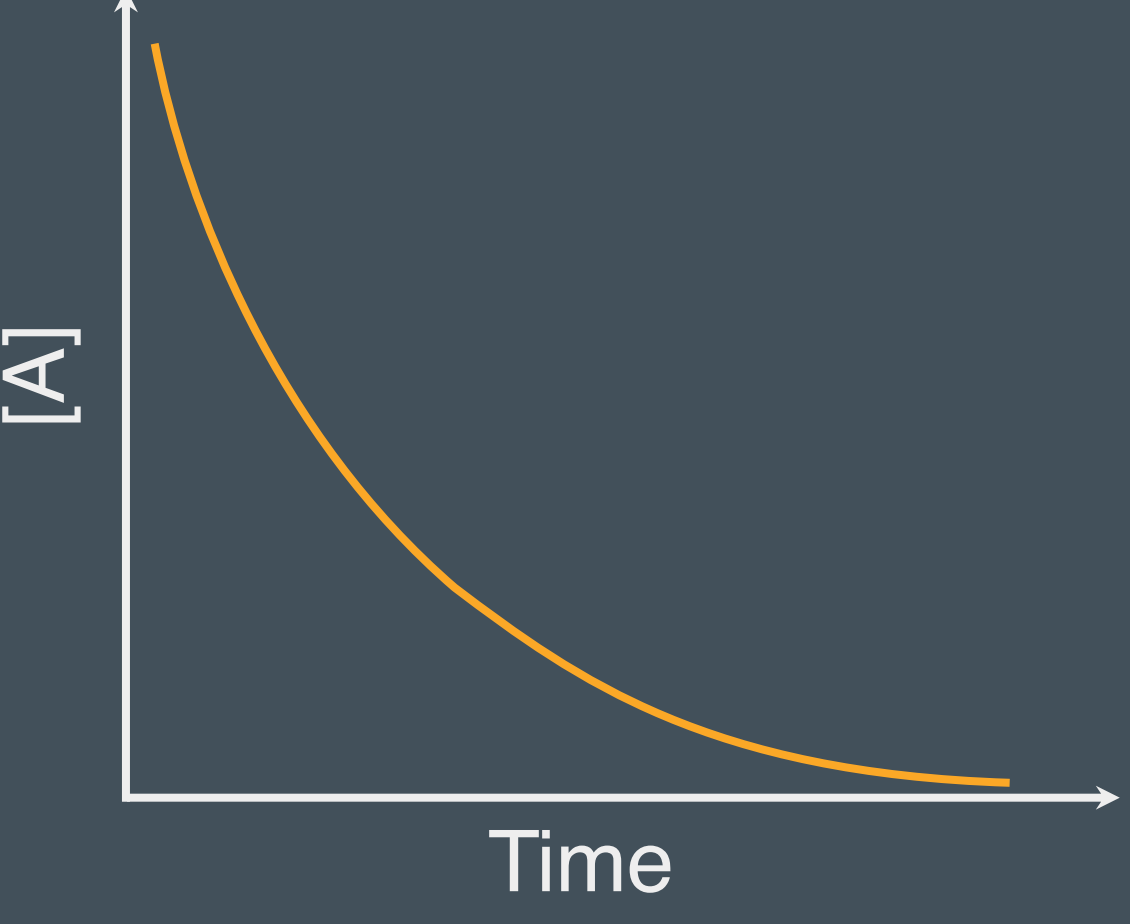
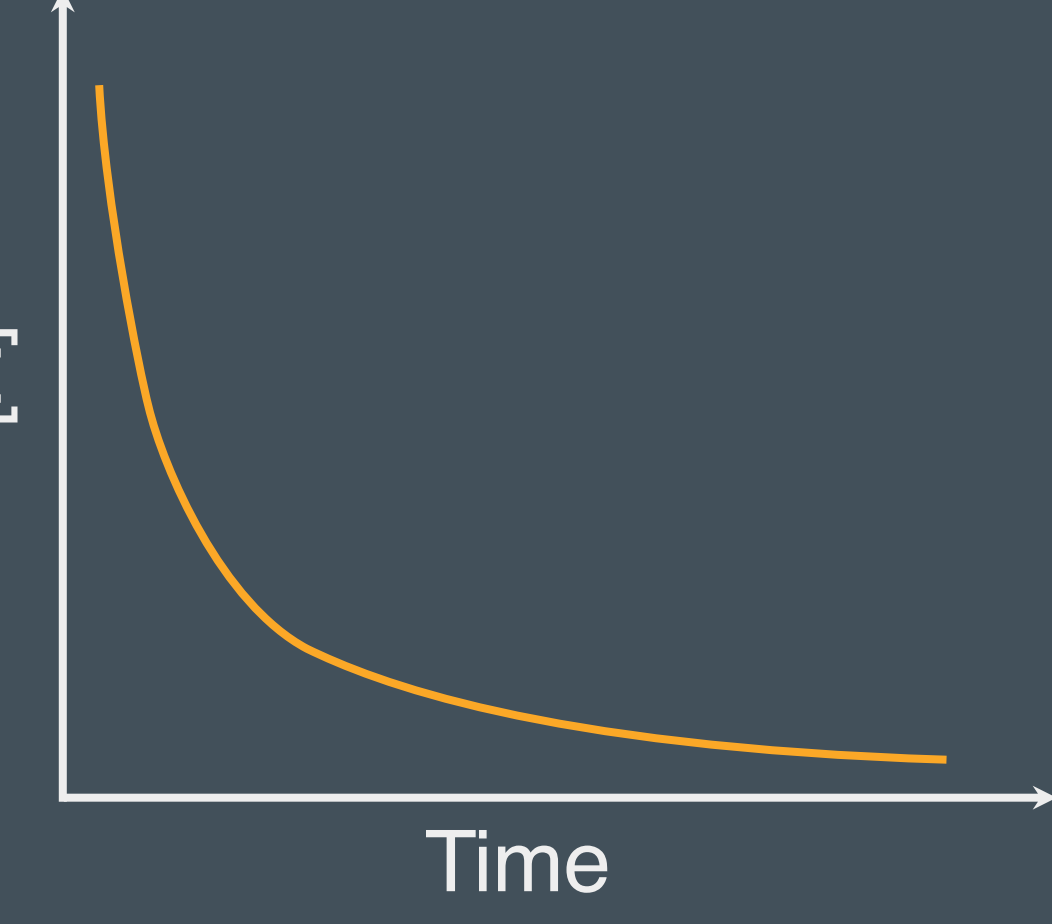
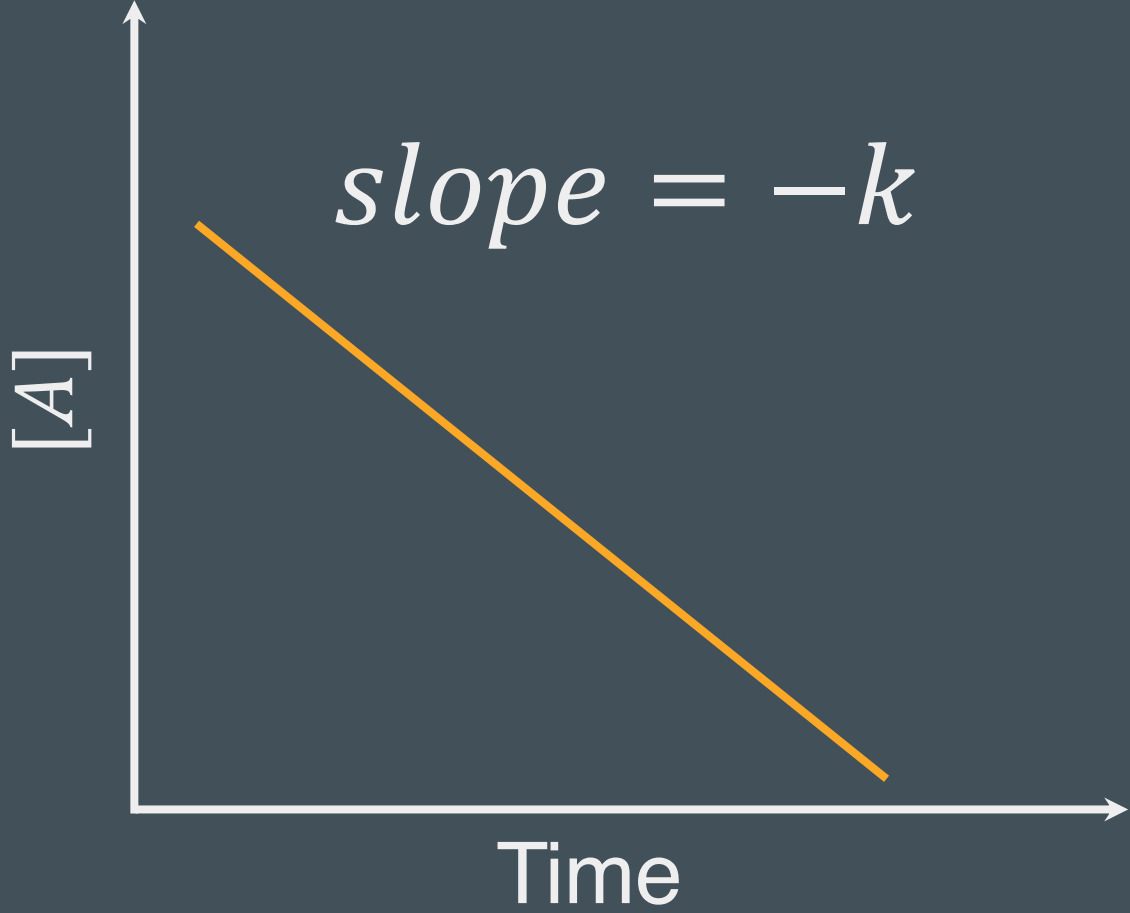
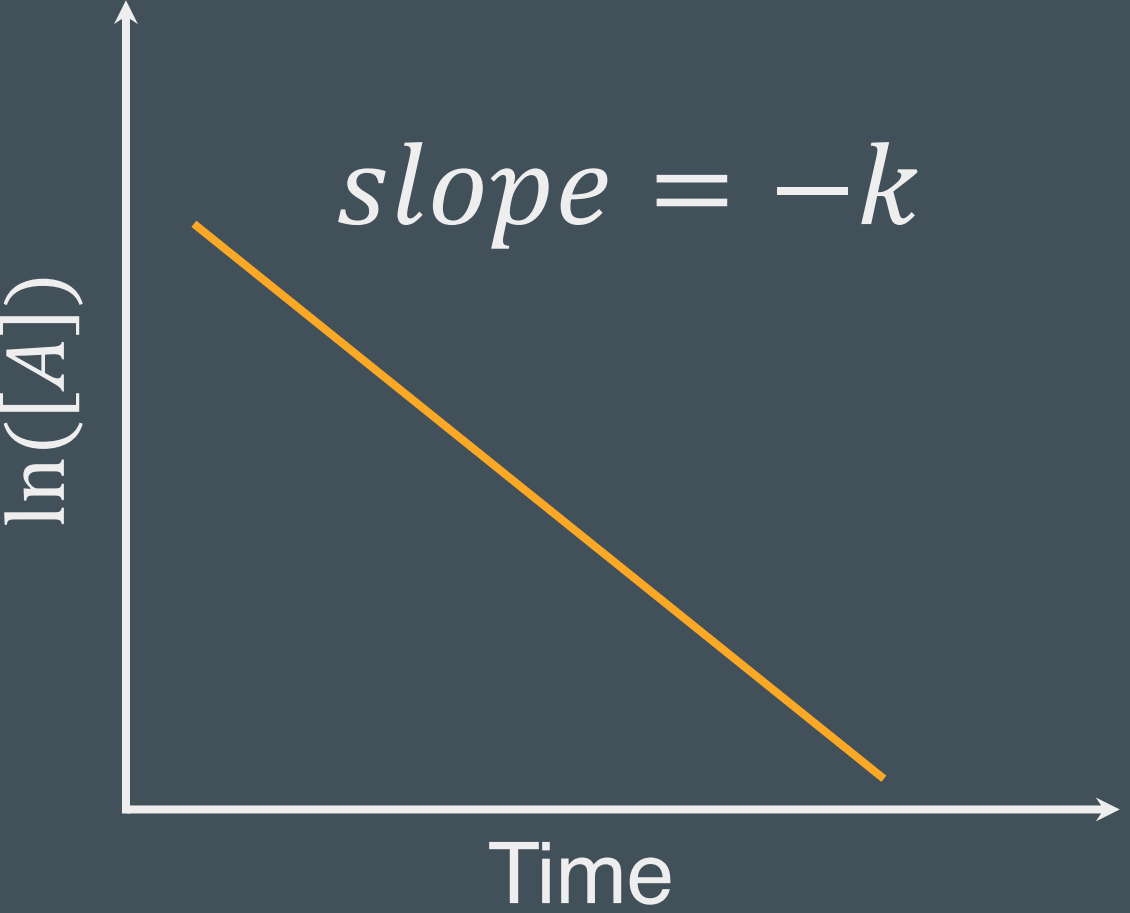
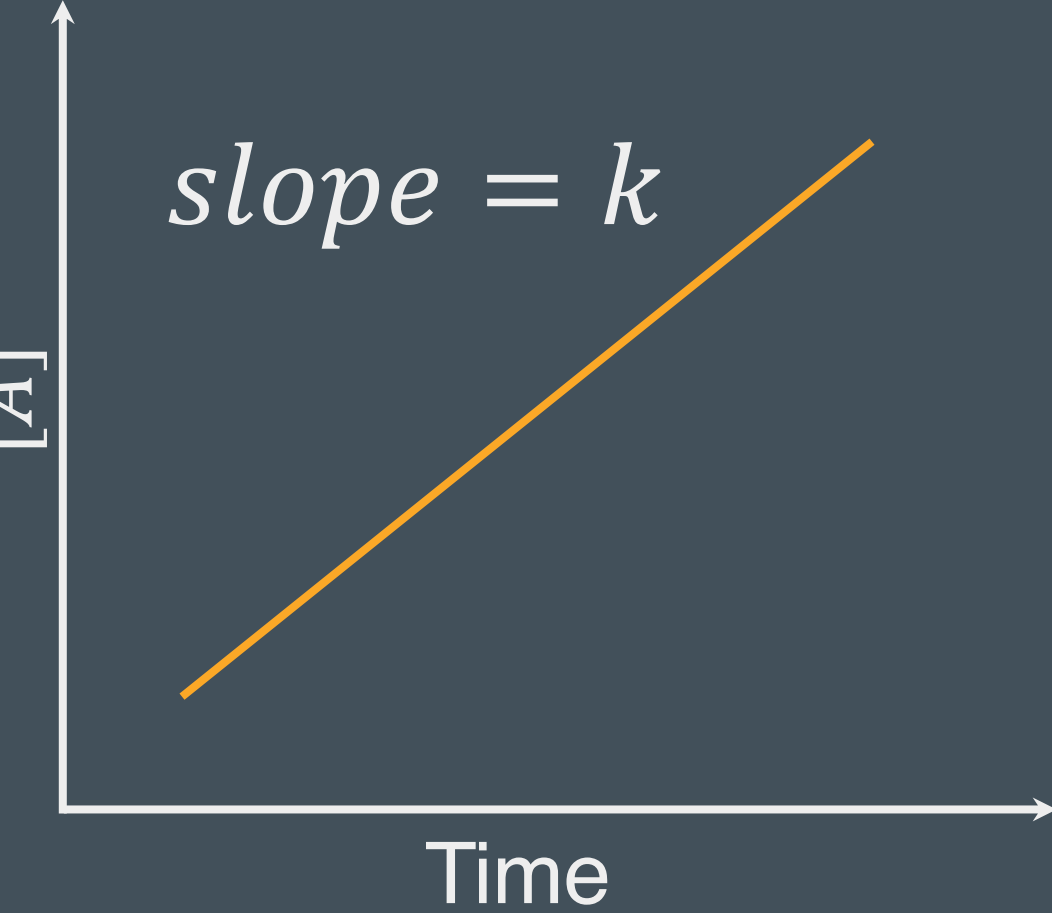


Example – rate law and order

Write the rate law for a zero, first, and second order reaction in which only reactant A appears in the rate law.

Integrating a first order rate law

$$\text{rate} = k[A]^0 = k$$

Order	Zeroth order	First order	Second order
Rate law	$rate = k[A]^0 = k$	$rate = k[A]^1$	$rate = k[A]^2$
Rate vs [A]			
[A] vs time			
Integrated rate law	$[A] = [A]_0 - kt$	$\ln([A]) = \ln([A]_0) - kt$	$\frac{1}{[A]} = \frac{1}{[A]_0} + kt$
Linearized integrated rate law plot			

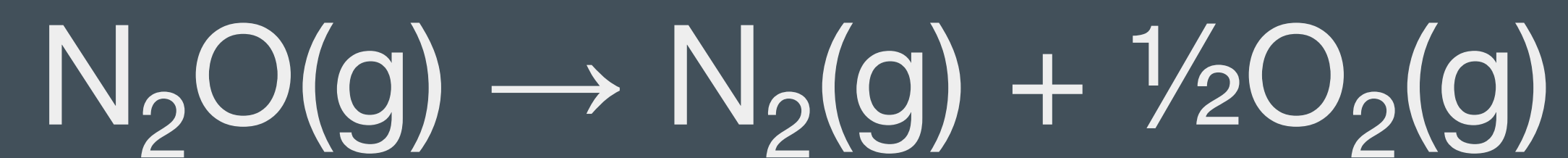
Integrated rate laws – problem solving

- ① If you know $[A]_0$ and k , you can calculate $[A]$ at any time t .
- ② If you know $[A]_0$ and $[A]$ at some time t , you can calculate the rate constant k .
- ③ If you know k and $[A]$ at some time t , you can calculate how much A you started with ($[A]_0$).

Example



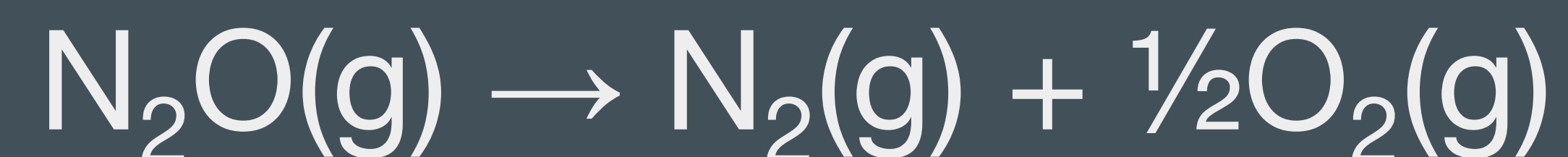
N_2O gas decomposes at $780\text{ }^\circ\text{C}$ following first-order kinetics. The rate law for the decomposition of N_2O is $\text{rate} = k[\text{N}_2\text{O}]$, where $k = 3.4\text{ s}^{-1}$. If the initial concentration of N_2O is 0.20 M , what will the concentration be after 100 ms ?



Example

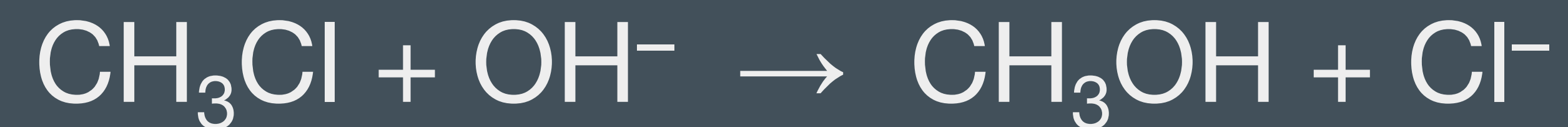


N_2O gas decomposes at 780°C following first-order kinetics. The rate law for the decomposition of N_2O is $\text{rate} = k[\text{N}_2\text{O}]$, where $k = 3.4\text{ s}^{-1}$. If the initial concentration of N_2O is 0.20 M , how long will it take for the N_2O concentration to drop to 1% of its original value?



Pseudo-first order kinetics

Consider the reaction rate of a second order reaction that depends on the concentrations of two different reactants:



$$\text{rate} = k[\text{OH}^-][\text{CH}_3\text{Cl}]$$

Pseudo-first order kinetics

When a reaction is carried out under conditions where one reactant is at a *much* higher concentration than the other, such as $[\text{OH}^-] = 2.0 \text{ M}$ and $[\text{CH}_3\text{Cl}] = 0.05 \text{ M}$, then $[\text{OH}^-]$ is *effectively constant*:

$$\text{rate} = k[\text{OH}^-][\text{CH}_3\text{Cl}] \approx k[2.0][\text{CH}_3\text{Cl}]$$

In these situations, we treat the second-order reaction like a first order reaction.

Recap: rate laws vs. integrated rate laws

Rate laws: Rate laws relate the concentrations of the reactants to the reaction rate at any given moment in time.

$$rate = k[A]^x[B]^y$$

Integrated rate laws: Integrated rate laws allow us to predict how long a reaction will take, or how much of the reactant remains after a certain amount of time.

$$[A] = [A]_0 - kt$$

$$\ln([A]) = \ln([A]_0) - kt$$

$$\frac{1}{[A]} = \frac{1}{[A]_0} + kt$$

Half-life ($t_{1/2}$)

How much time it takes for *one half* of $[A]_0$ to react away.

After 1 half-life $[A] = \frac{1}{2}[A]_0$

After 2 half lives $[A] = \frac{1}{4}[A]_0$

After 3 half-lives $[A] = \frac{1}{8}[A]_0$

The amount of reactant remaining after n half-lives is

$$[A] = \left(\frac{1}{2}\right)^n [A]_0$$

Example



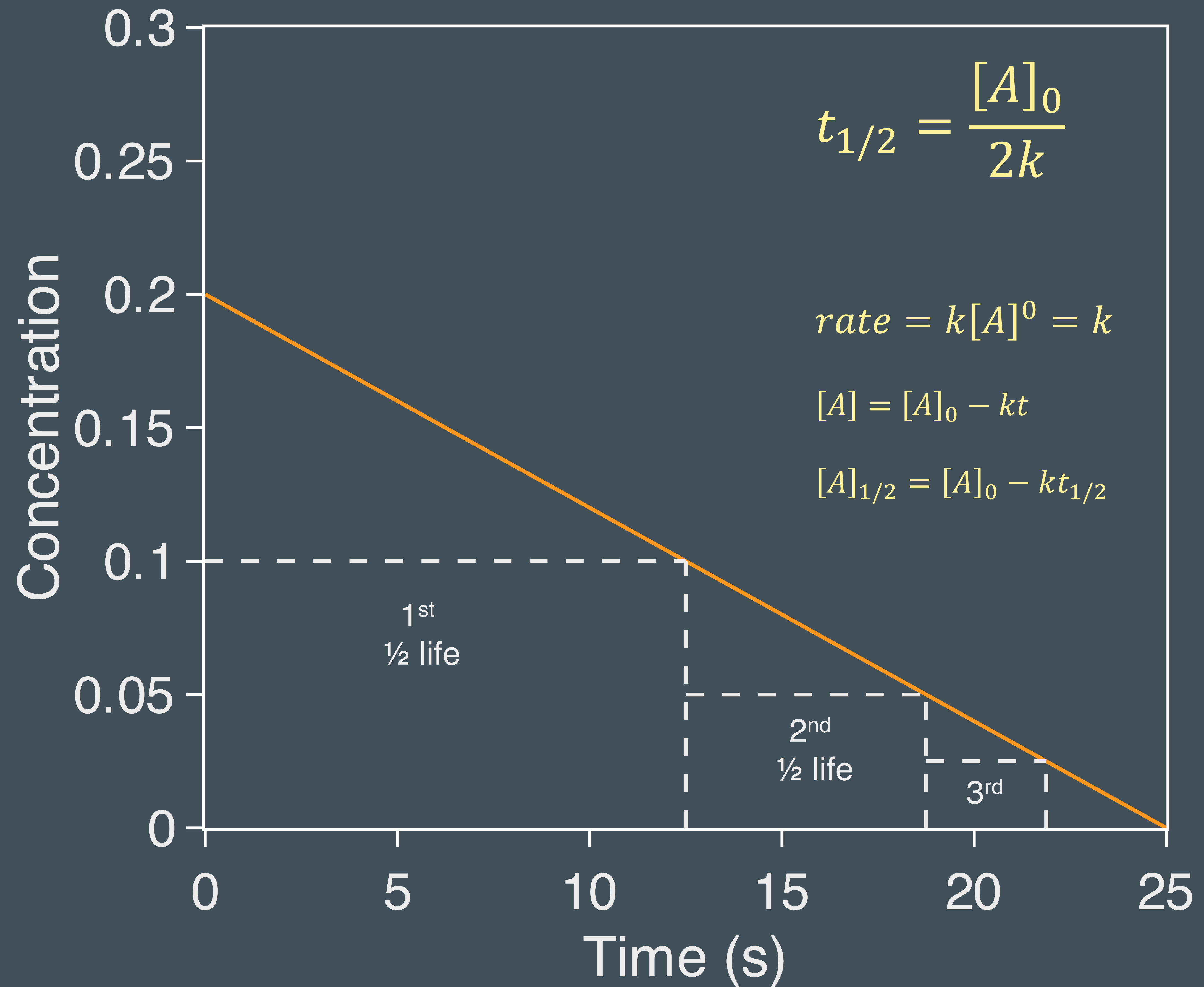
What percentage of a reactant will remain after five half-lives have passed?

Half-life ($t_{1/2}$)

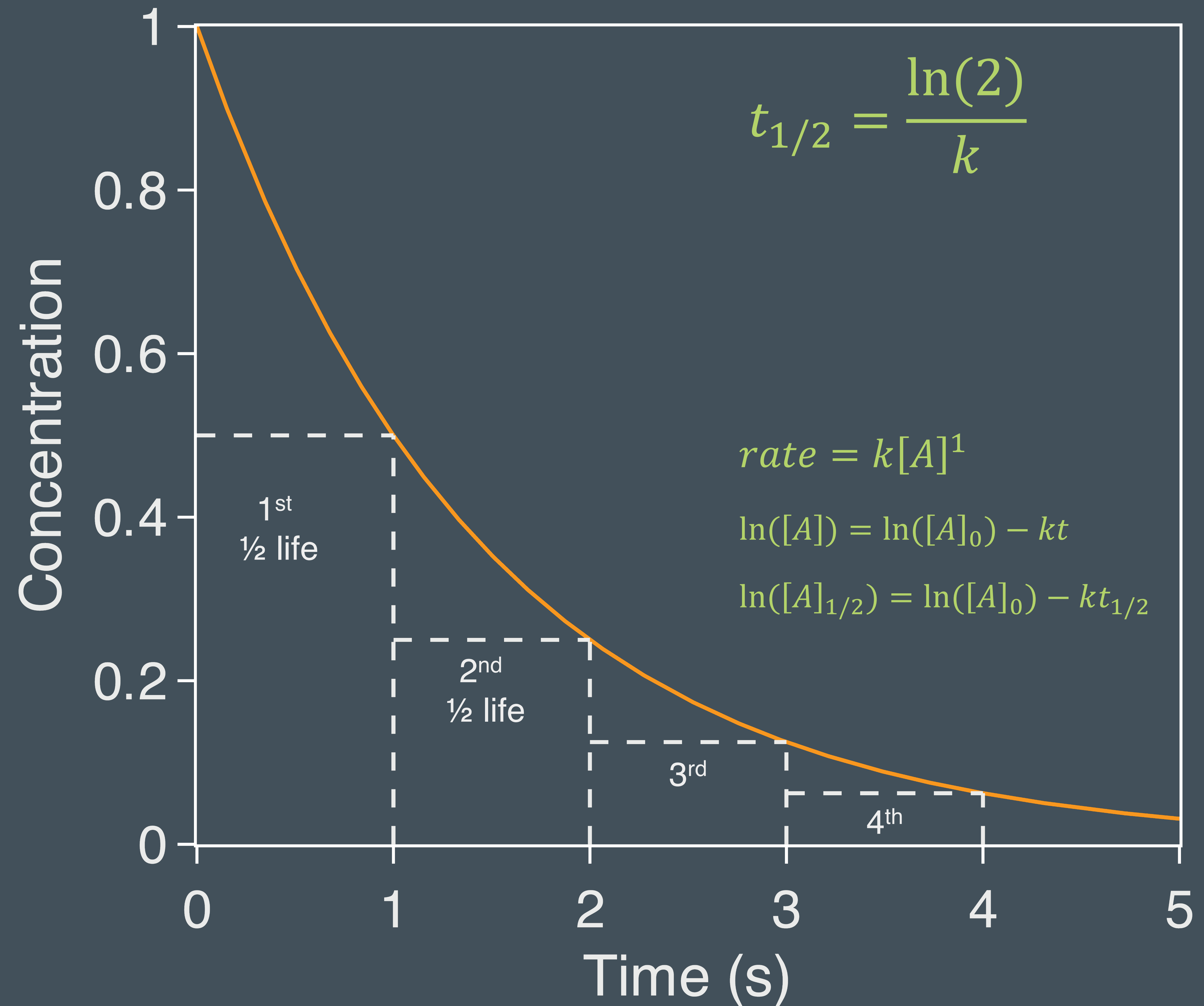
At $t_{1/2}$, $[A] = \frac{1}{2}[A]_0$

We can substitute $\frac{1}{2}[A]_0$ into the integrated rate laws and derive an equation to calculate the half-life for each order of reaction.

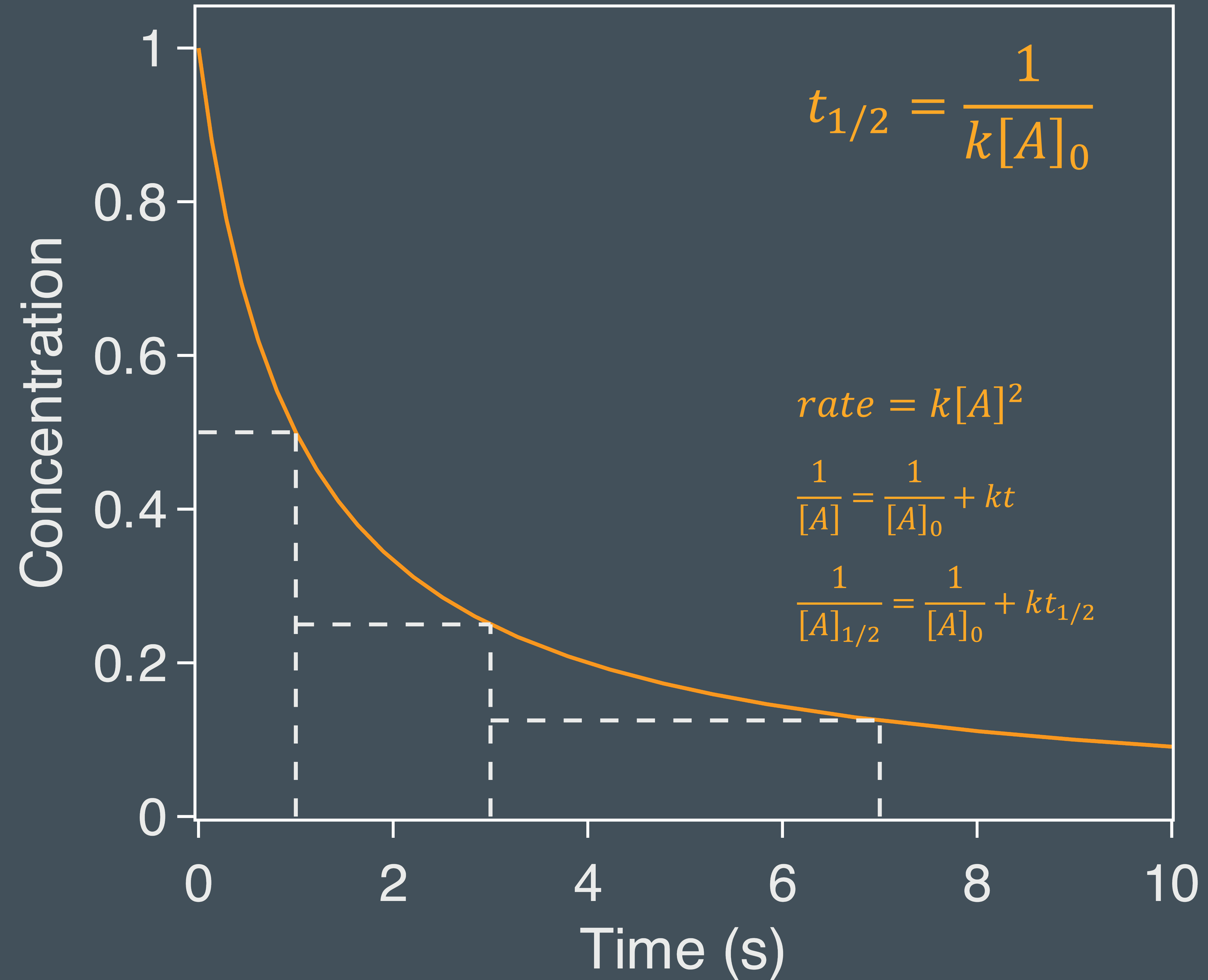
Zero Order Half-lives



First order half-lives



Second order half-lives



Summary: Half-lives

Zero order:

As the concentration decreases, the half-life time **decreases**

First order:

As the concentration decreases, the half-life time **remains constant**

Second order:

As the concentration decreases, the half-life time **increases**

Recap: half-lives

	Zeroth order	First order	Second order
Rate law	$rate = k[A]^0 = k$	$rate = k[A]^1$	$rate = k[A]^2$
Integrated rate law	$[A] = [A]_0 - kt$	$\ln([A]) = \ln([A]_0) - kt$	$\frac{1}{[A]} = \frac{1}{[A]_0} + kt$
First half-life	$[A]_{1/2} = [A]_0 - kt_{1/2}$ $t_{1/2} = \frac{[A]_0}{2k}$	$\ln([A]_{1/2}) = \ln([A]_0) - kt_{1/2}$ $t_{1/2} = \frac{\ln(2)}{k}$	$\frac{1}{[A]_{1/2}} = \frac{1}{[A]_0} + kt_{1/2}$ $t_{1/2} = \frac{1}{k[A]_0}$

Question



Compounds A and B react to form C and D in a reaction that was found to be **second order overall** and **second order in A** . The rate constant k at $30\text{ }^\circ\text{C}$ is $0.622\text{ M}^{-1}\text{ min}^{-1}$. What is the half-life of A when 0.0410 M A is mixed with excess B ?

Second order

$$\text{rate} = k[A]^2$$

$$\frac{1}{[A]} = \frac{1}{[A]_0} + kt$$

$$\frac{1}{[A]_{1/2}} = \frac{1}{[A]_0} + kt_{1/2}$$

$$t_{1/2} = \frac{1}{k[A]_0}$$

Radioactive Half-life

Recall: *Half-life is the time required to use one-half of the reactant*

[A]

When talking about radioactivity, the “concentration” can be expressed as:

- one half of the *mass* ($m = \frac{1}{2}m_0$)
- one half of the *number of atoms* ($N = \frac{1}{2}N_0$)
- the half of the *activity* ($A = \frac{1}{2}A_0$). The activity refers to the decay rate (e.g. counts per second or disintegration per second)

Radioactive Half-lives

Radioactive half-lives are *constant* and do not depend on how much material is present

A longer half-life indicates a more stable isotope

Radioisotope	Half-life
Uranium-238	4.5×10^9 years
Potassium-40	1.3×10^9 years
Plutonium-239	24,110 years
Carbon-14	5730 years
Cesium-137	30.2 years
Strontium-90	28.8 years
Cobalt-57	270 days
Radon-222	3.82 days
Iodine-131	8.04 days
Plutonium-231	8.5 minutes
Polonium-214	0.00016 seconds

Next time

- Measuring the Rate of Nuclear Decay
- Uses of Radioisotopes
- Types of Radioactivity
- Multistep Reactions