CHEM 102

Jussi Eloranta
Jussi.Eloranta@csun.edu
Course web page:
http://aa6kj.hopto.org/eloranta_lab/CHEM102/

Chapter 15: Chemical Kinetics I

Math Review

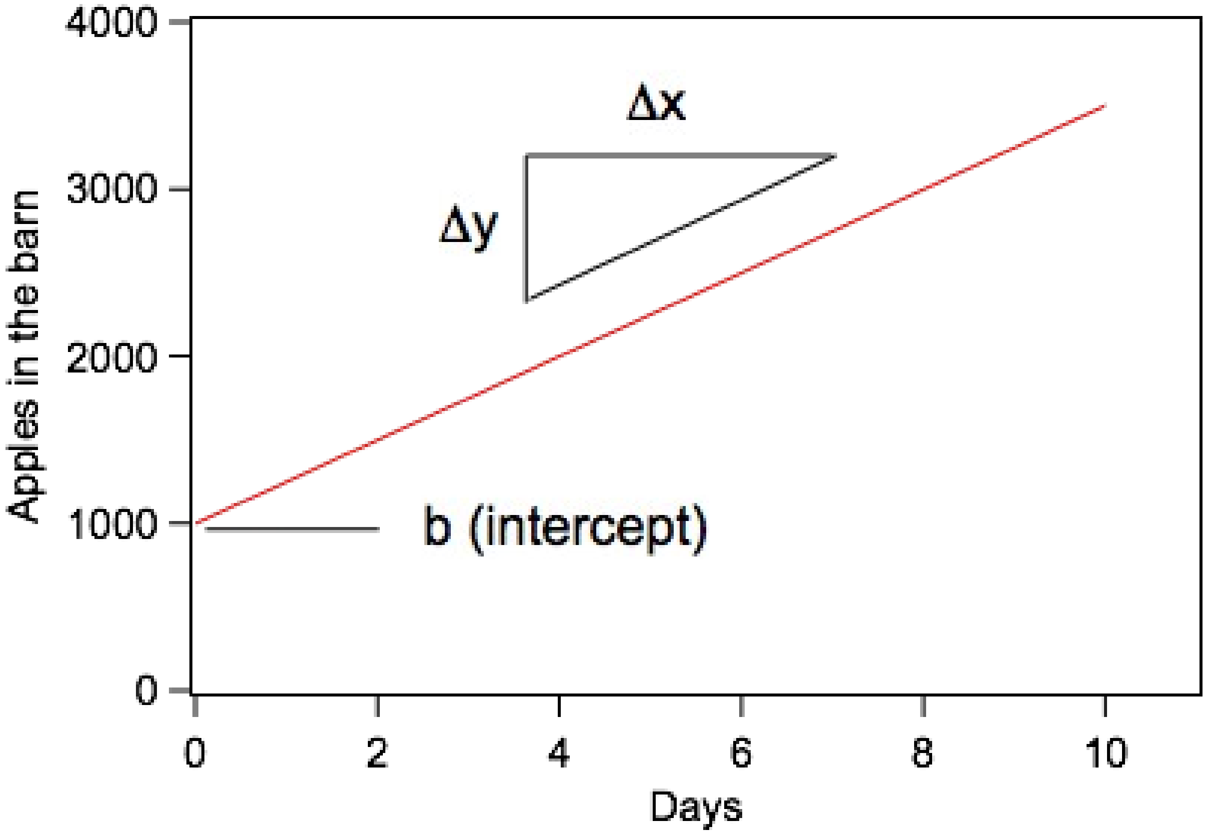
Equation of a line:

- Say you pick apples from your orchard, starting with 1000 apples in the barn and you pick 250 additional apples per day

$$y = mx + b$$

$$m = \frac{\Delta y}{\Delta x}$$

$$b = y \ at \ x = 0$$

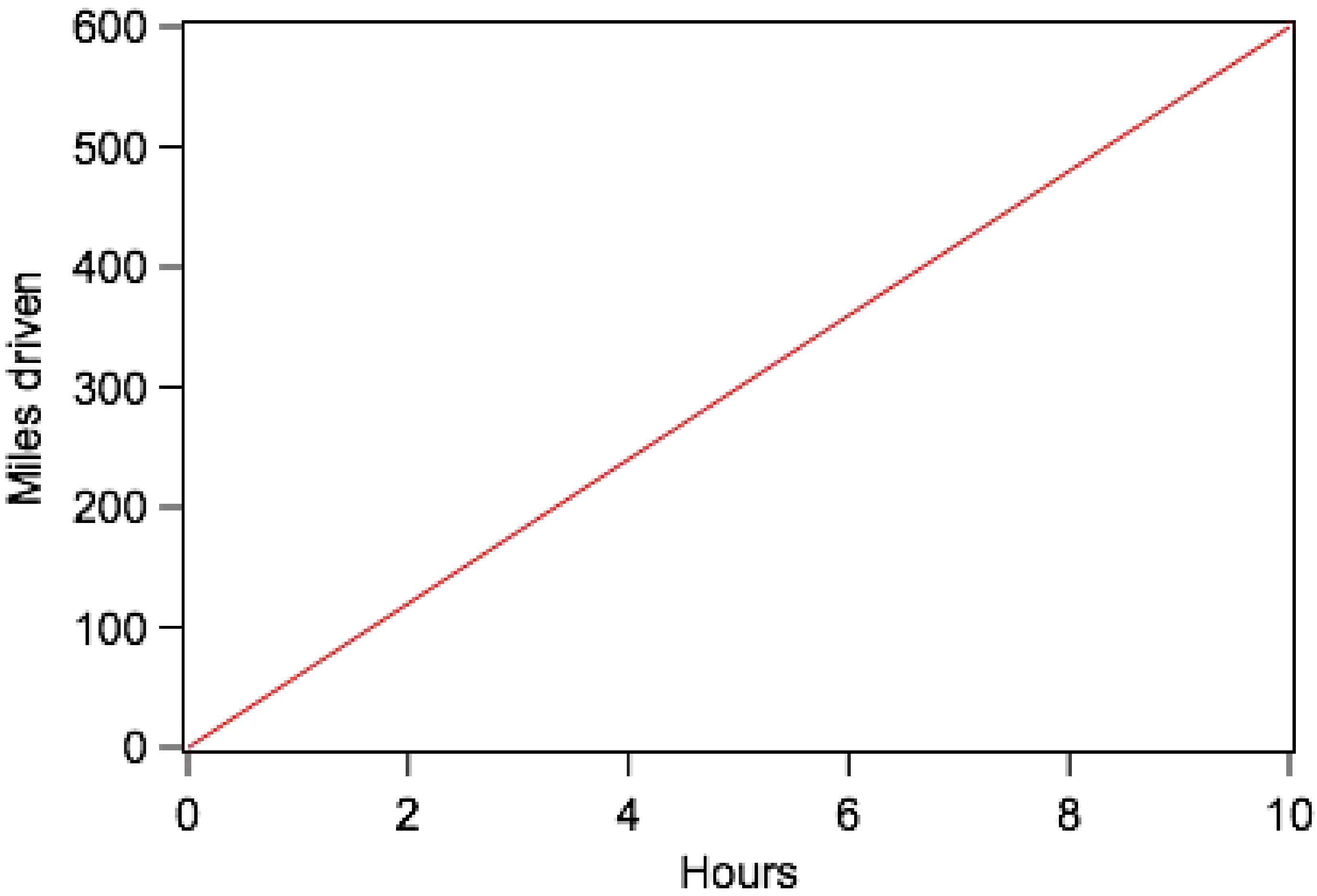


“Rise over run”

Math Review

Slope is a **rate of change**:

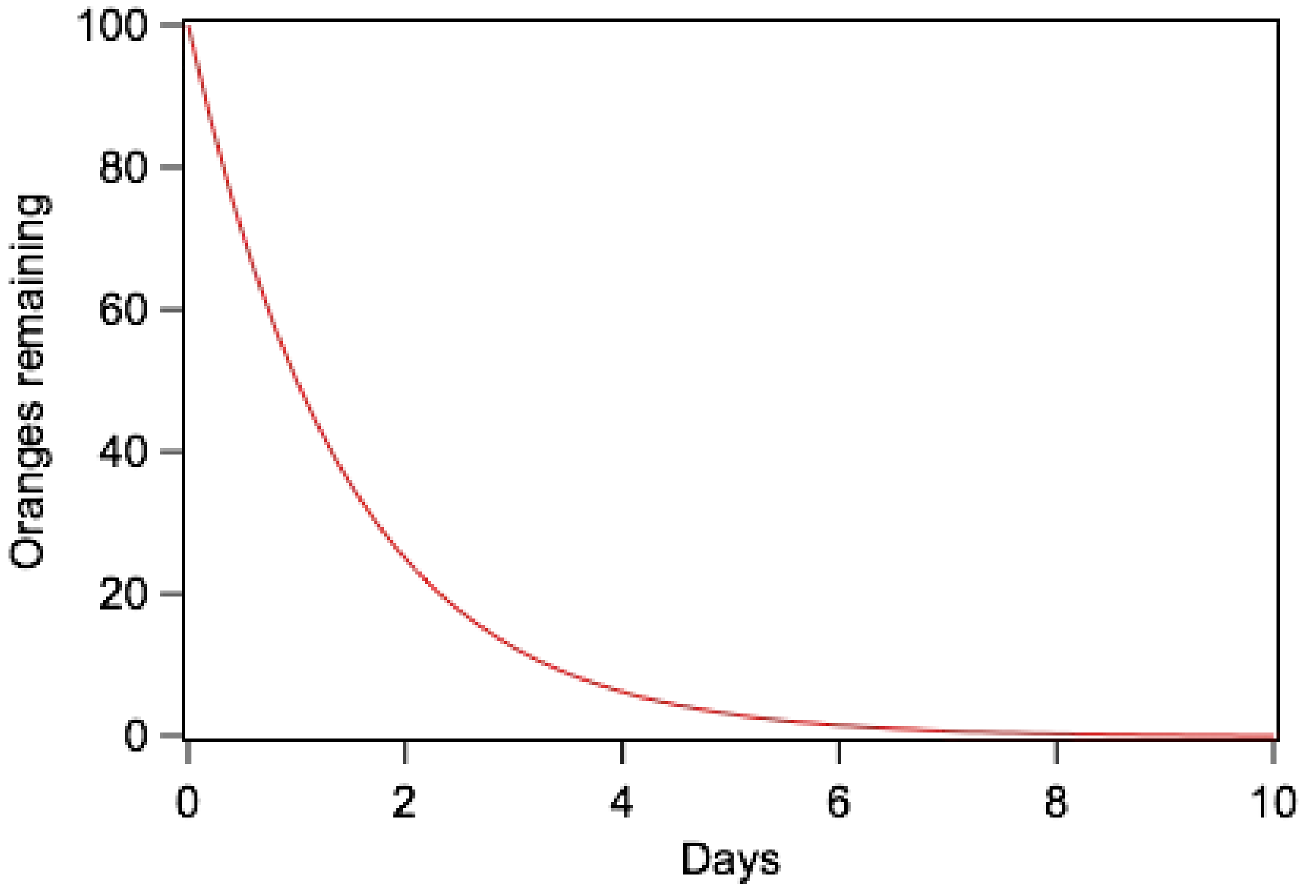
- Say you drive 60 miles per hour for 10 hours at constant speed then the plot of distance vs. time is:



Math Review

Slope of a curve:

- Now say you start with 100 oranges, but you eat half of them every day. 100 to 50 to 25 to 12.5, etc. for 10 days. 0.098 remain after 10 days.

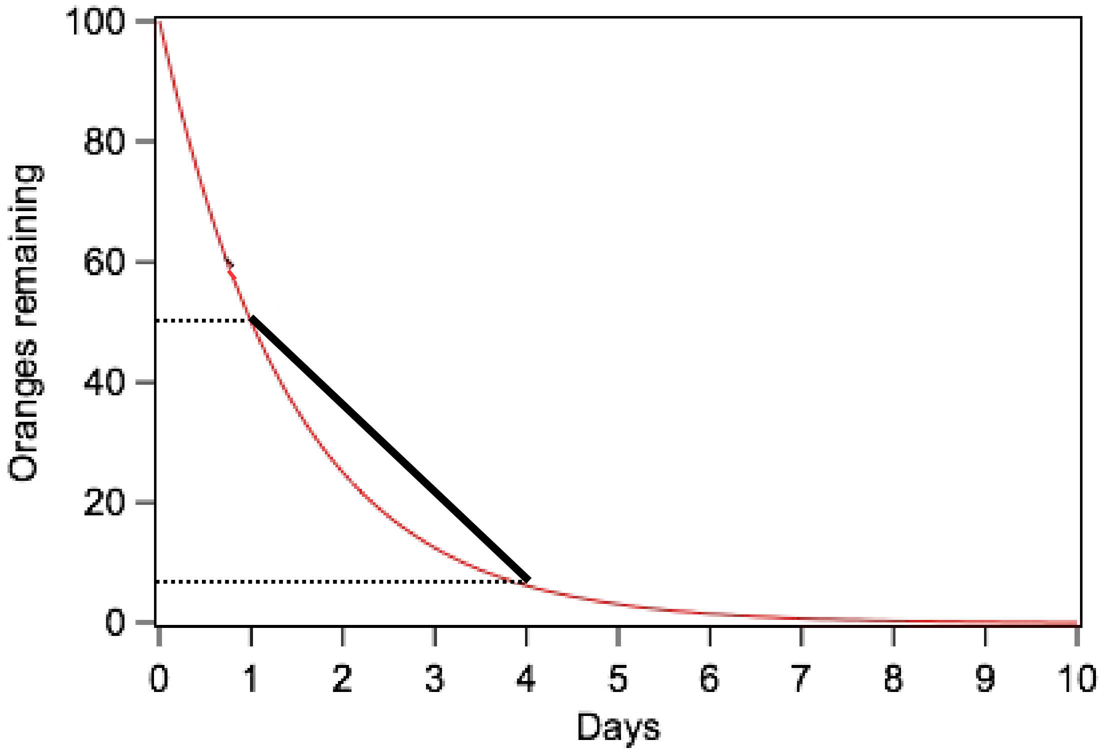


Math Review

Slope of a curve:

- Now say you start with 100 oranges, but you eat half of them every day. 100 to 50 to 25 to 12.5, etc. for 10 days. 0.098 remain after 10 days.

Average rate from day 1 to day 4:

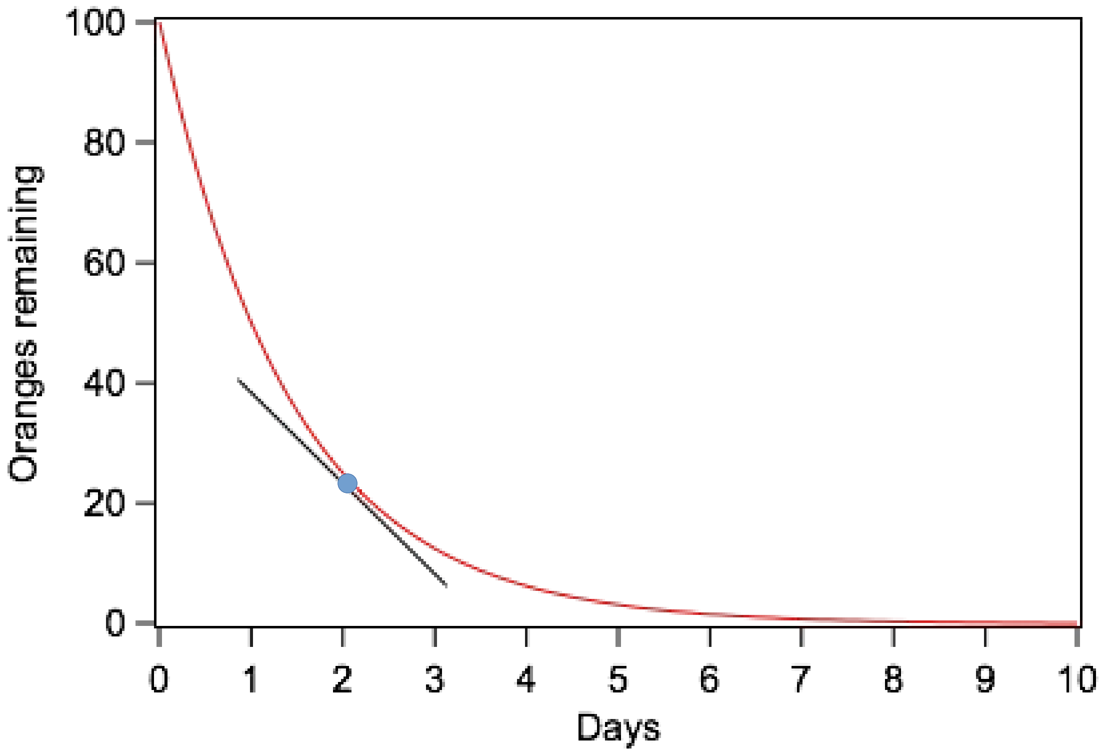


$$\frac{\Delta y}{\Delta x} = \frac{(6-50)\text{ oranges}}{(4-1)\text{ days}} = \frac{-44\text{ oranges}}{3\text{ days}} = -15\frac{\text{oranges}}{\text{day}}$$

Math Review

Slope of a curve:

- Now say you start with 100 oranges, but you eat half of them every day. 100 to 50 to 25 to 12.5, etc. for 10 days. 0.098 remain after 10 days.



Instantaneous rate on day 2:

Slope of the tangent line drawn at day 2 (blue circle)

Algebra Review

$$x^0 = 1$$

0^0 not defined!

$$10^{log(x)} = x \qquad log(10^x) = x$$

$$e^{ln(x)} = x \qquad ln(e^x) = x$$

$$\frac{x^n}{y^n} = \left(\frac{x}{y}\right)^n$$

$$log(x^n) = n\ log(x)$$

$$log\left(\frac{x}{y}\right) = log(x) - log(y)$$

$$log(xy) = log(x) + log(y)$$

Chemistry Review

- Concentration of a solute in a solution:
  - Molarity (M) = moles of solute / volume of solution
  - Unit: mol/L

- Pressure of a gas:
  - Units are Pascal (Pa; SI unit), atmospheres (atm), Torr, bar, pounds per square inch (psi), etc.

- Ideal gas law:

$$PV = nRT$$

Chemical Reaction Fundamentals

$$\underbrace{A + B}_{Reactants} \rightarrow \underbrace{C + D}_{Products}$$

- Thermodynamics (Later)
  - Does a reaction take place? Is it favored energetically? Are there other factors to consider?
- Equilibrium (Later)
  - How far does a reaction go before it stops?
- Kinetics (Now)
  - How fast does a reaction occur?

Energy

- **Energy**: Capacity to do work (unit Joule; J = Nm)
- **Work**: Force applied across a distance (unit Joule; J)
- **Force**: Push or pull on an object (unit Newton; N)

- Changes in matter (chemical reaction) result in the matter gaining or losing energy.

- Energy is either in kinetic or potential form.
- It can be converted from one form to another but usually total energy is conserved (closed system).

Chemical Energy

Usually we are discussing potential energy stored in the bonds between atoms or in the electrons:

$$2\ H_2(\ell) + O_2(\ell) \rightarrow 2\ H_2O(g)$$

$$10Al(s) + 6NH_4ClO_4(s) \rightarrow 4\ Al_2O_3(s) + 2\ AlCl_3(s) + 12\ H_2O(g) + 3N_2(g)$$

Chemical Kinetics

- Study of the **rate** (speed) at which chemical reactions occur:

  How fast or slow do reactions happen?

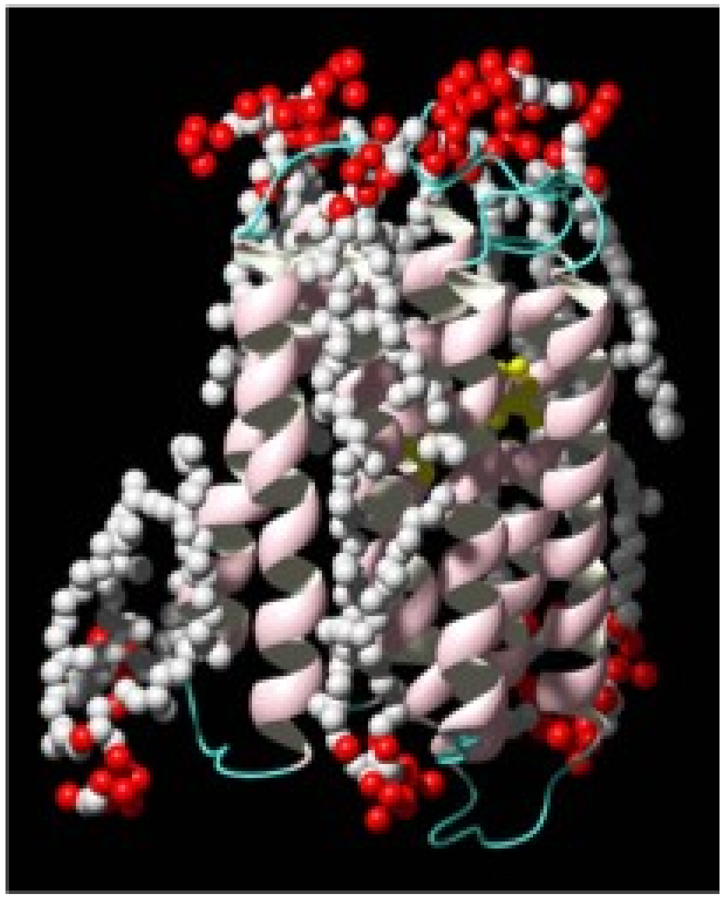
- Study of the **mechanisms** that cause reactions to occur:

  How do reactions happen on a molecular level?

- **Temperature dependence** of chemical reactions:

  How do reaction rates vary at different temperatures?

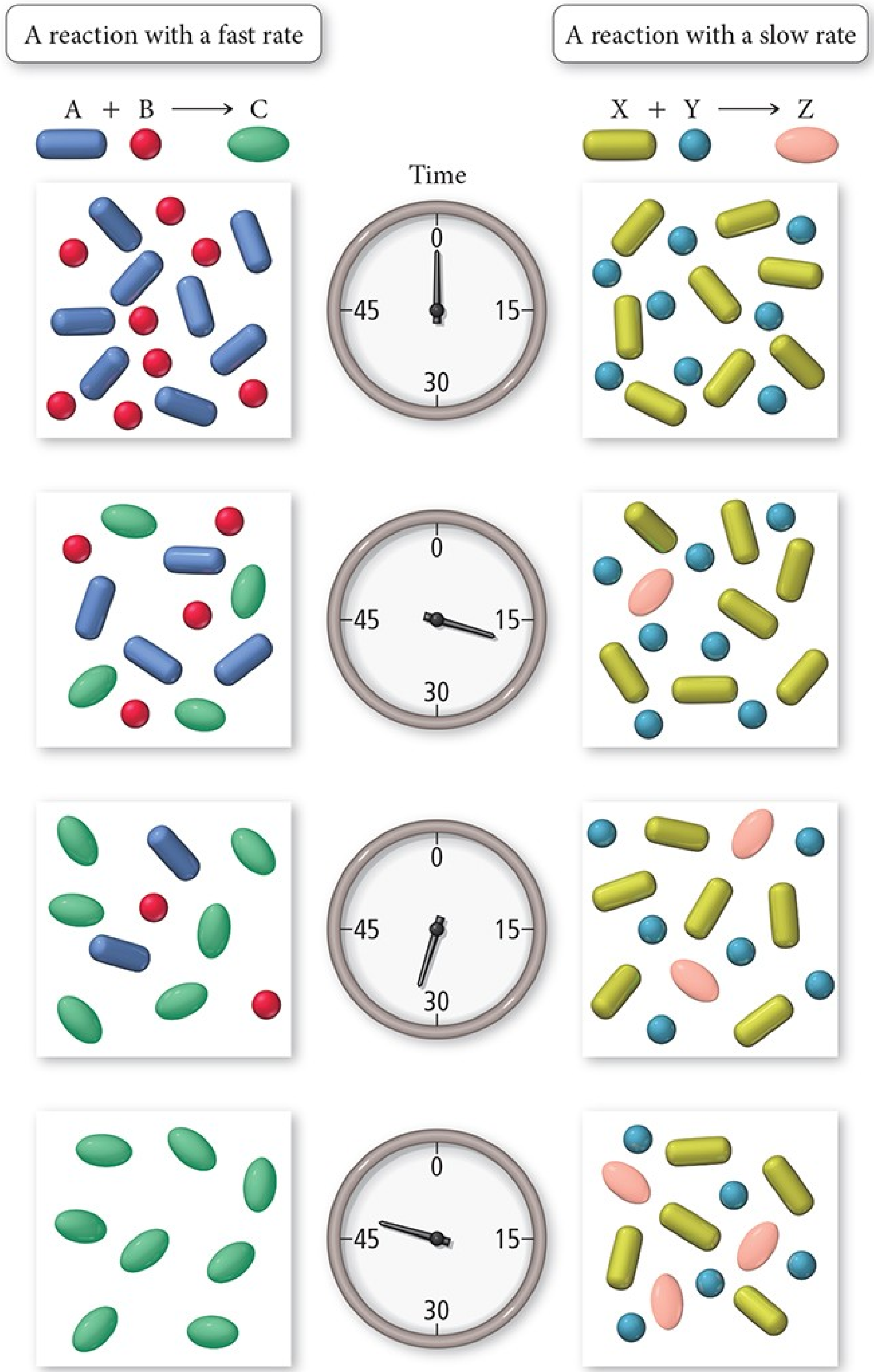
What kind of speeds are we talking about?



Ultrafast: rhodopsin in your eye isomerizes in 200 fs (2 x 10^{-13} s) after it absorbs a photon!

Fast: it takes less than 10^{-6} seconds to destroy a molecule of acetylene in a flame

Ultraslow: oxidation of diamond (C) to CO_2 is immeasurably slow at room temperature


A reaction with a fast rate
A reaction with a slow rate
A + B ⟶ C
X + Y ⟶ Z
Time
0
15
30
45

Rate of reaction

$$Reaction\ Rate = \frac{Change\ in\ concentration}{Change\ in\ time}$$

- Units of rate might be: $M \cdot s^{-1}$ or $molecules \cdot cm^{-3} \cdot s^{-1}$,etc.

Molarity (mol/L)

- Usually we will use: $mol \cdot L^{-1} \cdot s^{-1}$ or M/s or $M \cdot s^{-1}$ (all of these are identical)
- Change: represented by the Greek letter Δ

Reaction rate is the number (mol) of chemical reactions in the system per reaction volume (L) per time (s).

Example rate of reaction

$$A \rightarrow B$$

- Start with some concentration of A, which decreases during the reaction (usually)
- Start with 0 (usually) of B, which increases during the reaction (usually)
- Rate: mol/L of A that are converted to B per second or mol/L of B that are produced per second:

$$Rate = -\frac{\Delta[A]}{\Delta t} = \frac{\Delta[B]}{\Delta t}$$

Generic Reaction - Rate expression

$$aA + bB \rightarrow cC + dD$$

$$Rate = -\frac{1}{a}\frac{\Delta[A]}{\Delta t} = -\frac{1}{b}\frac{\Delta[B]}{\Delta t} = +\frac{1}{c}\frac{\Delta[C]}{\Delta t} = +\frac{1}{d}\frac{\Delta[D]}{\Delta t}$$

Negative sign because A and B are reactants
(they decrease in concentration during the reaction)

Reaction rate is always positive

IMPORTANT!

If you know the rate of change in concentration of one reactant or product, you can get the rate of change of any other product or reactant (or the reaction rate).

BUT:

- Reaction rate cannot be determined from the balanced equation alone!
- Must be determined experimentally!
- Reaction rate is not necessarily constant during reaction!

Reaction rates and stoichiometry

$$2\ NO_2(g) \rightarrow 2\ NO(g) + O_2(g)$$

- For every “mol” of reactions occurring per second:
  - 2 mol/L of NO_2 lost per second,
  - 2 mol/L of NO form and 1 mol/L of O_2 form per second.

- For each “mol” of reactions occurring, we must correct for the stoichiometry

$$Rate = -\frac{1}{2}\frac{\Delta[NO_2]}{\Delta t} = +\frac{1}{2}\frac{\Delta[NO]}{\Delta t} = +\frac{\Delta[O_2]}{\Delta t}$$

Reaction rates and stoichiometry

Given the reaction rate is 2.5 M/s, calculate the rate of change of each reactant and product for:

$$2\ NO_2(g) \rightarrow 2\ NO(g) + O_2(g)$$

Solution: Use the formula on previous slides with *a* = 2, *c* = 2, and *d* = 1 (note that *b* does not apply since there is only one reactant):

$$rate = -\frac{1}{2}\frac{\Delta[NO_2]}{\Delta t} = \frac{1}{2}\frac{\Delta[NO]}{\Delta t} = \frac{\Delta[O_2]}{\Delta t}$$

Here *rate* = 2.5 M/s, which gives:

$$\frac{\Delta[NO_2]}{\Delta t} = -5.0\ \mathrm{M/s}, \frac{\Delta[NO]}{\Delta t} = 5.0\ \mathrm{M/s}, \frac{\Delta[O_2]}{\Delta t} = 2.5\ \mathrm{M/s}.$$

Example reaction

$$H_2(g) + I_2(g) \rightarrow 2\ HI(g)$$

$$Rate = -\frac{\Delta[H_2]}{\Delta t} = -\frac{[H_2]_{t_2} - [H_2]_{t_1}}{t_2 - t_1}$$

$$Rate = -\frac{\Delta[I_2]}{\Delta t}$$

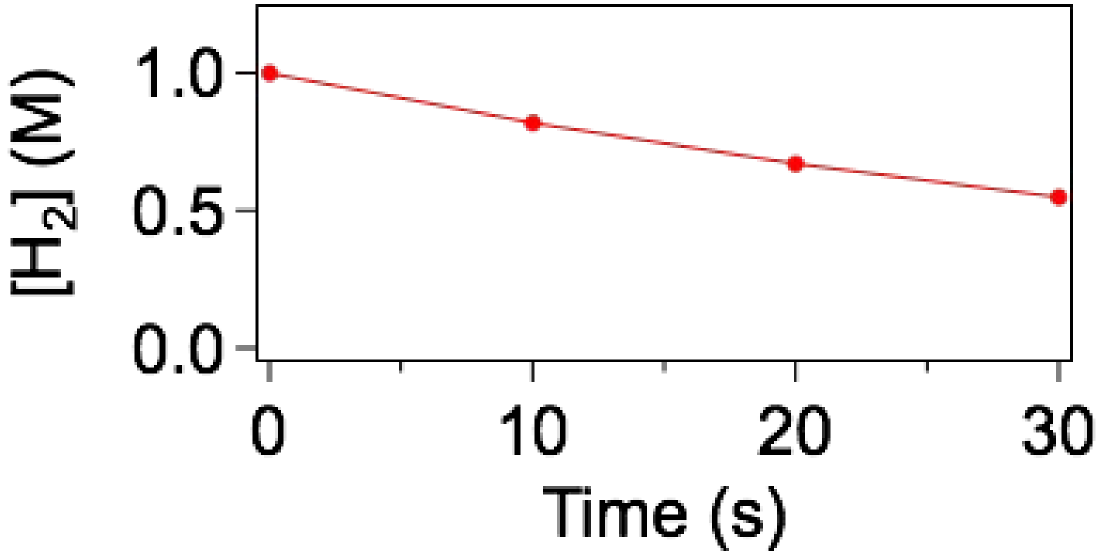
$$Rate = +\frac{1}{2}\frac{\Delta[HI]}{\Delta t}$$

$$H_2(g) + I_2(g) \rightarrow 2\ HI(g) \quad Rate = -\frac{\Delta[H_2]}{\Delta t} = -\frac{[H_2]_{t_2} - [H_2]_{t_1}}{t_2 - t_1}$$

t (s)	$[H_2]$ (M)
0	1.000
10	0.819
20	0.670
30	0.549

$\Delta[H_2]$ (M)	Δt (s)	Rate (M/s)
-0.181	10	0.0181
-0.149	10	0.0149
-0.121	10	0.0121

Avg. rate from 0 to 10 s

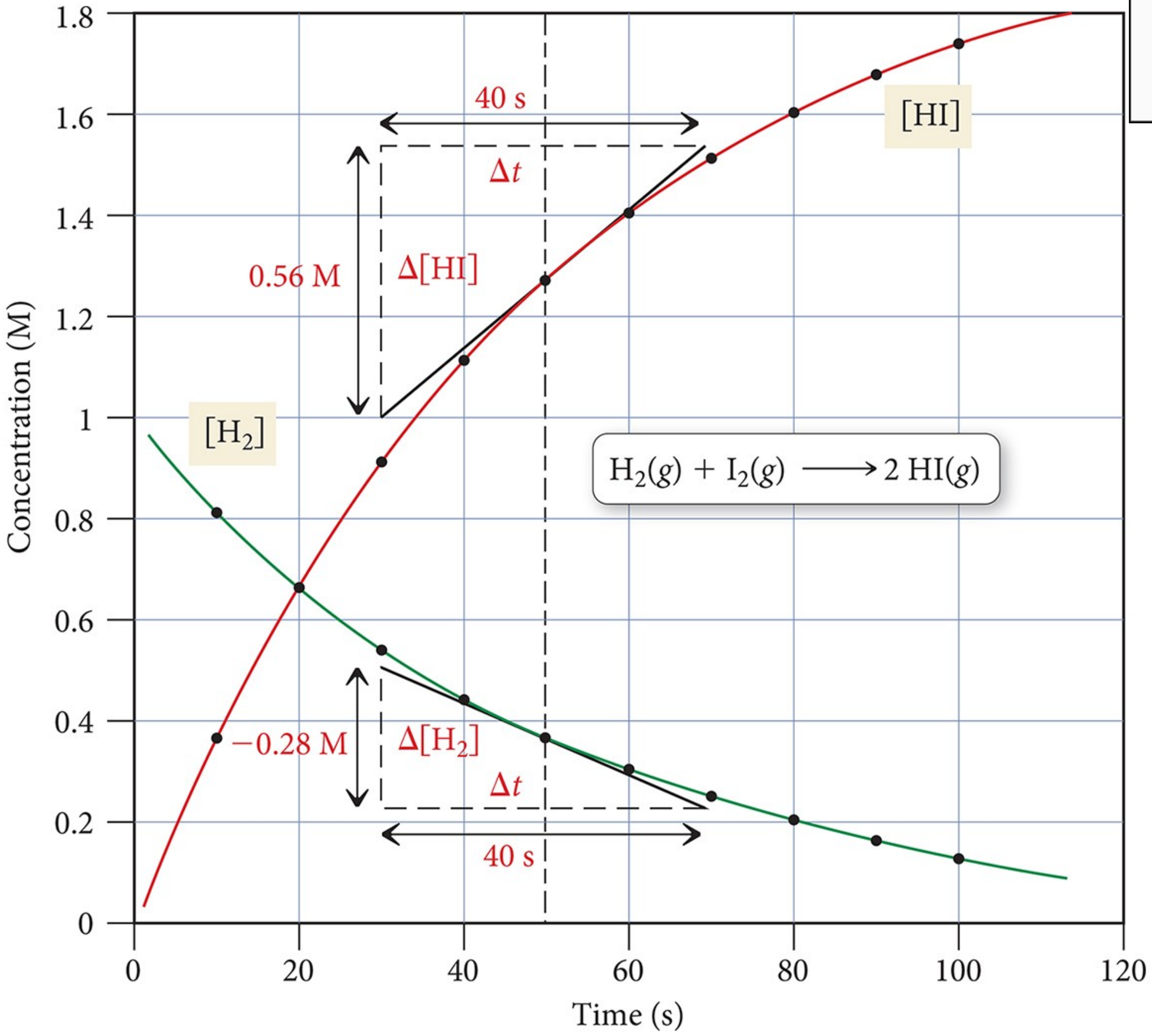


Average vs. Instantaneous Rate

- So far, we have been talking about <u>average</u> rates of reaction. We are using Δ for change over some range of concentration and time.
- But we could define rate as <u>instantaneous</u>, use differential *d* (instead of Δ) for change at a given time.
- In other words, it is given by the <u>slope of the tangent</u> to the curve, which you may be able to estimate from plotting (or use calculus; derivative).

$$H_2(g) + I_2(g) \rightarrow 2\ HI(g) \quad Rate = -\frac{\Delta[H_2]}{\Delta t} = -\frac{[H_2]_{t_2} - [H_2]_{t_1}}{t_2 - t_1}$$

Instantaneous rate <u>at 50 s</u> is equal to slope of tangent line at this point.



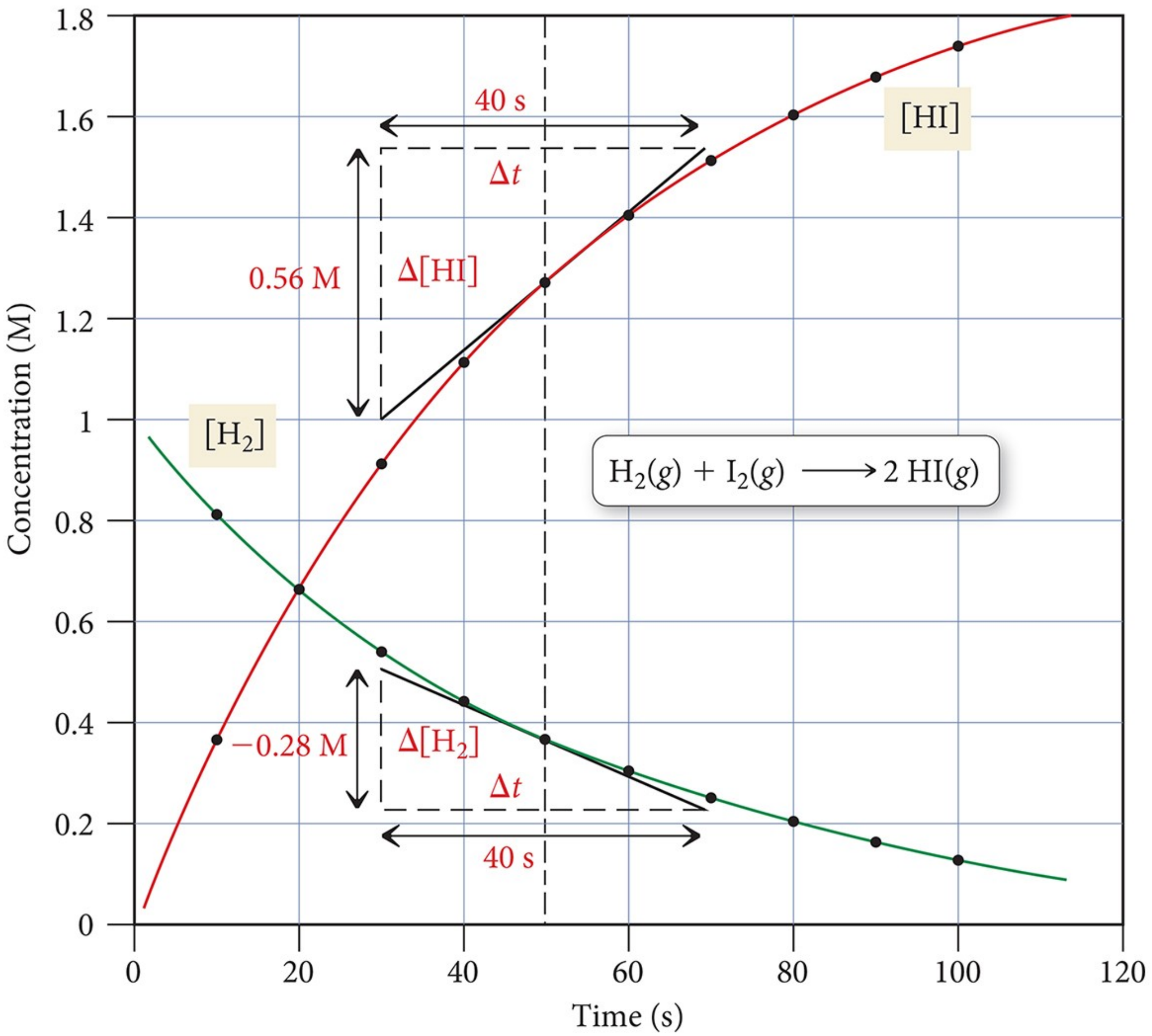
© 2017 Pearson Education, Inc.

$$Rate = -\frac{d[H_2]}{dt} = -\frac{-0.28\ M}{40\ s} = 0.0070\ M/s$$

General tips for this section

- You should be able to write:
  - A balanced reaction
  - Rate expression given for a reaction
- You should be able to calculate:
  - Average rate of reaction given a table of concentrations (reactants or products) over time
  - Rate of loss or formation of reactants/products given a reaction rate
- You should be able to estimate:
  - Instantaneous rate (or average rate) by reading a plot of concentration vs. time

Why do reaction rates change over time?



Example: Rate (left) is <u>decreasing</u> over time.

Why?

Intuitively, you might realize that reaction rate might depend on the concentration of the reactants (which are decreasing).

Note: Sometimes it does not!

The rate law

If reaction rate depends on the concentration of the reactants, we can write this as a mathematical expression called the “rate law”.

Example:

$$A \rightarrow Products$$

$$Rate \propto [A]^n$$

Rate is proportional to a power of [A], but we don’t know the exact relationship so we use “*n*”

$$Rate = k[A]^n$$

If rate is proportional to $[A]^n$, we can introduce a “constant”, *k*, so we can use an equal sign

The Rate Law for Single Reactant

$$A \rightarrow Products$$

$$\boxed{Rate = k[A]^n = \frac{-\Delta[A]}{\Delta t}}$$

- *k* is the "rate constant", which does not change during a reaction (even if the rate does).
- *n* is called the "reaction order":
  - *n* is usually an integer (there are some exceptions)
  - *n* can <u>only</u> be determined by experiment
  - *n* cannot be determined by reaction stoichiometry alone
  - *n* is generally defined for <u>reactants</u>, not products

The Rate Law for Generic Reaction

$$aA + bB \rightarrow cC + dD$$

$$\boxed{Rate = k[A]^m[B]^n}$$

- *k* is the "rate constant":
  - rate can vary over time, but rate constant does not change
- *m*+*n* is the "overall reaction order":
  - *m* order in A, *n* order in B
- Reaction order can only be determined by experiment:
  - usually (but not always) an integer or fraction (e.g., 1/2)
  - not necessarily related to the stoichiometry!

PITFALL!

Reaction order is usually determined experimentally and <u>cannot</u> be predicted from stoichiometry

$$F_2(g) + 2\ ClO_2(g) \rightarrow 2\ FClO_2(g)$$

$$\cancel{Rate = k[F_2][ClO_2]^2}$$

Not necessarily!

$$Rate = k[F_2][ClO_2]$$

Determined from experiment

Units of the rate constant, *k*

- Units of *k* can vary, depending on the reaction order
- Remember: Rate has units of mol L^{-1} s^{-1} (or similar)

  Use that to determine the units of *k*.

Example:

$$F_2(g) + 2\ ClO_2(g) \rightarrow 2\ FClO_2(g)$$

$$\underbrace{Rate}_{\left(\frac{mol}{L\cdot s}\right)} = \underbrace{k}_{?}\ \underbrace{[F_2]}_{\frac{mol}{L}}\ \underbrace{[ClO_2]}_{\frac{mol}{L}}$$

Overall reaction order = 2nd order

So, *k* must have units of ? (L mol^{-1} s or M^{-1} s)

Reaction order - Zero Order, Single Reactant

$$A \rightarrow Products$$

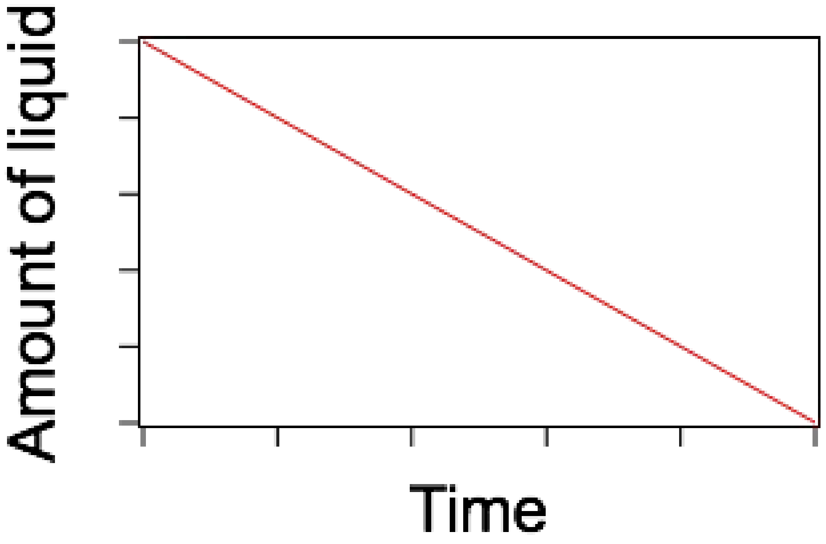
$$Rate = k[A]^0 = k = -\frac{\Delta[A]}{\Delta t}$$

Reaction rate (slope) has no dependence on [A]

- Unit of *k*: M•s^{-1} (or similar)
- Example: Evaporation;

  rate of evaporation does not depend on how much water is in the glass.

$$H_2O(\ell) \rightarrow H_2O(g)$$



Evaporation is limited by surface area.

Reaction order - First Order, Single Reactant

$$A \rightarrow Products$$

$$Rate = k[A]^1 = k[A]$$

Reaction rate is directly (linearly) proportional to [A]:

- Unit of *k*: s^{-1} (“events / second”)
- Example: Radioactive & fluorescence decay;

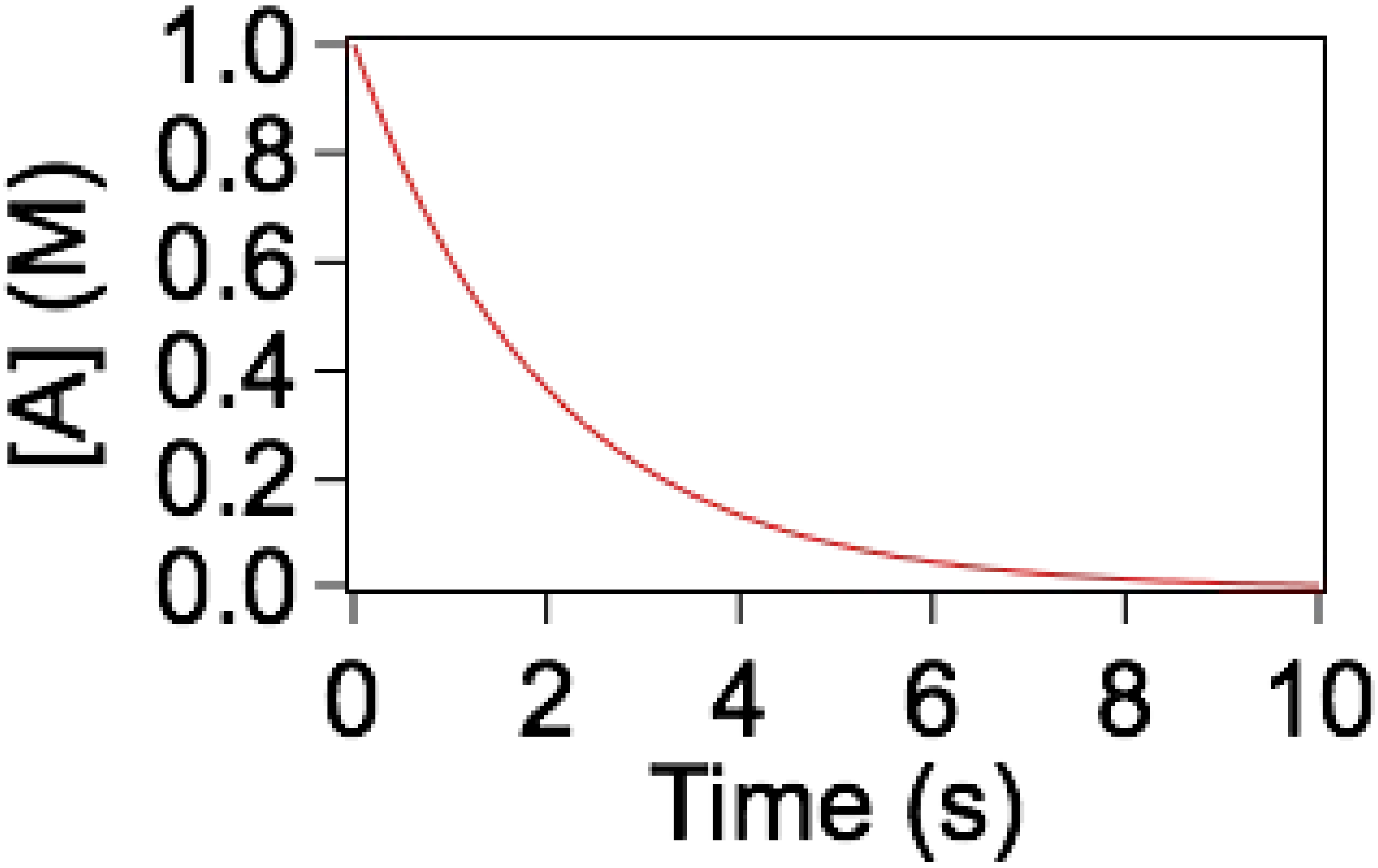
  rate of decay depends linearly on how much material is present.

Side note: What do we mean by “linearly” related?

First order (*n* = 1): $$Rate = k[A]^1 = k[A] = -\frac{\Delta[A]}{\Delta t}$$

Reaction rate (slope) is directly proportional to [A]:

- If you double [A], the rate should double
- If you halve [A], the rate should halve
- If you change [A] to 0.1 x [A], the rate becomes 0.1 x rate



Reaction order - Second Order, Single Reactant

$$A \rightarrow Products$$

Second order (*n* = 2): $Rate = k[A]^2$

Reaction rate is proportional to [A] squared:

- Unit of *k*: $M^{-1} \bullet s^{-1}$ (or similar)
- Example: Bimolecular reaction with one reactant;

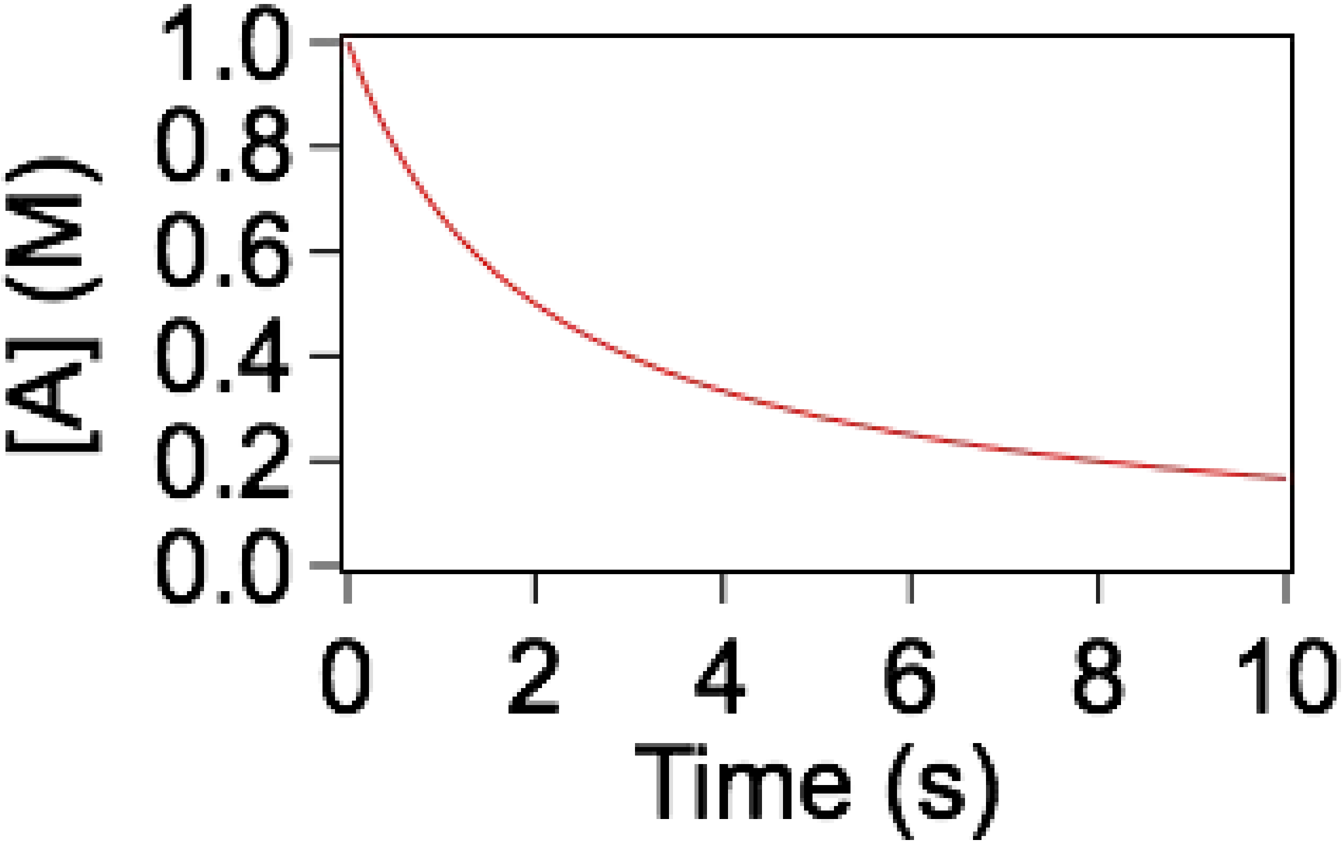
$H + H \rightarrow H_2$

Reaction order - Second Order, Single Reactant

$$Rate = k[A]^2 = -\frac{\Delta[A]}{\Delta t}$$

Reaction rate (slope) is proportional to $[A]^2$:

- If you double [A], the rate should quadruple
- If you halve [A], rate should change by 1/4



Determining Reaction Order: Method of Initial Rates

- Determine reaction order and rate constant experimentally by varying the concentrations and measuring the initial rates
- For example, see how the rate varies as a function of the initial concentration:
  - If rate does not change when concentration doubles, must be **zeroth** order.
  - If rate doubles when concentration doubles, must be **first** order.
  - If rate quadruples when concentration doubles, must be **second** order.

- Or: Solve using the algebra-based method.

Method of Initial Rates: Example 1

$$A \rightarrow Products \qquad Rate = k[A]^n = \frac{-\Delta[A]}{\Delta t}$$

[A] (M)	Initial Rate (M/s)
0.10	0.015
0.20	0.030
0.40	0.060

$$\frac{Initial\ Rate\ 2}{Initial\ Rate\ 1} = \frac{k[A]_2^n}{k[A]_1^n}$$

Inspect: Double [A], double rate:

- Must be first order in [A], solve for *k*
- Check

Or solve algebraically

Method of Initial Rates: Example 2

$$A \rightarrow Products \qquad Rate = k[A]^n = \frac{-\Delta[A]}{\Delta t}$$

[A] (M)	Initial Rate (M/s)
0.10	0.015
0.20	0.060
0.40	0.240

$$\frac{Initial\ Rate\ 2}{Initial\ Rate\ 1} = \frac{k[A]_2^n}{k[A]_1^n}$$

Inspect: Double [A], 4 x rate

- Must be second order in [A], solve for *k*
- Check

Or solve algebraically

Method of Initial Rates: Example 3

$$CHCl_3(g) + Cl_2(g) \rightarrow CCl_4(g) + HCl(g)$$

$[CHCl_3]$ (M)	$[Cl_2]$ (M)	Initial Rate (M/s)
0.010	0.010	0.0035
0.020	0.010	0.0069
0.020	0.020	0.0098
0.040	0.040	0.027

$$Rate = k[CHCl_3]^n[Cl_2]^m$$

- Plan: Inspect one by one to determine order in each reactant
- Find the experiments where only one reactant changes at a time

Method of Initial Rates: Example 3

$$CHCl_3(g) + Cl_2(g) \rightarrow CCl_4(g) + HCl(g)$$

$[CHCl_3]$ (M)	$[Cl_2]$ (M)	Initial Rate (M/s)
0.010	0.010	0.0035
0.020	0.010	0.0069
0.020	0.020	0.0098
0.040	0.040	0.027

$$Rate = k[CHCl_3]^n[Cl_2]^m$$

$[CHCl_3]$ increased 2x
$[Cl_2]$ did not change
Rate increased ~2x

Must be 1st order in $CHCl_3$

$$Rate = k[CHCl_3][Cl_2]^m$$

Method of Initial Rates: Example 3

$$CHCl_3(g) + Cl_2(g) \rightarrow CCl_4(g) + HCl(g)$$

$[CHCl_3]$ (M)	$[Cl_2]$ (M)	Initial Rate (M/s)
0.010	0.010	0.0035
0.020	0.010	0.0069
0.020	0.020	0.0098
0.040	0.040	0.027

$$Rate = k[CHCl_3]^n[Cl_2]^m$$

$[CHCl_3]$ did not change
$[Cl_2]$ increased 2x
Rate increased ~1.42x
~$2^{(1/2)}$

Must be 0.5 order in Cl_2

$$\frac{Rate\ 2}{Rate\ 1} = \frac{k[CHCl_2][Cl_2]_2^m}{k[CHCl_2][Cl_2]_1^m}$$

$$Rate = k[CHCl_3][Cl_2]^{0.5}$$

Method of Initial Rates: Example 3

$$CHCl_3(g) + Cl_2(g) \rightarrow CCl_4(g) + HCl(g)$$

$[CHCl_3]$ (M)	$[Cl_2]$ (M)	Initial Rate (M/s)
0.010	0.010	0.0035
0.020	0.010	0.0069
0.020	0.020	0.0098
0.040	0.040	0.027

$$Rate = k[CHCl_3]^n[Cl_2]^m$$

$$Rate = k[CHCl_3][Cl_2]^{0.5}$$

$$k = \frac{Rate}{[CHCl_3][Cl_2]^{0.5}} = \frac{0.0035\ M/s}{(0.010M)(0.010M)^{0.5}} = 0.00011\ M^{-0.5}s^{-1}$$

A few important points

- There is always some uncertainty in the experimental values, so you may wish to calculate *k* for all experiments and average
- Because of the uncertainty, sometimes you end up with strange coefficients. OK to round; they are commonly:

  0, 0.5, 1, or 2
- Think in terms of if you double (2x) concentration, multiplying by 2 raised to what power gives you the new rate?

Tips for this section

- Understand rate law, rate constant and different units of *k*
- Understand reaction order:
  - find reaction order and rate constant from experimental data
  - method of initial rates