Unit 2 – Day 1

Kinetics

Rates of Chemical Reactions

Lecture Topics

Measuring Rates

- Concentration
- Reactions Rates
- Spectroscopy

Average, unique average, and instantaneous rates

- Instantaneous Rate of Reaction

Rate Laws

- Reaction Order
- Rate Laws
- Rate Constant

Thermodynamics vs. Kinetics

Thermodynamics tells us if a reaction is energetically favorable (spontaneous).

Thermodynamics cannot tell us how fast or slow that reaction will occur.

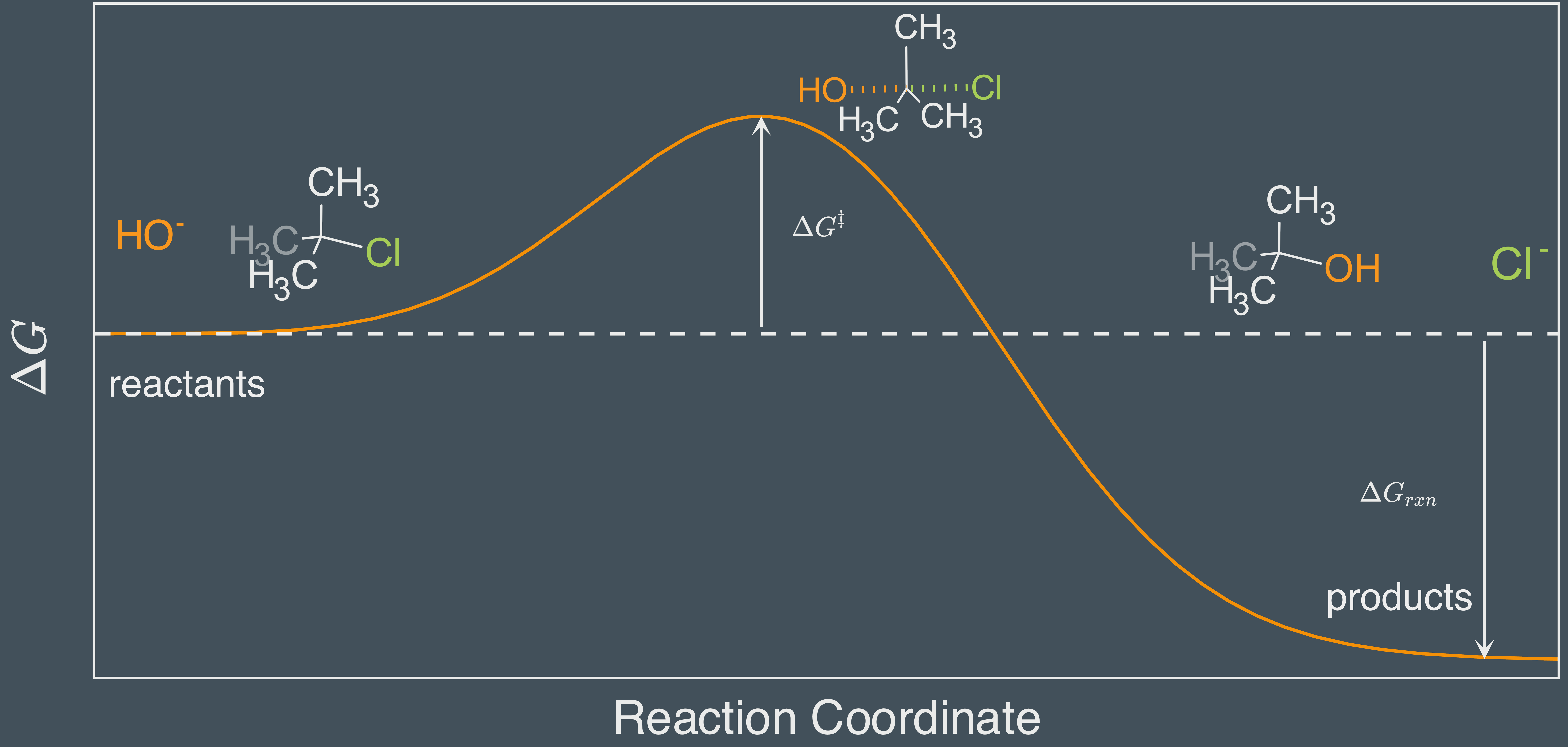
Kinetics

We use *Kinetics* to determine how quickly chemical reactions will occur and how long you have to wait form your reaction to complete.

Measuring the rates of reactions (macroscopic) gives us insight into what is happening on a molecular scale as the reaction occurs (microscopic).

Kinetic theory of atomistic reactions

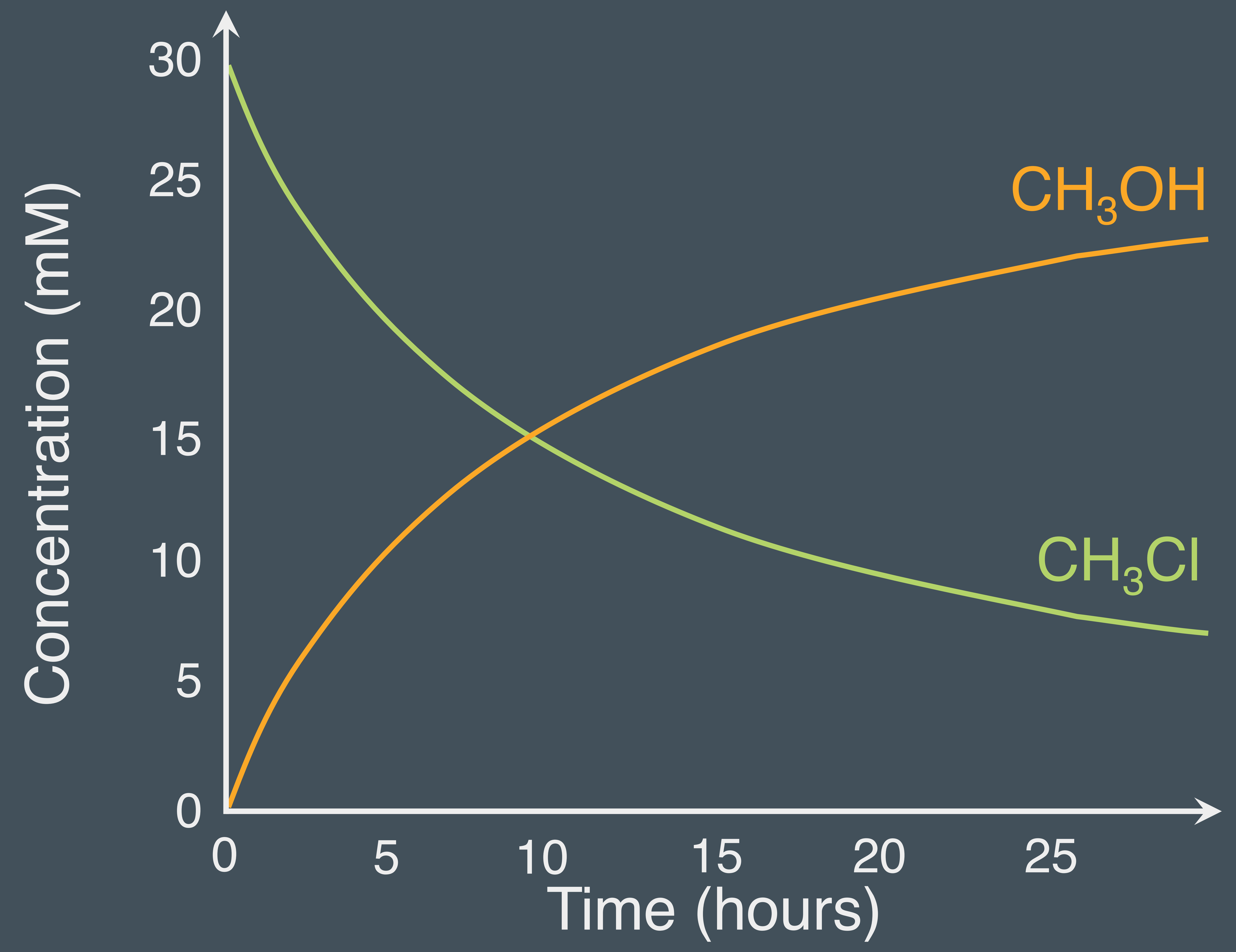
$$CH_3Cl + OH^- \rightarrow CH_3OH + Cl^-$$



Example

This graph shows the reactant and product concentrations changing with time for the reaction:

$CH_3Cl + OH^- \rightarrow CH_3OH + Cl^-$



1. How would you determine the rate of the reaction from this graph?
2. Where is the reaction rate the fastest?

Reaction Rate

$$CH_3Cl + OH^- \rightarrow CH_3OH + Cl^-$$

$$rate = -\frac{\Delta[CH_3Cl]}{\Delta t} = \frac{\Delta[CH_3OH]}{\Delta t}$$

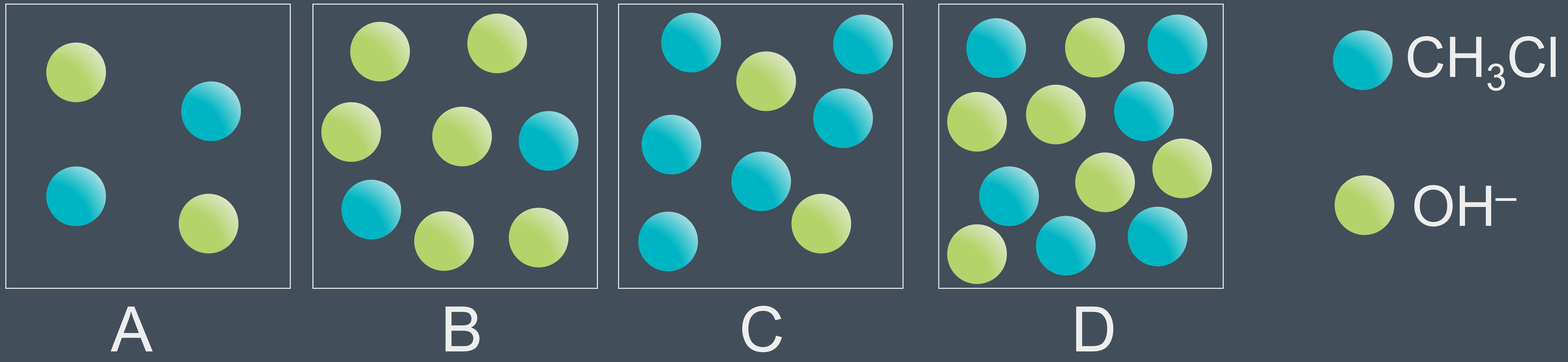
Macroscopic

(measured in the lab)

Concentration and Reaction Rate

For this reaction to occur, let's assume that there must be a collision between a methyl chloride molecule and a hydroxide ion. These images represent four different solutions containing CH_3Cl and OH^-.

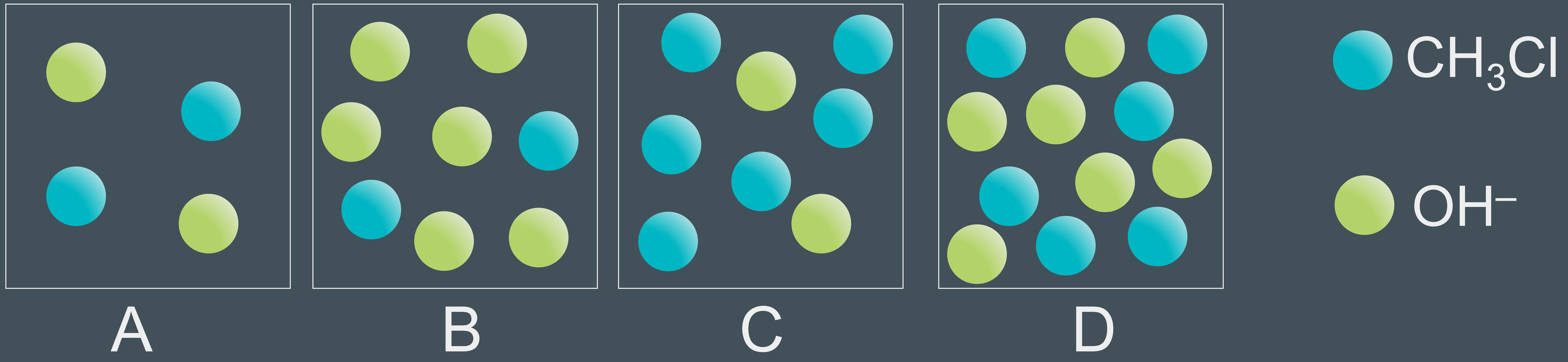
$$CH_3Cl + OH^- \rightarrow CH_3OH + Cl^-$$



Example

If the rate of the reaction depends on a collision occurring between CH_3Cl and OH^-, which solution would have the initial highest reaction rate?

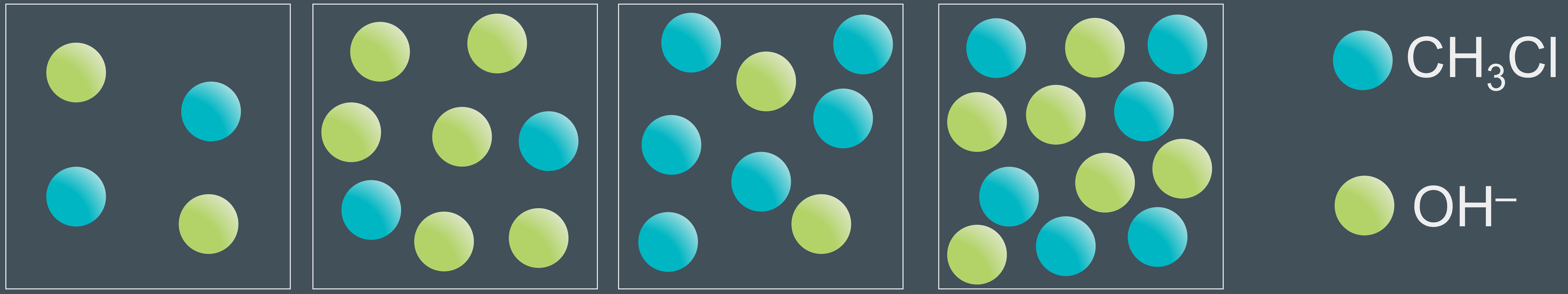
$$CH_3Cl + OH^- \rightarrow CH_3OH + Cl^-$$



Example

How much faster would the initial reaction rate be in solution B compared to solution A?

$$CH_3Cl + OH^- \rightarrow CH_3OH + Cl^-$$

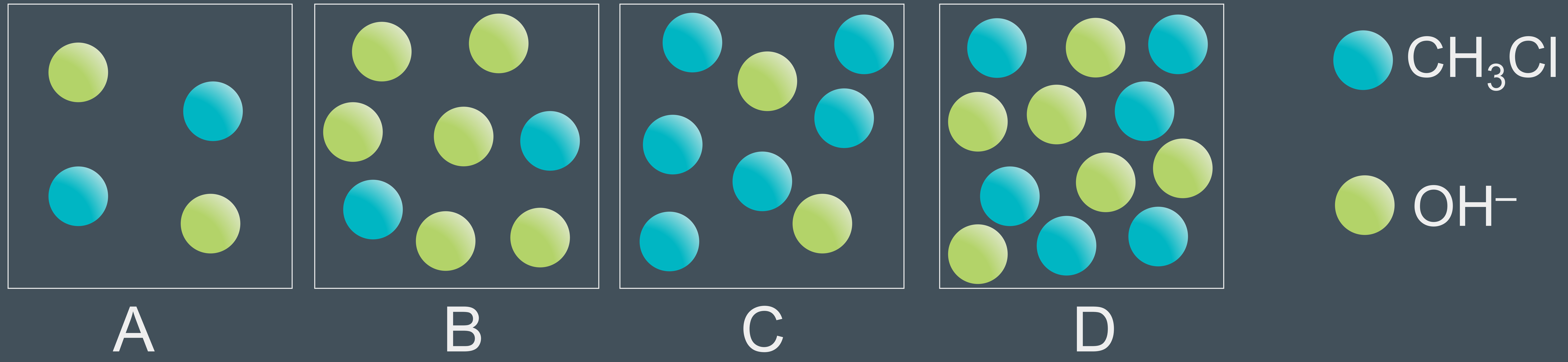


A B C D

Example

How much faster would the initial reaction rate be in solution D compared to solution A?

$$CH_3Cl + OH^- \rightarrow CH_3OH + Cl^-$$



Definitions

Reaction Rate: the change in concentration of one of the reactants or products at a selected stage of the reaction divided by the time interval over which the change takes place

- Instantaneous: the reaction rate at a specific moment in time
- Average: the reaction rate over a defined time interval
- Unique average reaction rate: a single unique average rate of reaction that is uniform across all reactants and products

In the lab

Two main factors when running kinetics experiments:

1. The reaction must be started at a precise time
2. The reaction must be monitored at precise instants after the reaction has been initiated

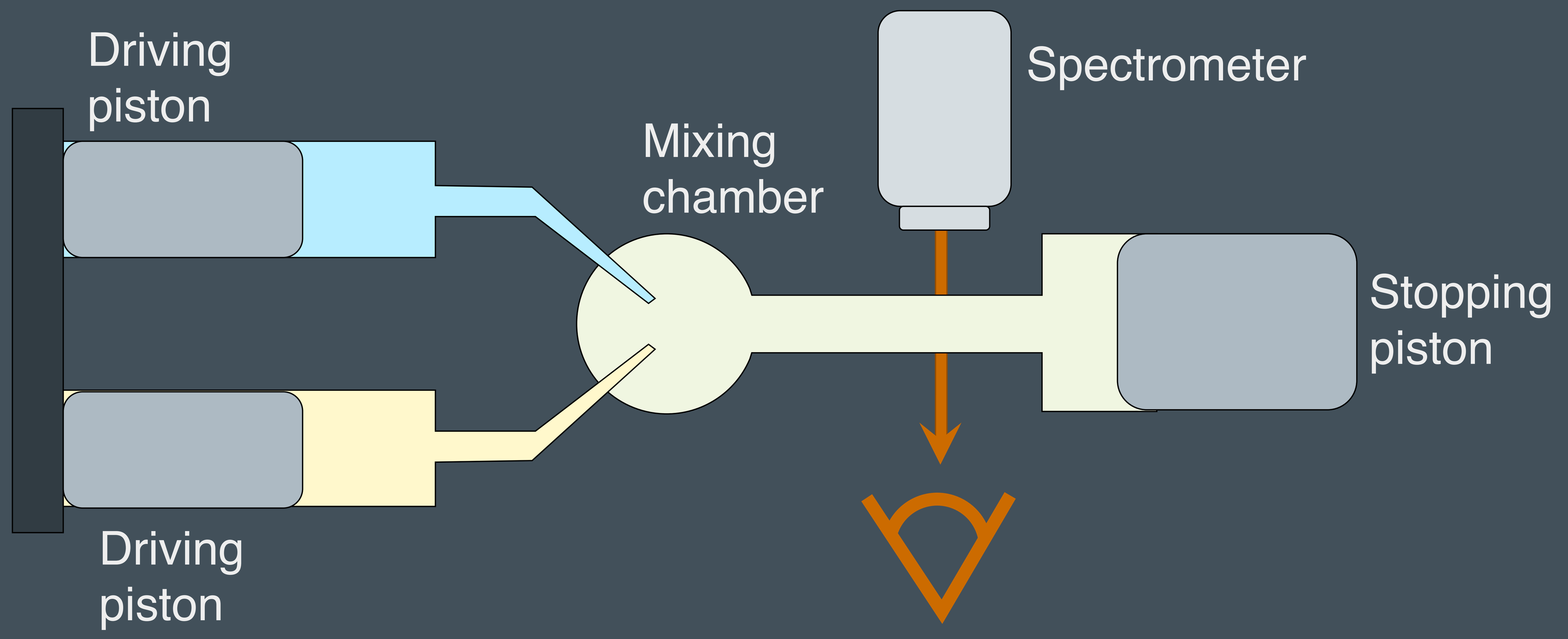
If the reaction is slow, this can be done manually.

Stopped-Flow technique

Solutions of the reactants are forced into a mixing chamber very rapidly, and the formation of products or loss of reactants is monitored.

Examples:

- protein folding
- enzyme reactions



Spectrometer

We often use spectrometers to determine concentrations by measuring the absorption of light by compounds in a sample

Many modern spectrometers have lasers that can initiate certain types of reactions

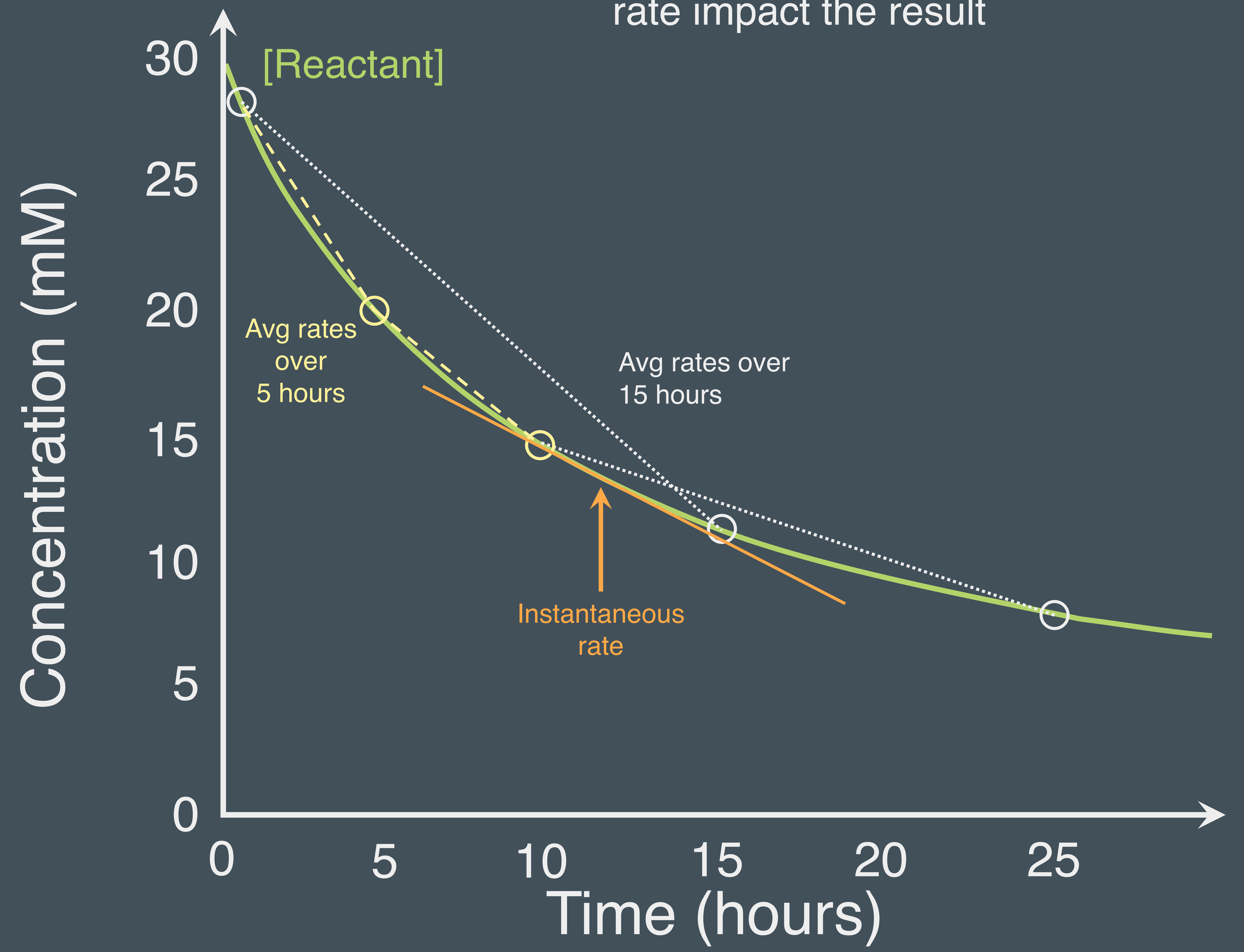
- Current detection limits: reactions that are complete in 1 picosecond (1 ps = 10^{-12} s)
- The newest technique can study reactions in a few femtoseconds (1 fs = 10^{-15} s)

Instantaneous rate of reaction

Arguably, the instantaneous rate of reaction is more useful than the overall rate of change

The instantaneous rate is the slope of the tangent to the curve at the time of interest

Start time and time range used to measure average rate impact the result



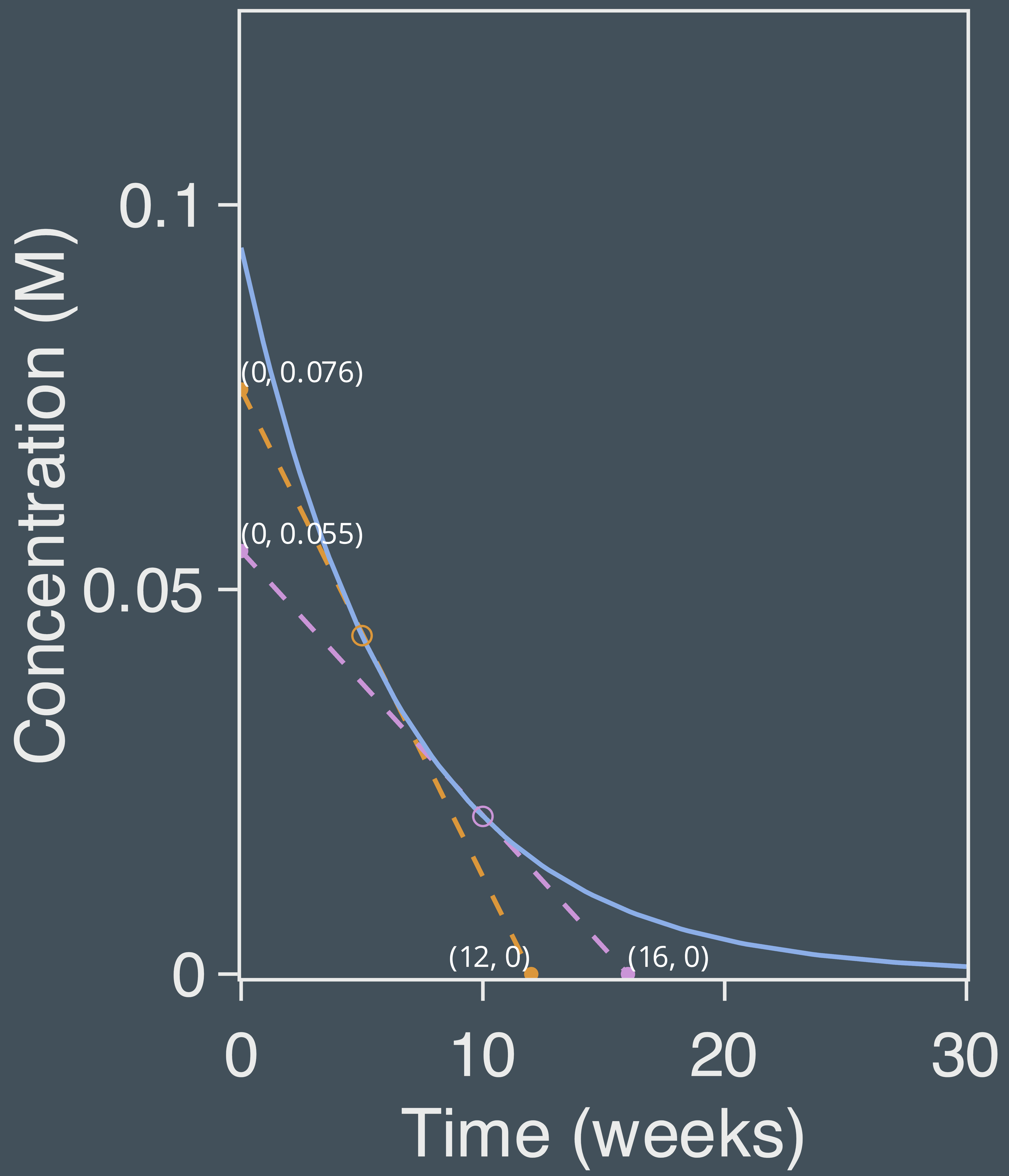
Instantaneous rates allow us to define a reaction rate consistently for a point in time

Example

Most instantaneous rates of reactants and products decrease as the reaction proceeds

The instantaneous rate of deterioration of penicillin during storage changes over time

- After 5 weeks: 0.0063 M/week
- After 10 weeks: 0.0034 M/week



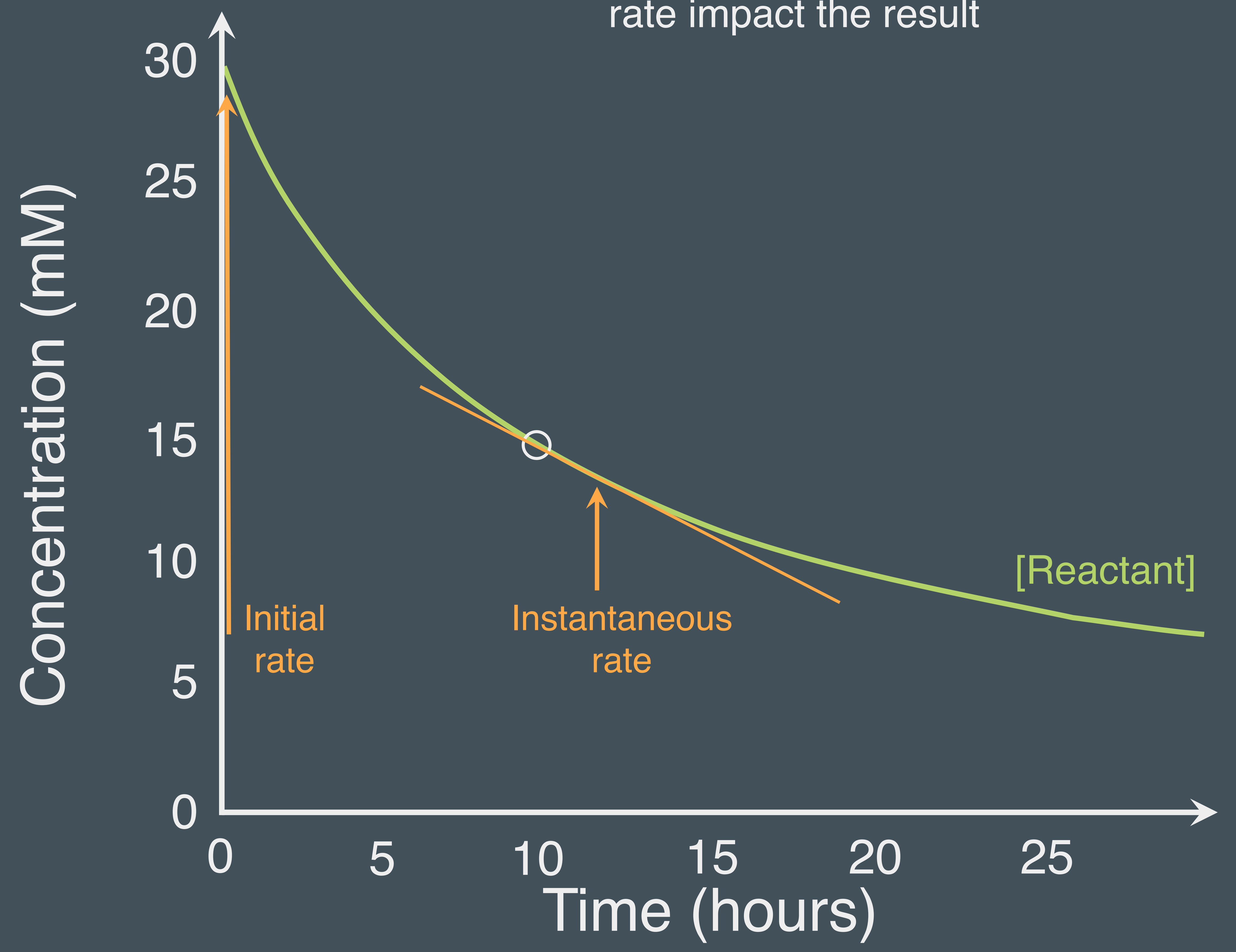
Initial rate of reaction

The instantaneous rate of reaction at the start of the reaction is called the <u>initial rate of reaction</u>

We can look at initial rates to determine patterns in reaction rate data

The initial rate always has the unit: concentration/time

Start time and time range used to measure average rate impact the result



Experiments in lab

$CH_3Cl + OH^- \rightarrow CH_3OH + Cl^-$

We can determine the **rate of the reaction** after we collect initial concentration vs time data in lab.

$$rate = -\frac{\Delta[CH_3Cl]}{\Delta t} = \frac{\Delta[CH_3OH]}{\Delta t}$$

Macroscopic
(measured in the lab)

If done properly, we can learn how quickly the reactants are being used up, or how quickly the products are being formed.

Experiment 1: measure a concentration and the time the measurement took place

Experiment 2: measure a rate directly and record the time the rate was measured.

Convert rate of reaction to rate law

$CH_3Cl + OH^- \rightarrow CH_3OH + Cl^-$

The rate of the reaction depends on the concentrations of the species in the reaction. This expression is known as the **rate law**.

Macroscopic $\Rightarrow$

$$\text{rate} = k[CH_3Cl][OH^-]$$

k is called the rate constant

Microscopic
(how the reaction occurs at molecular level)

Empirical Rate Law

For a generic reaction $A + B \rightarrow C + D$

$$\text{rate} = k[A]^{x}[B]^{y}$$

What are x and y?

Reaction order

Some reaction rates depend on the concentrations of the reactants, while other reactions' rates do not. The **reaction order** is the degree to which the reaction rate depends on the concentrations.

$$\text{rate} = k[A]^x[B]^y$$

Order of each species

Overall reaction order

Rate constant

The rate constant, k, is unique to each rate law. The units on k depend on the overall order of the reaction.

Remember: The initial rate always has units of concentration/time.

$$\text{rate} = k[A]^x[B]^y$$

Example

The empirical rate law for the following reaction is rate = $k[CO][H_2O]$.

$$CO + H_2O \rightarrow CO_2 + H_2$$

1. What is the order with respect to each reactant?

2. What is the overall order of reaction?

3. What are the units for the rate constant?

The rate law

$CH_3Cl + OH^- \rightarrow CH_3OH + Cl^-$

In a previous slide, we wrote the below rate law for the reaction between CH_3Cl and OH^-.

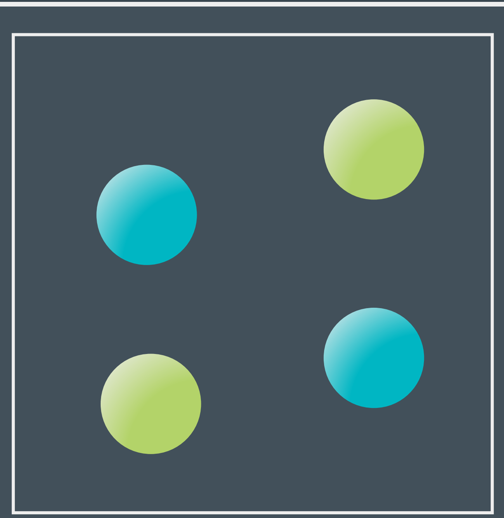
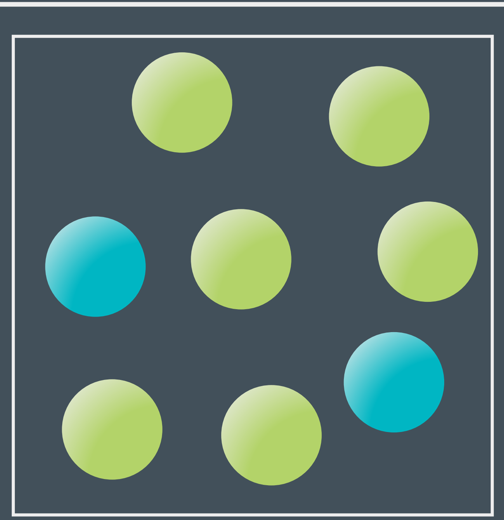
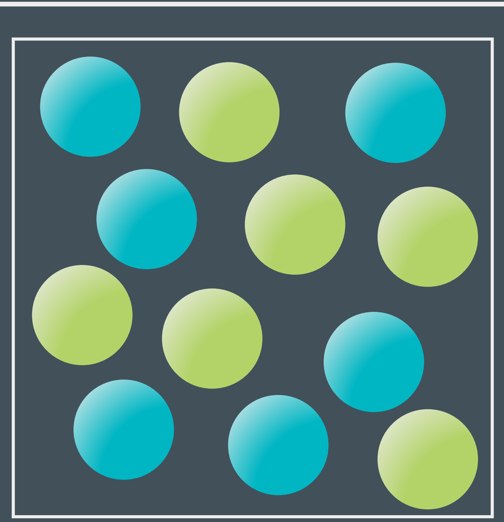
$$\text{rate} = k[CH_3Cl][OH^-]$$

For this to be true, the rate must be directly proportional to the concentrations of each reactant.

Let's see if the empirical data supports that assumption.

Example: Determine the rate law

$CH_3Cl + OH^- \rightarrow CH_3OH + Cl^-$ ● CH_3Cl ● OH^-

Experiment	Initial $[CH_3Cl]$	Initial $[OH^-]$	Initial Rate M/min
1 	0.1 M	0.1 M	5.0×10^{-6}
2 	0.1 M	0.3 M	1.5×10^{-5}
3 	0.3 M	0.1 M	1.5×10^{-5}
4 	0.3 M	0.3 M	4.5×10^{-5}

Example: Determine the rate law (solution)

Poll: Determine the rate law

Determine the rate law for $A + 2B \rightarrow C$

Experiment	[A]	[B]	Initial Rate [$M\ s^{-1}$]
1	0.1 M	0.1 M	2.73
2	0.15 M	0.1 M	6.14
3	0.1 M	0.2 M	2.74

Poll: Determine the rate law (solution)

Next Time

- First Order Integrated Rate Laws
- Half-Lives of First-Order Reactions
- Second Order Integrated Rate Laws