Kinetics

Chapter 12

“Kinetic”

The study of how things change or move over time.

KINETIC ENERGY

The energy an object has because of its motion, involving the movement of the object over a specific period of time.

$$KE = \frac{1}{2}mV^2$$

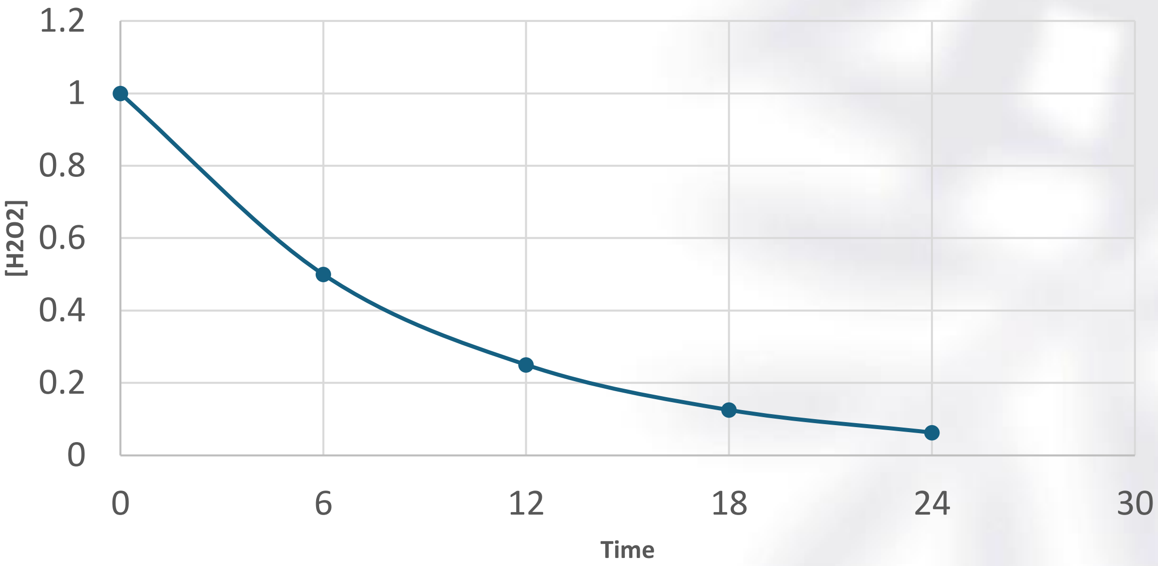
m = mass (kg)

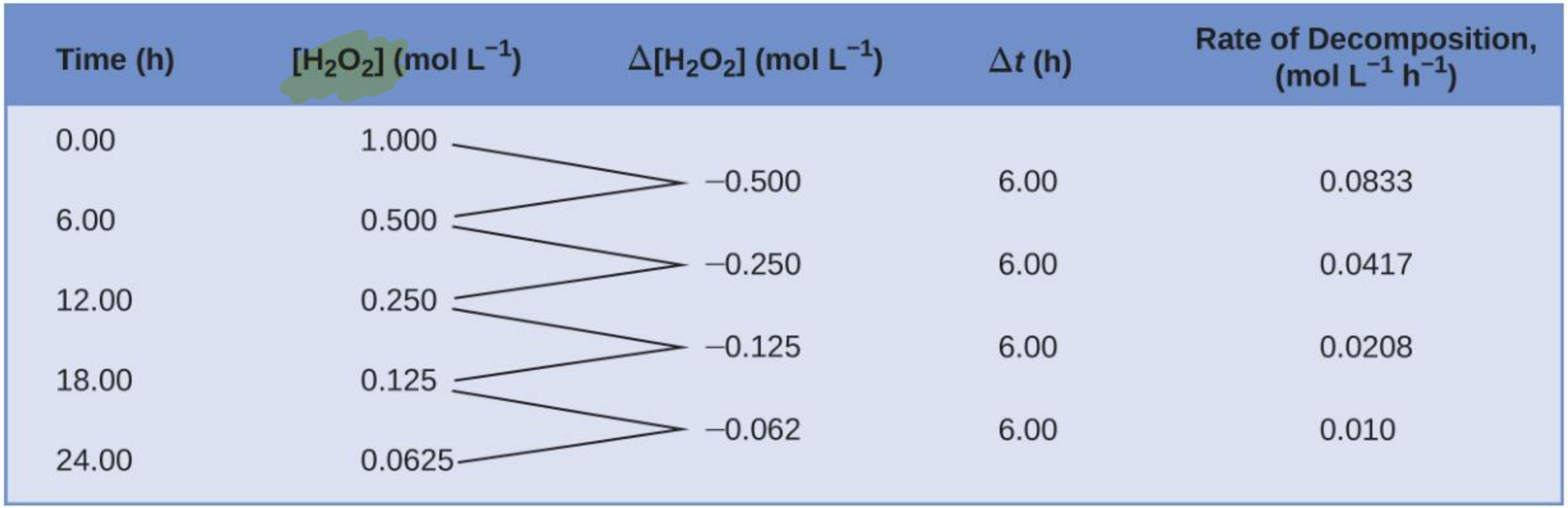
V = Velocity (m/s)

CHEMICAL KINETICS

$M = \frac{mol}{L}$

The study of how the concentration of substances changes over time during a chemical reaction.





Time (h)	$[H_2O_2]$ (mol L^{-1})	$\Delta[H_2O_2]$ (mol L^{-1})	Δt (h)	Rate of Decomposition, (mol L^{-1} h^{-1})
0.00	1.000			
		−0.500	6.00	0.0833
6.00	0.500			
		−0.250	6.00	0.0417
12.00	0.250			
		−0.125	6.00	0.0208
18.00	0.125			
		−0.062	6.00	0.010
24.00	0.0625			

RATE EXPRESSION

the change in concentration of reactants or products over time in a chemical reaction.

$$2H_2O_{2(aq)} \rightarrow 2H_2O_{(l)} + O_{2(g)}$$

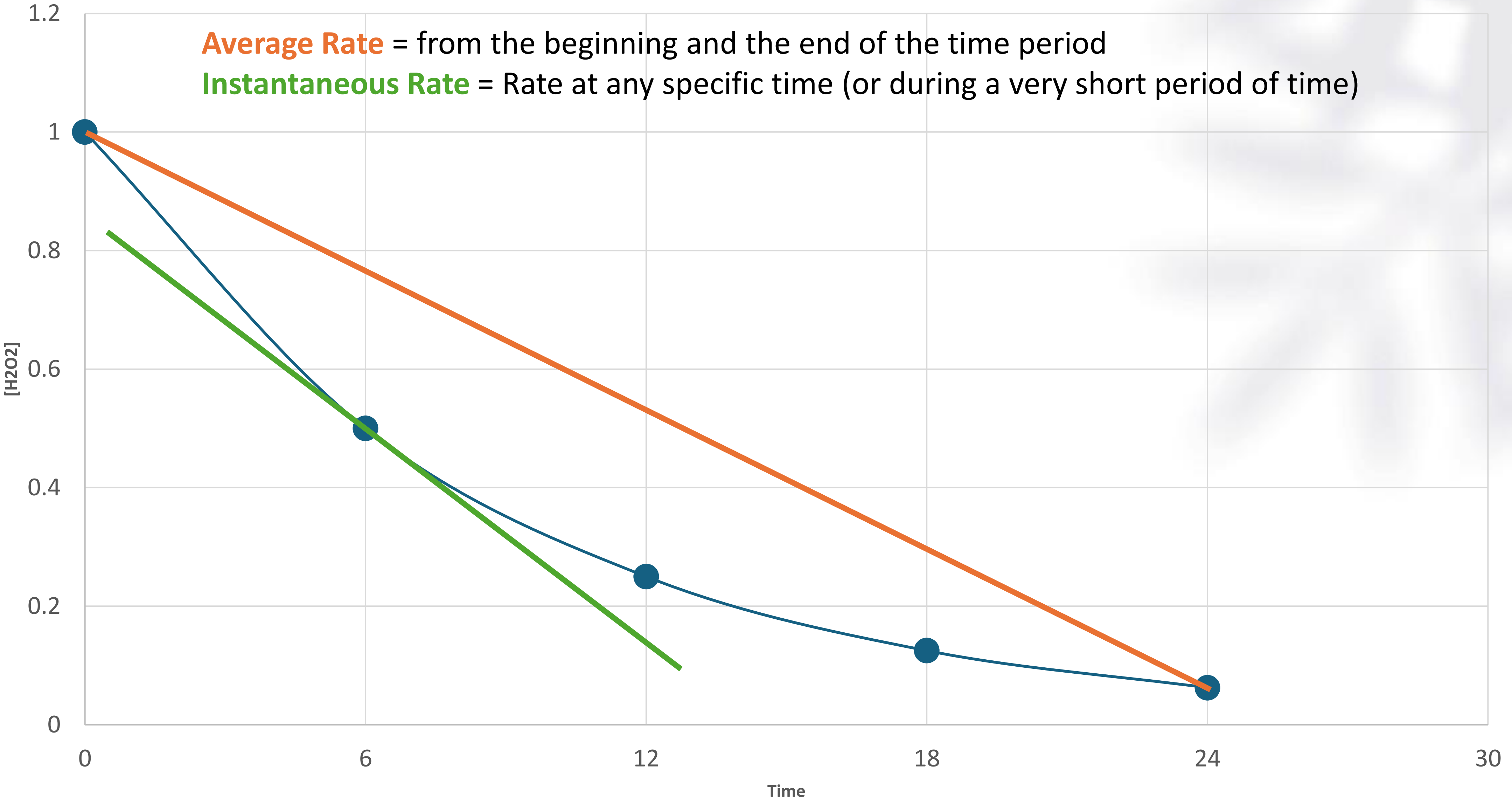
$$\text{Rate of decomposition of } H_2O_2 = -\frac{\text{change in concentration of reactant}}{\text{time interval}}$$

$$= -\frac{[H_2O_2]_{t2} - [H_2O_2]_{t1}}{t_2 - t_1}$$

$$= -\frac{\Delta[H_2O_2]}{\Delta t}$$

Δ = “change in” or “final – initial”

The bracket [] indicates molarity (mol/L)



Average Rate = from the beginning and the end of the time period

Instantaneous Rate = Rate at any specific time (or during a very short period of time)

RELATIVE RATES OF REACTION

$$N_2 + O_2 \xrightarrow{\times 2} 2\,NO$$

$$\begin{array}{ccc} N_2 & O_2 & NO \\ 1 & 1 & (0) \\ -1 & -1 & +2 \\ \hline 0 & 0 & (2)\ \text{mol} \end{array}$$

$$-\frac{\Delta[N_2]}{\Delta t} = \frac{1}{2}\,\frac{\Delta[NO]}{\Delta t}$$

$$(1/2)\,\Delta[NO]/\Delta t = -\Delta[N_2]/\Delta t = -\Delta[O_2]/\Delta t$$

$$\frac{1}{\text{Coeff.}}\,\frac{\Delta[\;]}{\Delta t}$$

Due to the coefficient (mol ratio),
every 1 mol of the reactant (N_2 and O_2) spent,
only ½ of the product (NO) is produced

The concentration of N_2 and O_2 decrease at half the rate at which the concentration of NO increases.

$$\frac{\Delta[NH_3]}{\Delta t} = -10\ M/s$$

Ex) Expressions for Relative Reaction Rates

The first step in the production of nitric acid is the combustion of ammonia:

$$4NH_{3(g)} + 5O_{2(g)} \rightarrow 4NO_{(g)} + 6H_2O_{(g)}$$

$$\frac{5 \cdot 10}{4} = \frac{4}{5} x$$

Write the equations that relate the rates of consumption of the reactants and the rates of formation of the products.

$$\frac{50}{4} = 12.5$$

$$-\overset{\times 4}{\frac{1}{4}}\frac{\Delta[NH_3]}{\Delta t} = -\overset{\times 4}{\frac{1}{5}}\frac{\Delta[O_2]}{\Delta t} = \overset{\times 4}{\frac{1}{4}}\frac{\Delta[NO]}{\Delta t} = \overset{\times 4}{\frac{1}{6}}\frac{\Delta[H_2O]}{\Delta t}$$

$$-\frac{\Delta[NH_3]}{\Delta t} = -\frac{4}{5}\frac{\Delta[O_2]}{\Delta t} = 1\frac{\Delta[NO]}{\Delta t} = \frac{4}{6}\frac{\Delta[H_2O]}{\Delta t}$$

$$10 = \qquad 10$$

Ex) $2H_2O_2 \rightarrow 2H_2O + O_2$

$$-\frac{1}{2}\frac{\Delta[H_2O_2]}{\Delta t} = \frac{1}{2}\underbrace{\frac{[H_2O]}{\Delta t}} = \frac{1}{1}\underbrace{\frac{\Delta[O_2]}{\Delta t}}$$

The instantaneous rate of decomposition of H2O2 at *t* = 11.1 h is determined to be 3.20 x 10^{-2} $\frac{\text{mol}}{\text{L} * \text{h}}$. That is:

H_2O : 3.2×10^{-2} M/h

O_2 : 0.016 M/h

$$-\frac{\Delta[\text{H2O2}]}{\Delta t} = 3.20\ x\ 10-2\ \frac{\text{mol}}{\text{L} * \text{h}}$$

M

What is the instantaneous rate of production of H_2O and O_2?

$$-\frac{1}{2}\left(3.20 \times 10^{-2}\ \text{mol}/\text{L}\cdot\text{h}\right) = \frac{1}{2}(H_2O\ \text{rate})$$

$$-\frac{1}{2}\left(\frac{\Delta[H_2O_2]}{\Delta t}\right) = 1\ \frac{\Delta[O_2]}{\Delta t}$$

$$-\frac{1}{2}\left(3.2 \times 10^{-2}\ \text{M}/\text{h}\right) : \text{rate of } O_2$$

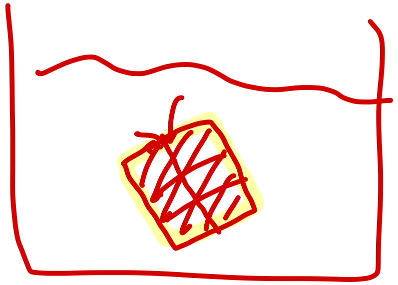
rate

FACTORS AFFECTING REACTION RATES

- **The chemical nature of the reacting substances**
  - Different substances have varying reactivities due to their chemical properties, such as bond strength, electron configurations, and types of bonds (ionic, covalent, etc.).
  - For example, sodium reacts more vigorously with water than magnesium due to its more reactive nature.

FACTORS AFFECTING REACTION RATES

- **The state of subdivision of the reactants (e.g., one large lump vs. many small particles)**
  - When reactants are in different physical states or phases (solid, liquid, gas), reactions occur only at the interfaces where the phases meet.
  - Smaller particles have a larger surface area relative to their volume, providing more area for reactions to occur. For example, powdered sugar dissolves faster in water than a sugar cube.
  - Increased surface area leads to more collisions between reactant molecules, thereby increasing the reaction rate.



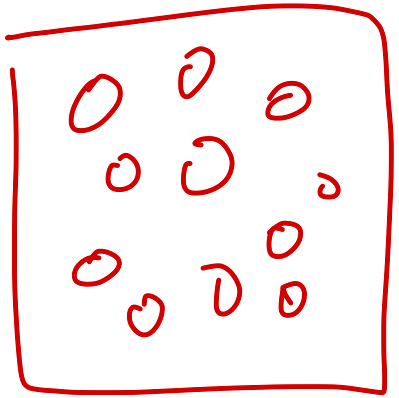
FACTORS AFFECTING REACTION RATES

- **The temperature of the reactants**
  - Higher temperatures provide reactant molecules with more kinetic energy, increasing their movement and the frequency of collisions.
  - More collisions mean a higher likelihood of reactant molecules overcoming the activation energy barrier, resulting in a faster reaction rate.
  - A general rule of thumb is that for many reactions, the rate doubles with every 10°C increase in temperature due to the increased kinetic energy of the molecules.

FACTORS AFFECTING REACTION RATES

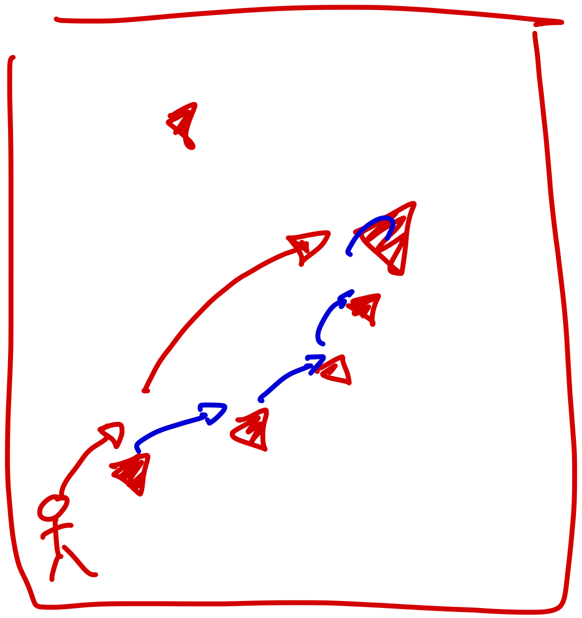
- **The concentration of the reactants**
  - Higher concentrations of reactants lead to more frequent collisions between reactant molecules.
  - In solutions, this means more reactant particles per unit volume, increasing the probability of successful collisions and, thus, the reaction rate.
  - For example, increasing the concentration of hydrochloric acid speeds up the reaction with magnesium.

$$M = \left[\frac{mol}{L}\right] \rightarrow$$



FACTORS AFFECTING REACTION RATES

- **The presence of a catalyst**
  - Catalysts provide an alternative reaction pathway with a lower activation energy, making it easier for reactants to convert into products.
  - Catalysts are not consumed in the reaction and can be used repeatedly.
  - For example, enzymes in biological systems act as catalysts to speed up biochemical reactions essential for life.

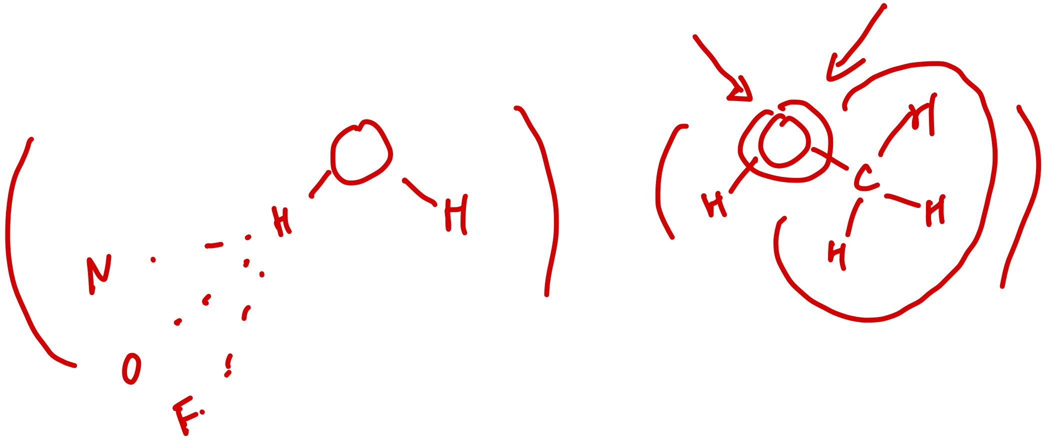


COLLISION THEORY

1. The reaction rate is proportional to the frequency of reactant collisions.
2. Reacting species must collide in a proper orientation for atoms to bond in the product.
3. Collisions must have sufficient energy to allow valence shell interaction and new bond formation.

$AB + CD \rightarrow AD + CB$

$BA \rightarrow \; \leftarrow CD$



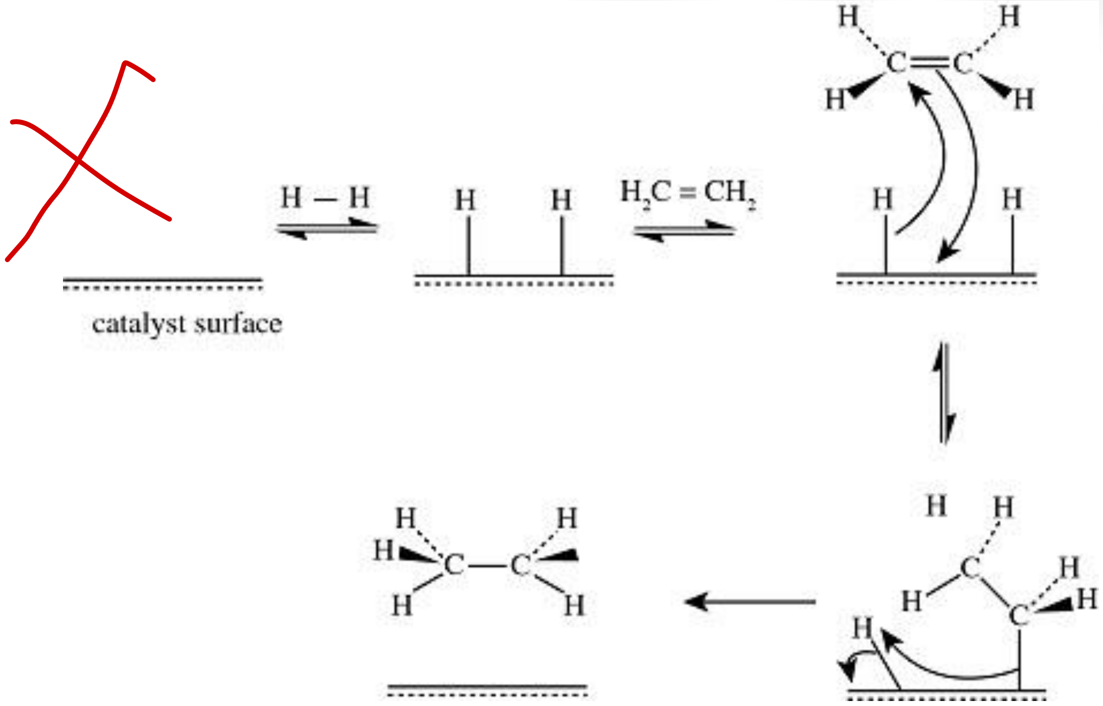
1. The rate of a reaction is proportional to the rate of reactant collisions:

- **The chemical nature of the reacting substances:**
  - Different substances have varying reactivities due to their molecular structures, which influence the frequency and energy of collisions.
  - For example, some molecules may inherently have higher rates of effective collisions due to their bond strengths and electron configurations. (N_2 requires more energy than H_2 because it has a triple bond)
- **The concentration of the reactants:**
  - Higher concentrations lead to more frequent collisions between reactant molecules.
  - In a solution, more reactant particles per unit volume increase the chance of collisions, thereby increasing the reaction rate.
- **The state of subdivision of the reactants (e.g., one large lump vs. many small particles):**
  - Smaller particles or a greater surface area allow for more frequent collisions.
  - Finely divided reactants have more surface area available for collisions, resulting in a higher rate of reaction.

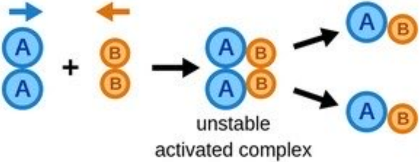
2. The reacting species must collide in an orientation that allows contact between the atoms that will become bonded together in the product:

- **The presence of a catalyst:**
    - Catalysts help orient the reacting species in a favorable position to ensure that collisions occur with the correct orientation for bond formation.
    - They provide a surface or an environment that increases the likelihood of properly oriented collisions.

In the catalytic hydrogenation of ethene (C_2H_4) to ethane (C_2H_6) using a palladium (Pd) catalyst, the catalyst adsorbs ethene and hydrogen, aligning them to facilitate effective collisions and bond formation, thereby speeding up the reaction.



Effective collision



Ineffective collision

3. The collision must occur with adequate energy to permit mutual penetration of the reacting species’ valence shells so that the electrons can rearrange and form new bonds (and new chemical species):

- **The temperature of the reactants:**
  - Higher temperatures increase the kinetic energy of molecules, leading to more energetic collisions.
  - A higher proportion of collisions will have sufficient energy to overcome the activation energy barrier, resulting in a faster reaction rate.
- **The presence of a catalyst:**
  - Catalysts lower the activation energy required for a reaction, meaning that a greater proportion of collisions will have enough energy to result in a reaction.
  - This increases the rate of the reaction without the need for an increase in temperature.

RATE LAW

Or differential rate laws or rate equations

Mathematical expressions that describe the relationship between the rate of a chemical reaction and the concentration of its reactants.

$2H_2O_2 \rightarrow$ ______

$\text{Rate} = k[H_2O_2]^{\cancel{2}}$

$\cancel{a}A + \cancel{b}B \rightarrow$ products

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

K = rate constant

m,n = reaction order

Note:
Unlike the exponents in a chemical equilibrium equation, the reaction orders of the reactants are not related to their coefficients in a balanced chemical equation. It must be determined experimentally.

EX)

Consider the rate law: Rate = $k[A]^2[B]^1$.

Reaction Orders:

$\times 4$

$8 = \text{rate} = (1)[\overset{\times 2}{2}]^2[2]^1$

$32 = \text{rate} = (1)[4]^2[2]^1$

- The reaction is second order with respect to A and first order with respect to B.
- If the concentration of A is doubled, the reaction rate increases by a factor of 4 (since $2^2 = 4$).
- If the concentration of B is doubled, the reaction rate doubles.

Rate Constant k:

- The magnitude of k determines how fast the reaction proceeds at a given concentration of reactants.
- If k is large, the reaction proceeds quickly and vice versa
- Changing the temperature or adding a catalyst can change the value of k.

Overall Reaction Order

The sum of orders for each reactant

The rate law:

$\text{rate} = k[H_2O_2]$

describes a reaction that is first order in hydrogen peroxide and first order overall. The rate law:

$\text{rate} = k[C_4H_6]^2$

describes a reaction that is second order in C_4H_6 and second order overall. The rate law:

1 + 2 = 3

$\text{rate} = \underbrace{k[H^+][OH^-]}$

describes a reaction that is first order in H^+, first order in OH^-, and second order overall.

Stop for today

$\text{rate} : \dfrac{\Delta[X]}{\Delta t}$ M/s

ex) $A + 2B \rightarrow 3C$ $\dfrac{1}{\text{coeff.}} \dfrac{\Delta[\;]}{\Delta t}$

$$\text{rate} = -\frac{1}{1}\frac{\Delta[A]}{\Delta t} = -\frac{1}{2}\frac{\Delta[B]}{\Delta t} = +\frac{1}{3}\frac{\Delta[C]}{\Delta t}$$

$$= K[A]^{x}[B]^{y}\,)$$

* experimentally determined

* if it is not a multi-step reaction, we can use coefficient (Law of Mass action)

$$\underset{\times 4}{\text{rate}} = K\underset{\times 2}{[A]}^{1}\underset{\times 2}{[B]}^{2}$$

METHOD OF RATE LAW DETERMINATION

- Method of initial Rates

Determines the rate law by comparing initial reaction rates at different reactant concentrations to see how changes in concentration affect the rate.

- Using integrated Raw Laws

Determines the rate law by analyzing how the concentration of reactants changes over time, fitting this data to integrated rate equations to find the reaction order and rate constant.

METHOD OF INITIAL RATES

Ex)

$A + 2B + C \rightarrow D$

Experiment	Initial Concentration of Reactants (M)			Initial Rates of Formation of D (M/s)
	[A]	[B]	[C]	
1	0.10	0.10	0.10	0.01
2	0.10	0.10	0.20	0.01
3	0.10	0.20	0.10	0.02
4	0.20	0.20	0.10	0.08

$$\text{Rate} = k[A]^x[B]^y[C]^z$$

Experiment	Initial Concentration of Reactants (M)			Initial Rates of Formation of D (M/s)
	[A]	[B]	[C]	
1	0.10	0.10	0.10	0.01
2	0.10	0.10	0.20	0.01
3	0.10	0.20	0.10	0.02
4	0.20	0.20	0.10	0.08

×2

×4

Let's look at [A]

Experiment 3 & 4

Why? [A] changes while the other reactant concentrations remain constant. For this reason, the rate change is solely based on [A]

When the concentration doubles (0.10 → 0.20), the rate quadruples (0.02 → 0.08)

($(2)^x = 4$ or $x = 2$)

$\text{Rate} = k[A]^{\textcircled{2}}[B]^y[C]^z$

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

×4 ×2

Experiment	Initial Concentration of Reactants (M)			Initial Rates of Formation of D (M/s)
	[A]	[B]	[C]	
1	0.10	0.10	0.10	0.01
2	0.10	0.10	0.20	0.01
3	0.10	0.20	0.10	0.02
4	0.20	0.20	0.10	0.08

×2

2x

Let’s look at [B]

$(2)^x = 2$ or $x = 1$

Experiment 1 & 3

$\text{Rate} = k[A]^2[B]^1[C]^z$

When the concentration doubles (0.10 → 0.20),
the rate doubles (0.02 → 0.04)

Experiment	Initial Concentration of Reactants (M)			Initial Rates of Formation of D (M/s)
	[A]	[B]	[C]	
1	0.10	0.10	0.10	0.01
2	0.10	0.10	0.20	0.01
3	0.10	0.20	0.10	0.02
4	0.20	0.20	0.10	0.08

×2

Let's look at [C]

Experiment 1 & 2

When the concentration doubles
(0.10 → 0.20),
the rate doesn't change
(0.02 → 0.02)

$(2)^x = 1$ or $x = 0$

$\text{Rate} = k[A]^2[B]^1\cancel{[C]^0}$

Or

$\text{Rate} = k[A]^2[B]^1$

Overall 3rd order.

Experiment	Initial Concentration of Reactants (M)			Initial Rates of Formation of D (M/s)
	[A]	[B]	[C]	
1	0.10	0.10	0.10	0.01
2	0.10	0.10	0.20	0.01
3	0.10	0.20	0.10	0.02
4	0.20	0.20	0.10	0.08

Rate Constant

$$\text{Rate} = k[A]^2[B]^1$$

Choose any experiment

Experiment 3

$$\text{Rate} = k[A]^2[B]^1$$

$$0.02\ \frac{M}{s} = k[0.10\cancel{M}]^2[0.20\cancel{M}]^1$$

$$\frac{M}{s\,\cancel{M^2}\,\cancel{M^1}}) \Rightarrow \frac{\cancel{M}\ 1}{s \cdot M^{\cancel{3}\,2}}$$

$$k = 10\ \frac{1}{M^2 s}$$

Ex) Using the initial rates method and the experimental data, determine the rate law and the value of the rate constant for this reaction:

$$2NO_{(g)} + Cl_{2(g)} \rightarrow 2NOCl_{(g)}$$

Trial	[NO]	[Cl2]	Initial Rate
1	0.10	0.10	0.00300
2	0.10	0.15	0.00450
3	0.15	0.10	0.00675

$$\text{Rate} = k[NO]^m[Cl_2]^n$$

Trial	[NO]	$[Cl_2]$	Initial Rate
1	0.10	0.10	0.00300
2	0.10	0.15	0.00450
3	0.15	0.10	0.00675

Let’s Look at [NO]

(Choose trial 1 & 3)

$$\frac{\text{rate}_3 = k\,[NO]^x[Cl_2]^y}{\text{rate}_1 = k\,[NO]^x[Cl_2]^y}$$

$$\frac{\text{rate law of trial 3}}{\text{rate law of trial 1}}$$

$$\frac{\text{Rate 3}}{\text{Rate 1}} = \frac{0.00675}{0.00300} = \frac{\cancel{k}(0.15)^m\cancel{(0.10)^n}}{\cancel{k}(0.10)^m\cancel{(0.10)^n}}$$

$$\left(\frac{0.00675}{0.00300}\right) = \frac{(0.15)^m}{(0.10)^m} = \left(\frac{0.15}{0.10}\right)^m$$

$$\ln 2.25 = \ln (1.5)^m$$

$$\ln(2.25) = m\ln(1.5)$$

$$\frac{\ln(2.25)}{\ln(1.5)} = m$$

$$m = 2$$

Trial	[NO]	$[Cl_2]$	Initial Rate
1	0.10	0.10	0.00300
2	0.10	0.15	0.00450
3	0.15	0.10	0.00675

$$\boxed{\text{rate} = k\,[NO]^2\,[Cl_2]}$$

Let's Look at $[Cl_2]$
(Choose trial 1 & 2)

$$\frac{\text{rate law of trial 2}}{\text{rate law of trial 1}}$$

$$\frac{\text{Rate 2}}{\text{Rate 1}} = \frac{0.00450}{0.00300} = \frac{\cancel{k}\cancel{(0.10)}^{\cancel{m}\,2}(0.15)^n}{\cancel{k}\cancel{(0.10)}^{\cancel{m}\,2}(0.10)^n}$$

$$\frac{0.00450}{0.00300} = \frac{(0.15)^m}{(0.10)^m} = \left(\frac{0.15}{0.10}\right)^m$$

$$1.5 = (1.5)^m$$

$$\ln(1.5) = m \ln(1.5)$$

$$\frac{\ln(1.5)}{\ln(1.5)} = m$$

$$m = 1$$

Trial	[NO]	$[Cl_2]$	Initial Rate
1	0.10	0.10	0.00300
2	0.10	0.15	0.00450
3	0.15	0.10	0.00675

Rate = $k[NO]^2[Cl2]^1$

Choose Any Trial For k

With trial 1,

$0.00300\ {}^{M}/_{s} = k\ (0.10\ M)^2(0.10\ M)^1$

$K = 3.0\ {}^{1}/_{M^2 s}$

$$2NO + O_2 \rightarrow 2\ NO_2$$

Experiment	[NO]	[O_2]	Initial Reaction Rate (M/s)
1	0.025	0.025	$1.6\times\cancel{10^{-5}}$
2	0.025	0.066	4.1×10^{-5}
3	0.050	0.025	$6.2\times\cancel{10^{-5}}$

NO: 1, 3

O_2: 1, 2

×2

3.875

×4

[NO]

$$\frac{1.6\times10^{-5}}{6.2\times10^{-5}} = \frac{\cancel{k}[.025]^x\cancel{[.025]^y}}{\cancel{k}[.05]^x\cancel{[.025]^y}}$$

$$0.25806 = (0.5)^x$$

$$\frac{\ln 0.25806}{\ln(0.5)} = x$$

$$x = 1.95 \approx \boxed{2}$$ ✓

$$\text{rate} = k[NO]^2[O_2]$$

[O_2]

$$\frac{\text{Ep }1}{\text{Ep }2} = \left(\frac{1.6\times10^{-5}}{4.1\times10^{-5}}\right) = \frac{\cancel{k[0.025]^x}[0.025]^y}{\cancel{k[0.025]^x}[0.066]^y}$$

$$= 0.3902 = \left(\frac{0.025}{0.066}\right)^y = (0.37879)^y$$

$$\frac{\ln 0.3902}{\ln(0\ 37879)} = y = 0.9694\ldots = \boxed{1}$$

$2NO + O_2 \rightarrow 2\ NO_2$

Experiment	[NO]	[O_2]	Initial Reaction Rate (M/s)
1	0.025	0.025	1.6×10^{-5}
2	0.025	0.066	4.1×10^{-5}
3	0.050	0.025	6.2×10^{-5}

$\text{rate} = k[NO]^2[O_2]$

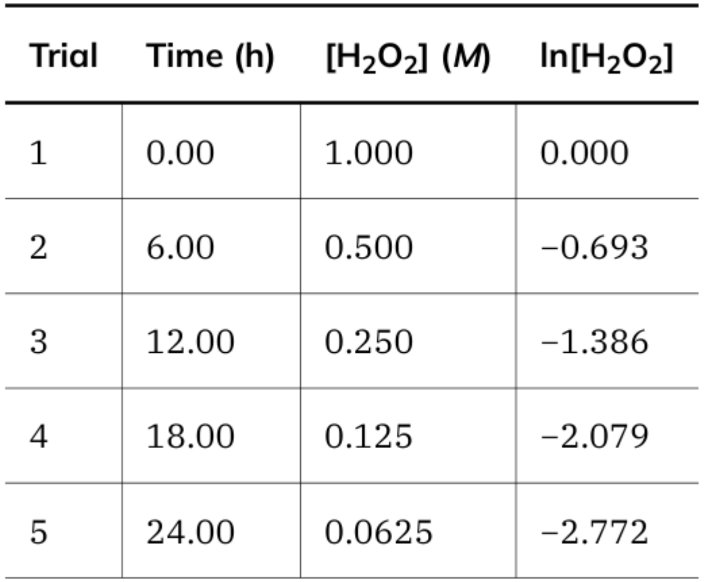
$\frac{M}{s} \quad \left(\frac{\cancel{M}}{s\cancel{M^3}}\right) \cancel{M^2} \quad M^1$

$1.6 \times 10^{-5} = k\ \underbrace{[0.025]^2[0.025]^1}$

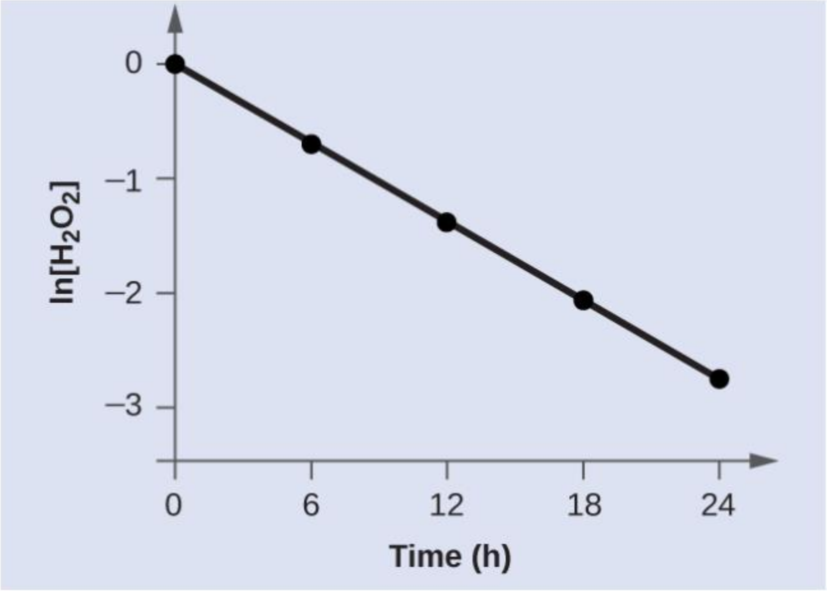
$\frac{1.6 \times 10^{-5}}{(1.5625 \times 10^{-5})} = k = \boxed{1.024} \left(\frac{1}{M^2 s}\right)$

INTEGRATED RATE LAW

- Determines the rate law by analyzing how the concentration of reactants changes over time, fitting this data to integrated rate equations to find the reaction order and rate constant.
- Uses plots of observed data that directly relate the time and reactant concentration.



Trial	Time (h)	$[H_2O_2]$ (*M*)	$\ln[H_2O_2]$
1	0.00	1.000	0.000
2	6.00	0.500	−0.693
3	12.00	0.250	−1.386
4	18.00	0.125	−2.079
5	24.00	0.0625	−2.772



	Zero-Order	**First-Order**	**Second-Order**
rate law	rate = k	rate = $k[A]$	rate = $k[A]^2$
units of rate constant	$M\,\mathrm{s}^{-1}$	s^{-1}	$M^{-1}\,\mathrm{s}^{-1}$
integrated rate law	$[A] = -kt + [A]_0$ Y = mX	$\ln[A] = -kt + \ln[A]_0$ Y = mX	$\frac{1}{[A]} = kt + \left(\frac{1}{[A]_0}\right)$ Y = mX

	Zero-Order	**First-Order**	**Second-Order**
plot needed for linear fit of rate data	$[A]$ vs. t	$\ln[A]$ vs. t	$\frac{1}{[A]}$ vs. t
relationship between slope of linear plot and rate constant	$k = -\text{slope}$	$k = -\text{slope}$	$k = \text{slope}$
half-life	$t_{1/2} = \frac{[A]_0}{2k}$	$t_{1/2} = \frac{0.693}{k}$	$t_{1/2} = \frac{1}{[A]_0 k}$

Derivation Of The First Order Integrated Rate Law

$$\text{Rate} = -\frac{d[A]}{dt} = k[A]$$

$$\frac{d[A]}{[A]} = -k\,dt$$

$$\int_{[A]_o}^{[A]} \frac{d[A]}{[A]} = -\int_{t_o}^{t} k\,dt$$

$$\int_{[A]_o}^{[A]} \frac{1}{[A]} d[A] = -\int_{t_o}^{t} k\,dt$$

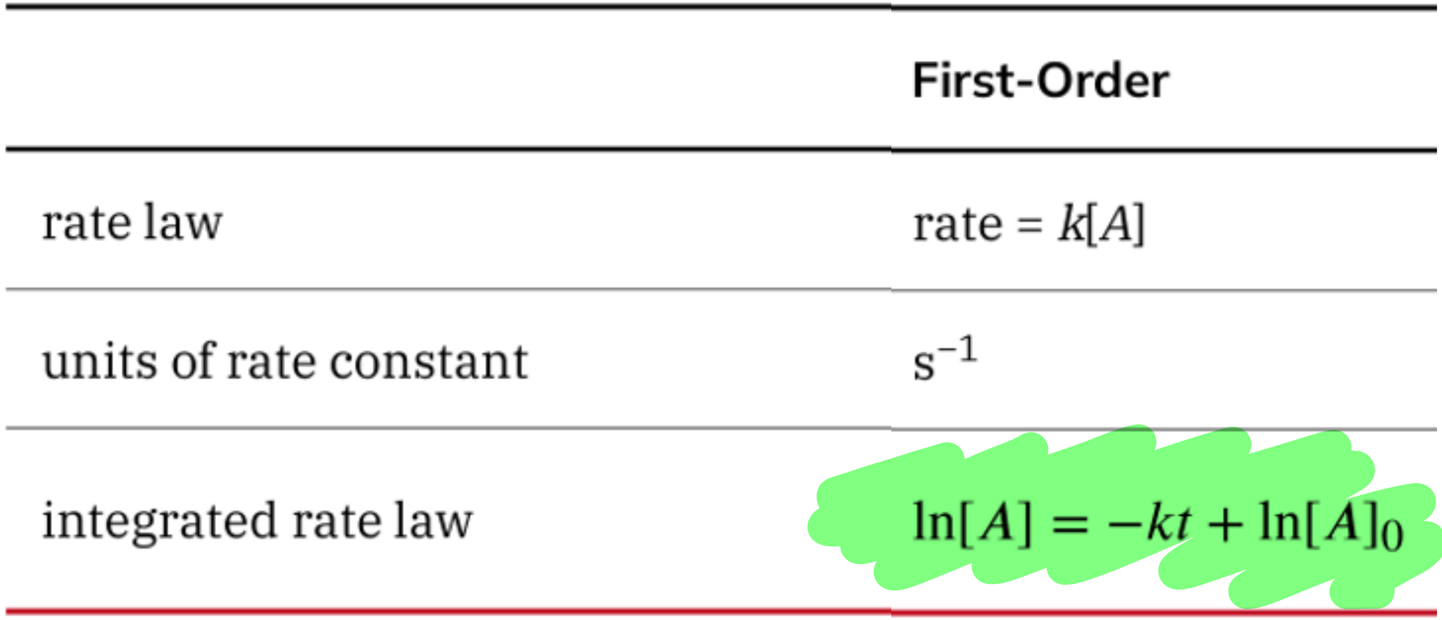
$$\int \frac{1}{x} = \ln(x) + C$$

$$\ln[A] - \ln[A]_o = -kt$$

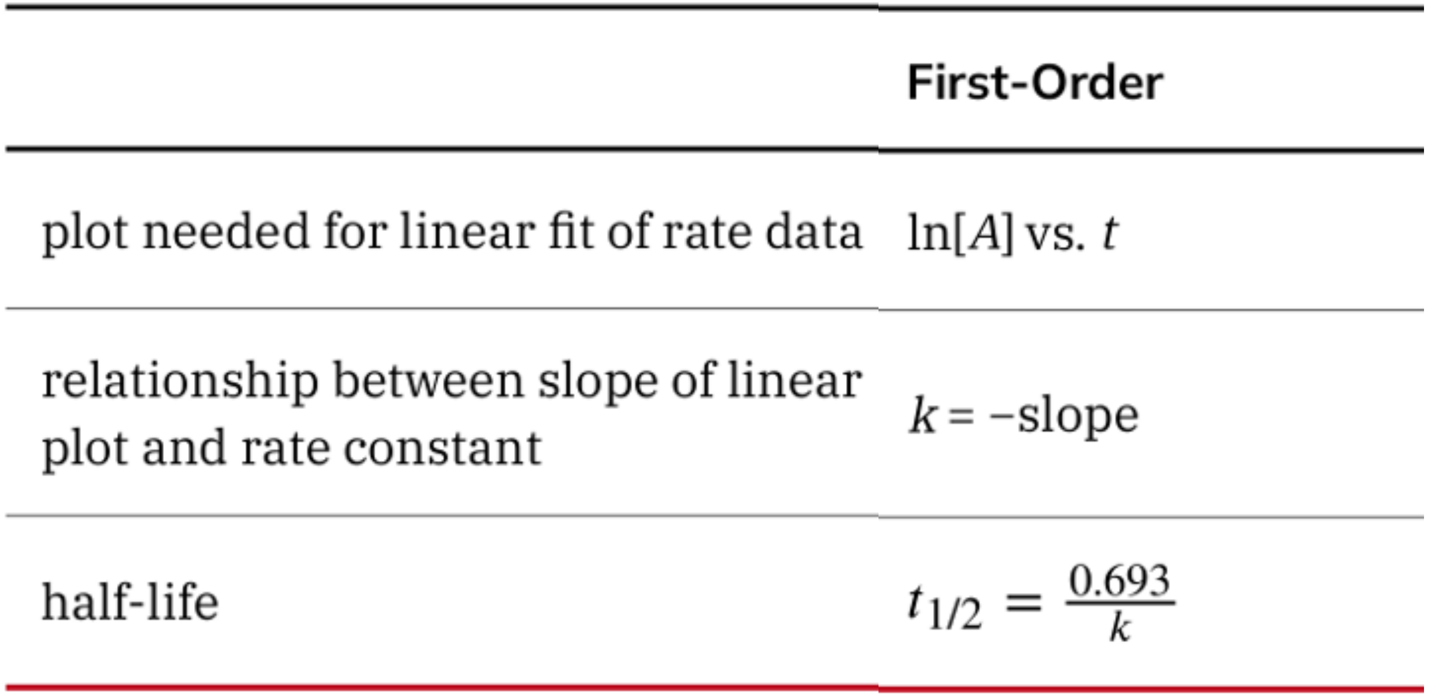
$$\ln[A] = \ln[A]_o - kt$$

$$\ln[A] = -kt + \ln[A]_o$$

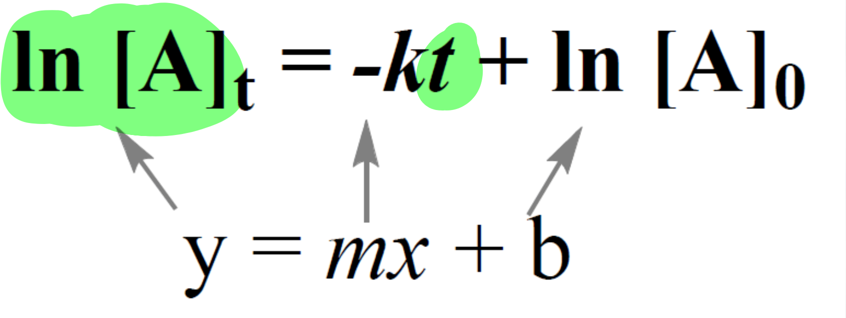
First-Order Reaction



	First-Order
rate law	rate = $k[A]$
units of rate constant	s^{-1}
integrated rate law	$\ln[A] = -kt + \ln[A]_0$

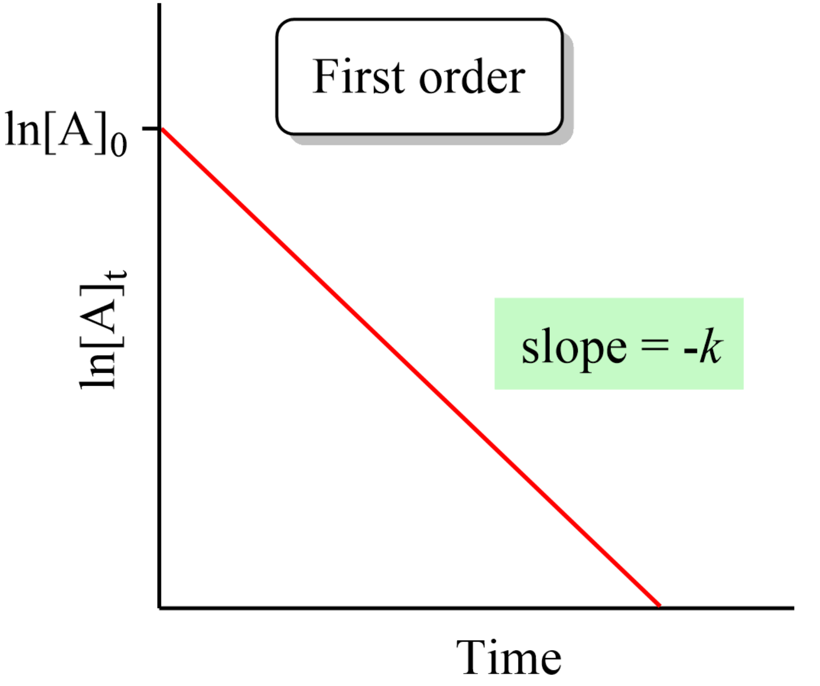


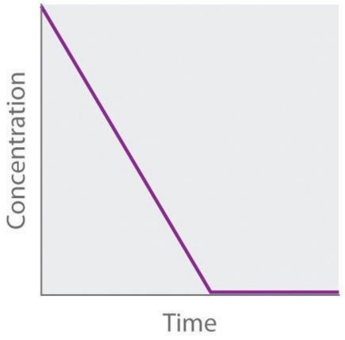
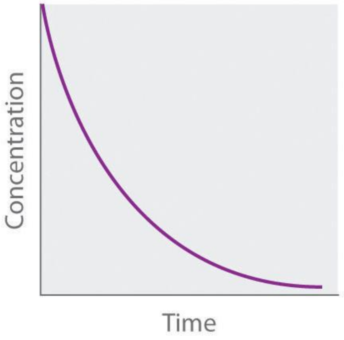
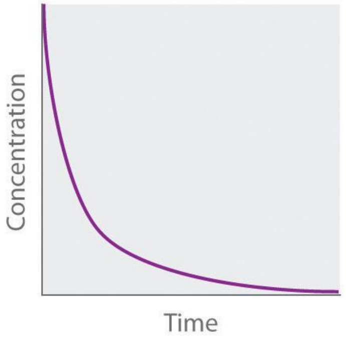
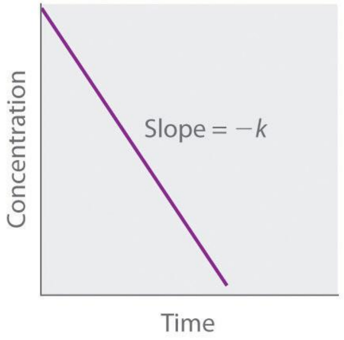
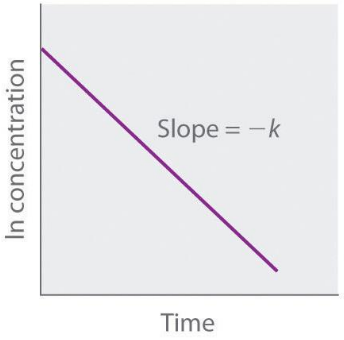
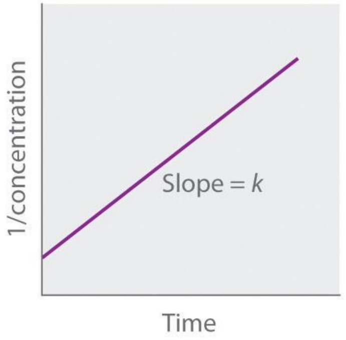
	First-Order
plot needed for linear fit of rate data	$\ln[A]$ vs. t
relationship between slope of linear plot and rate constant	$k = -\text{slope}$
half-life	$t_{1/2} = \frac{0.693}{k}$



$$\ln [A]_t = -kt + \ln [A]_0$$

$$y = mx + b$$

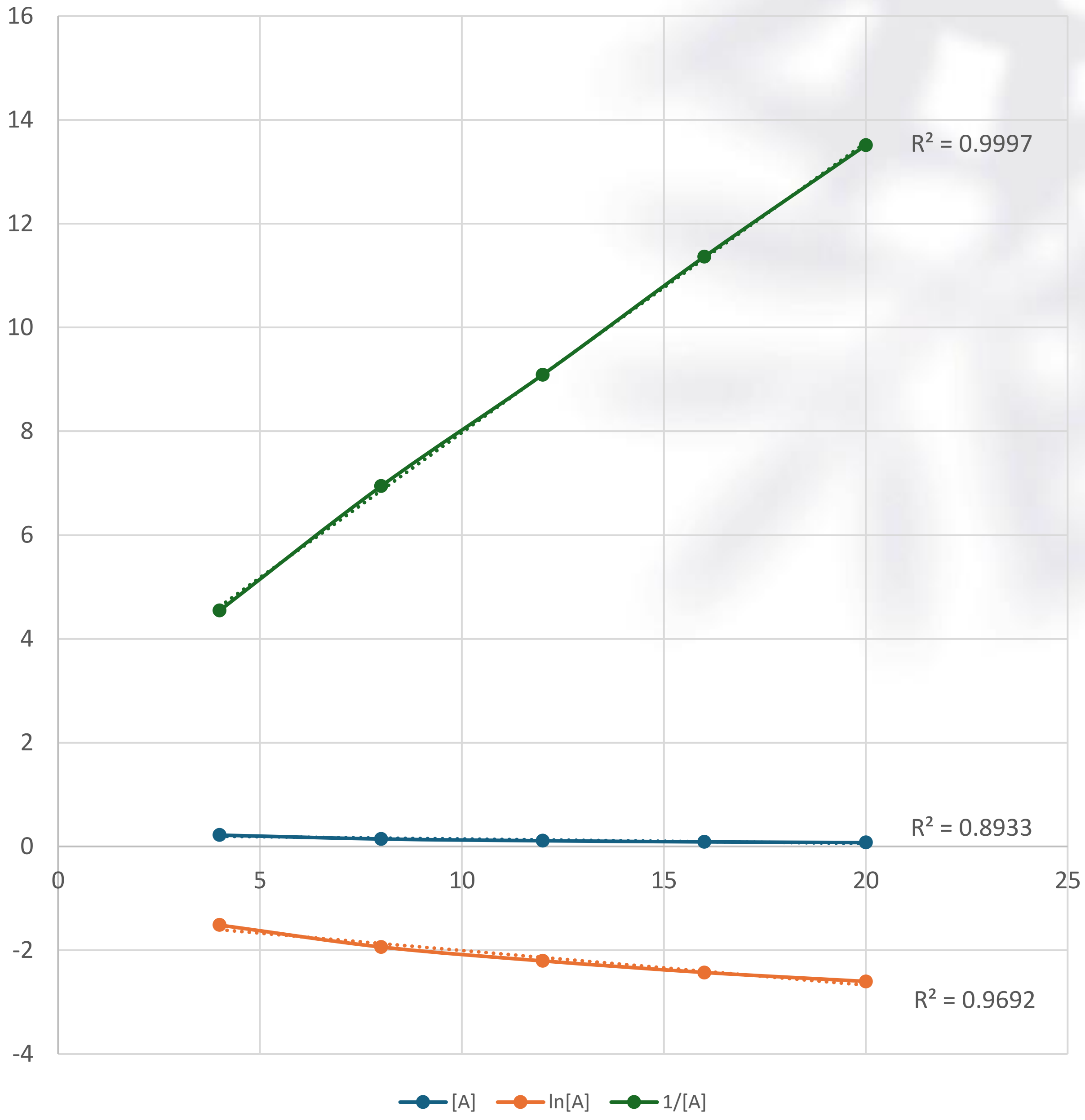


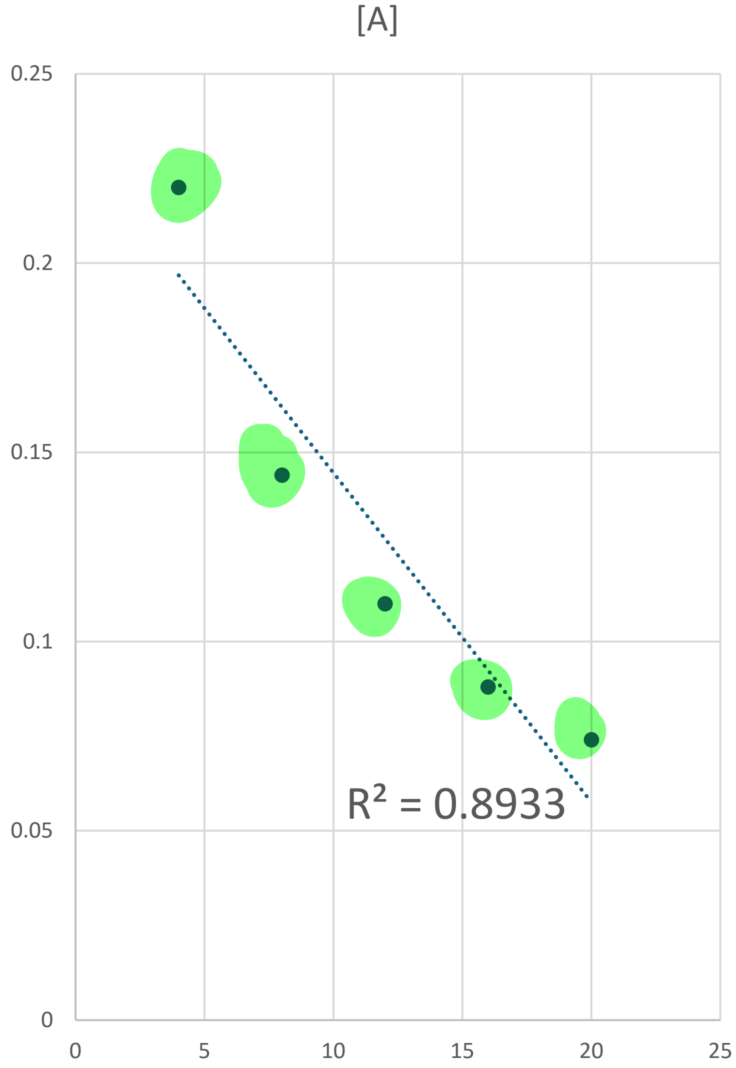
	Zeroth Order	First Order	Second Order
Differential rate law	$\text{Rate} = -\frac{\Delta[A]}{\Delta t} = k$	$\text{Rate} = -\frac{\Delta[A]}{\Delta t} = k[A]$	$\text{Rate} = -\frac{\Delta[A]}{\Delta t} = k[A]^2$
Concentration vs. time			
Integrated rate law	$[A] = [A]_0 - kt$	$[A] = [A]_0e^{-kt}$ or $1\text{n}[A] = 1\text{n}[A]_0 - kt$	$\frac{1}{[A]} = \frac{1}{[A]_0} + kt$
Straight-line plot to determine rate constant			

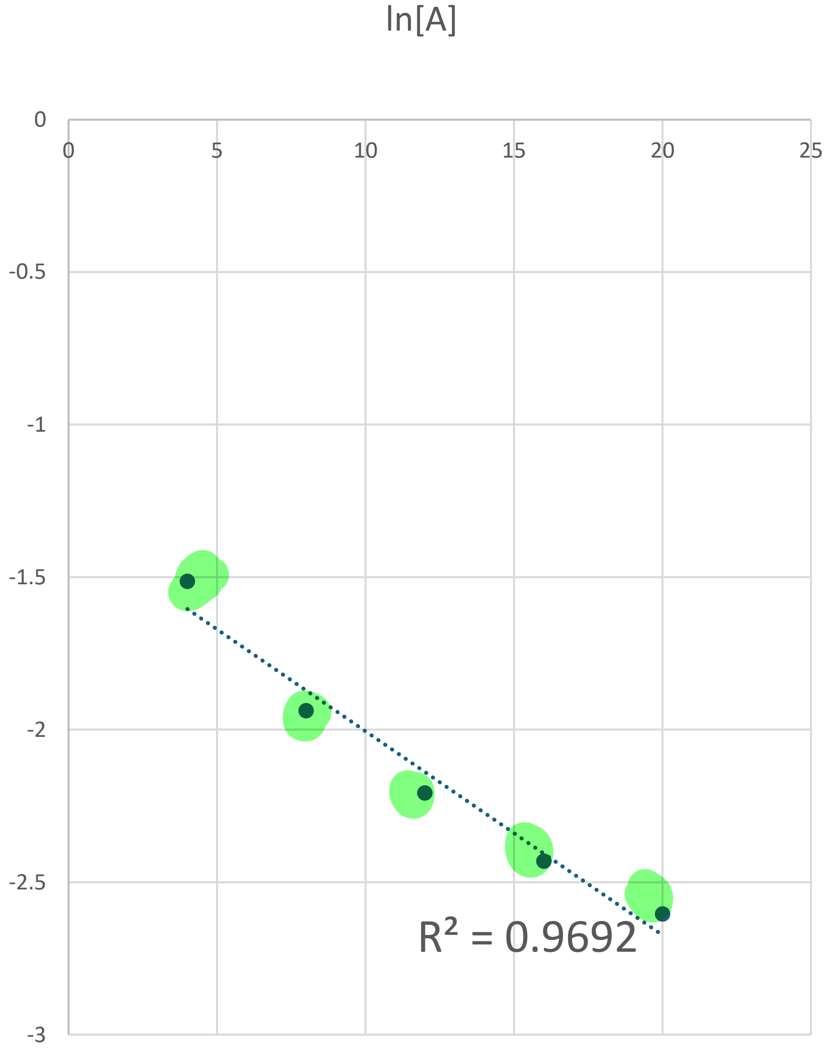
	Zeroth Order		First Order		Second Order	
Relative rate vs. concentration	[A], *M*	Rate, M/s	[A], *M*	Rate, M/s	[A], *M*	Rate, M/s
	1	1	1	1	1	1
	2	1	2	2	2	4
	3	1	3	3	3	9

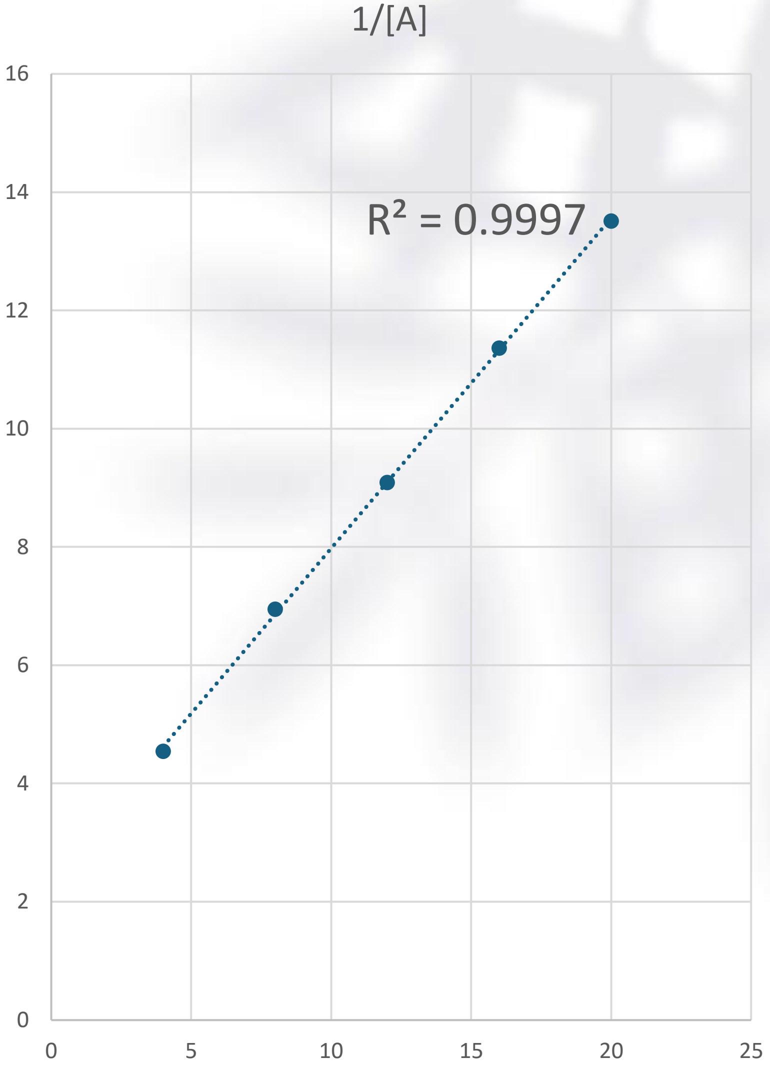
Ex) Graph the following data to determine whether the reaction, $A \rightarrow B + C$ is first order.

Trial	Time (s)	[A]
1	4.0	0.220
2	8.0	0.144
3	12.0	0.110
4	16.0	0.088
5	20.0	0.074









	Zero-Order	**First-Order**	**Second-Order**
plot needed for linear fit of rate data	$[A]$ vs. t	$\ln[A]$ vs. t	$\frac{1}{[A]}$ vs. t

FIRST-ORDER REACTIONS

k

Ex) The rate constant for the first-order decomposition of cyclobutane, C_4H_8 at 500 °C is $9.2 \times 10^{-3}\ s^{-1}$:

$$C_4H_8 \rightarrow 2C_2H_4$$

How long will it take for 80% of a sample of C_4H_8 to decompose?

	First-Order
rate law	rate = $k[A]$
units of rate constant	s^{-1}
integrated rate law	$\ln[A] = -kt + \ln[A]_0$

Ex) The rate constant for the first-order decomposition of cyclobutane, C_4H_8 at 500 °C is $9.2 \times 10^{-3}\ s^{-1}$:

$$C_4H_8 \rightarrow 2C_2H_4$$

How long will it take for 80% of a sample of C_4H_8 to decompose? t

$$\underbrace{\ln[A]_t}_{20\%} = -\overset{\checkmark\ ?}{kt} + \underbrace{\ln[A]_0}_{100\%} \rightarrow$$

80% used.

$$\ln\left(\frac{\overset{100}{[A]_0}}{\underset{20}{[A]_t}}\right) = kt \rightarrow \ln\left(\frac{[A]_{100\%}}{[A]_{20\%}}\right) = kt$$

$$t = \ln\left(\frac{x}{0.2x}\right) \times \frac{1}{k}$$

$$t = \ln(5) \times \frac{1}{9.2 \times 10^{-3} s^{-1}}$$

$$t = 1.609 \times \frac{1}{9.2 \times 10^{-3} s^{-1}}$$

$$t = 1.7 \times 10^2\ s$$

$$\ln\left(\frac{1}{0.2}\right) \times \frac{1}{k} = t$$

Iodine-131 is a radioactive isotope that is used to diagnose and treat some forms of thyroid cancer. Iodine-131 decays to xenon-131. The decay is first-order with a rate constant of 0.138 d^{-1}. How many days will it take for 90% of the iodine−131 in a 0.500 M solution of this substance to decay to Xe-131?

$$\ln\left(\frac{[A]_0}{[A]_t}\right) = kt$$

$$\ln\left(\frac{1}{0.1}\right) = (0.138\ d^{-1})(t)$$

$$2.303 = 0.138\ t$$

$$t = \boxed{16.69\ \text{days}}$$

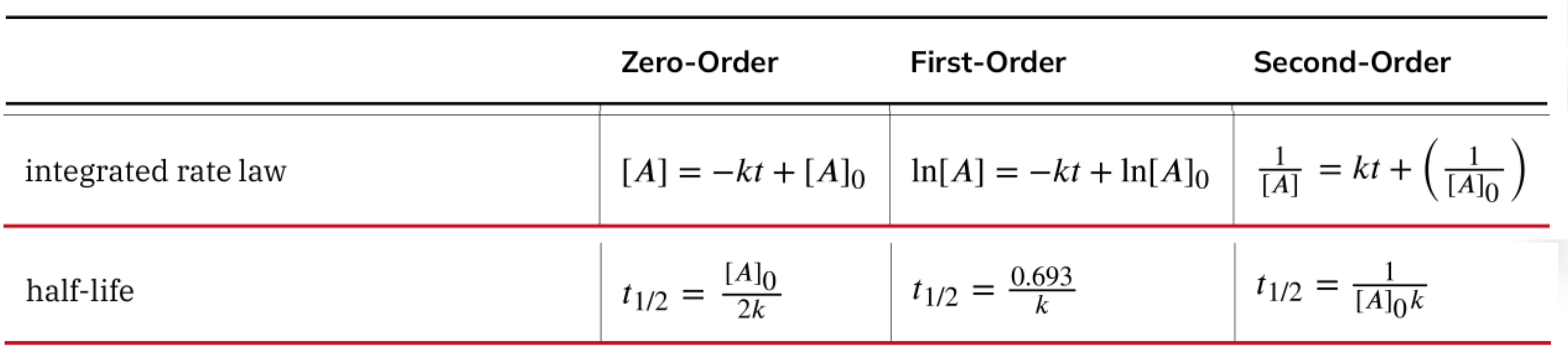
THE HALF-LIFE OF A REACTION ($T_{1/2}$)

The time required for one-half of a given amount of reactant to be consumed.

First-Order Reactions

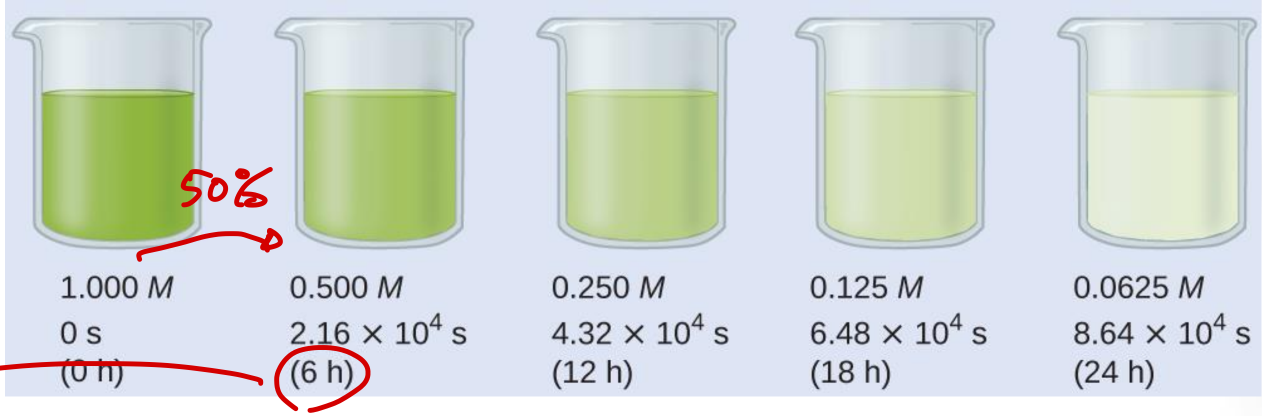
$$\ln[A]_t = -kt + \ln[A]_0 \rightarrow \ln\left(\frac{[A]_0}{[A]_t}\right) = kt \rightarrow \ln\left(\frac{[A]_{100\%}}{[A]_{50\%}}\right) = kt \rightarrow \underbrace{\ln\left(\frac{\overset{1}{[A]_{100\%}}}{\underset{0.5}{[A]_{50\%}}}\right)} \times \frac{1}{k} = t$$

$$T_{1/2} = \frac{0.693}{k}$$



	Zero-Order	First-Order	Second-Order
integrated rate law	$[A] = -kt + [A]_0$	$\ln[A] = -kt + \ln[A]_0$	$\frac{1}{[A]} = kt + \left(\frac{1}{[A]_0}\right)$
half-life	$t_{1/2} = \frac{[A]_0}{2k}$	$t_{1/2} = \frac{0.693}{k}$	$t_{1/2} = \frac{1}{[A]_0 k}$

Ex) Calculate the rate constant for the first-order decomposition of hydrogen peroxide in water at 40 °C



$$T_{1/2} = \frac{0.693}{k} \rightarrow k = \frac{0.693}{t_{1/2}} = \frac{0.693}{2.16 \times 10^{4} s} = 3.21 \times 10^{-5}\ s^{-1}$$

days^{-1}

Ex) The first-order radioactive decay of iodine-131 exhibits a rate constant of 0.138 d^{-1}. What is the half-life for this decay?

$$T_{1/2} = \frac{0.693}{k}$$

$$\frac{0.693}{0.138\, d^{-1}} \quad 5.02 \text{ days}$$

$$\frac{0.693}{0.138\, \frac{1}{\text{days}}}$$

Stop Here

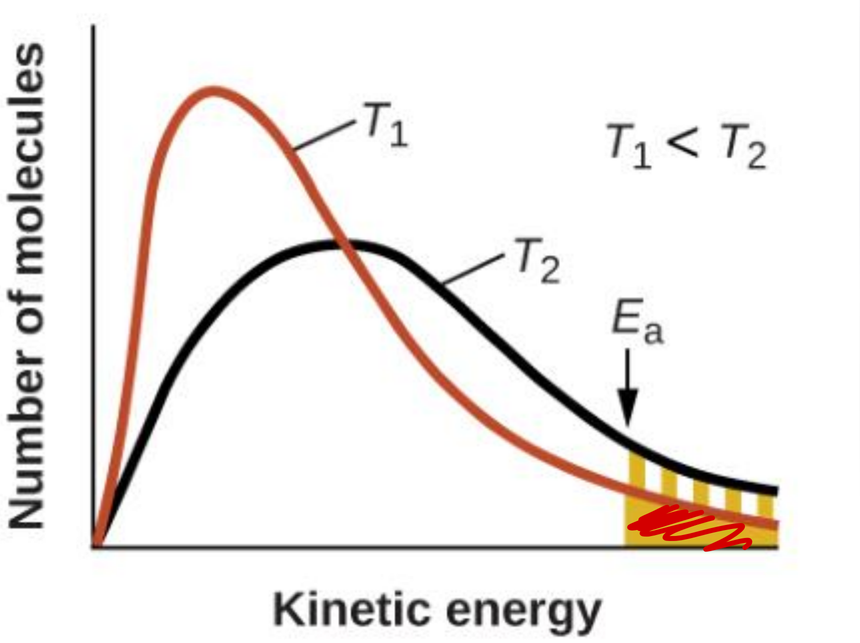
ACTIVATION ENERGY (E_a)

The minimum energy necessary to form a product during a collision between reactants

A → ← B

↳ AB

- High activation energy compared to average kinetic energy:
  - Reaction occurs slowly
  - Few molecules have enough energy to react
- Low activation energy compared to average kinetic energy:
  - Reaction occurs rapidly
  - Many molecules have sufficient energy to react



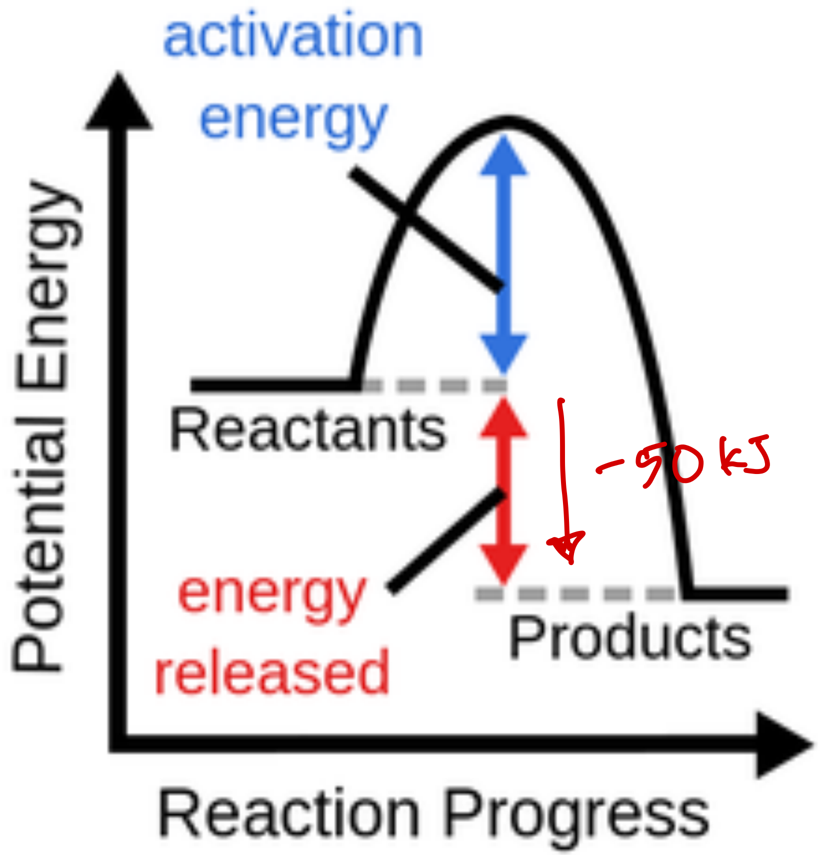
REACTION DIAGRAM

$2H_2 + O_2 \rightarrow 2H_2O$

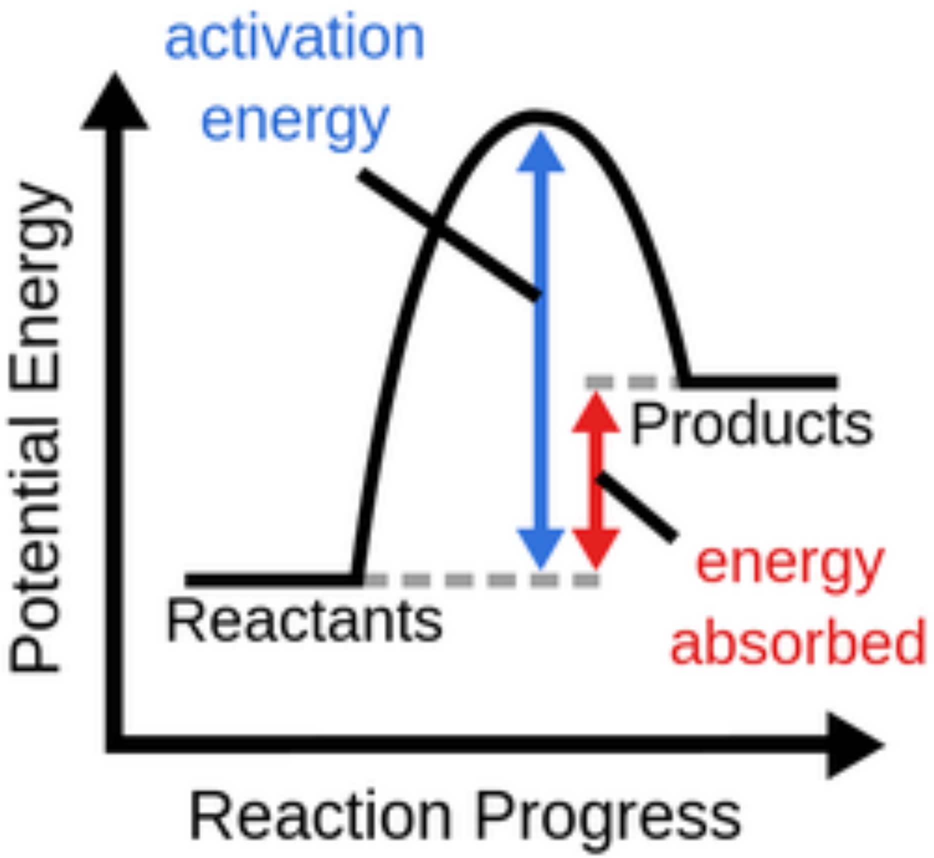
H–H

H–H

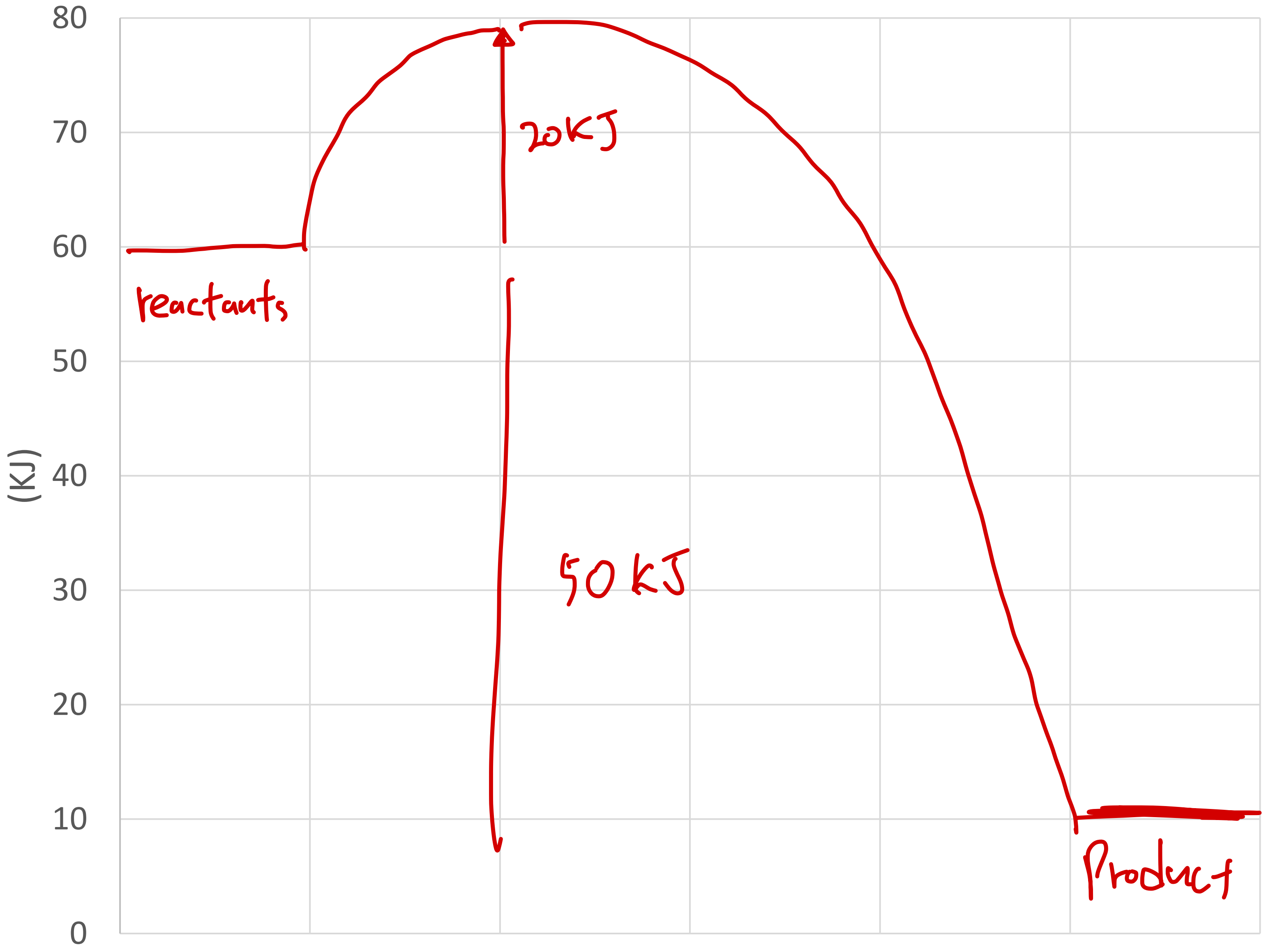
O=O



Exothermic reaction



Endothermic reaction



The $E_{a(forward)}$ is 20 kJ, and the ΔH_{rxn} for the reaction is -50 kJ. Draw a reaction energy diagram for this reaction, and calculate $E_{a(reverse)}$.

ARRHENIUS EQUATION

$$k = Ae^{-E_a/RT}$$

R = ideal gas constant, 8.314 $^{J}/_{mol \cdot K}$

$0.08206 \frac{atm \cdot L}{mol \cdot K}$

T = Temperature (kelvin) °C + 273.15 =

Ea = the activation energy $^{J}/_{mol}$

e = 2.7183

A = frequency factor (related to the frequency of collisions and the orientation of the reacting molecules)

k = rate constant

K_1 K_2

Ex) For the reaction $CH_4 + 2S_2 \rightarrow CS_2 + 2H_2S$ The rate constant is 1.1 $M^{-1}s^{-1}$ at 550 °C. What would be the rate constant at 625 °C? E_a =1.4 x 10 ^{5} J/mol

Step 1. Solve for A using the Arrhenius equation

$k = Ae^{-E_a/RT}$

$1.1 = (A)e^\wedge\frac{-1.4 \times 10^5}{8.314 \times (550+273.15)}$

$1.1 = A \times (1.2 \times 10^{-9})$

$A = 9.17 \times 10^8 \frac{1}{Ms}$

Step 2. Use A to find the rate constant at the new temperature

$k_2 = (9.17 \times 10^8)e^\wedge\frac{-1.4 \times 10^5}{8.314 \times (625+273.15)}$

$k_2 = 9.17 \times 10^8 \times 6.95 \times 10^{-9}$

$k2 = 6.37 \frac{1}{Ms}$

$$\frac{k = \cancel{A} e^{-\frac{E_a}{RT}}}{k = \cancel{A}(e^{+\frac{E_a}{RT}})}$$

$$\frac{k_2}{k_1} = e^{-\frac{E_a}{RT}} e^{+\frac{E_a}{RT}}$$

$$\ln\left(\frac{K2}{K1}\right) = \frac{E_a}{R}\left(\frac{1}{T1} - \frac{1}{T2}\right)$$

Can be used to bypass solving for A

② ①

Ex) The rate constant for the decomposition of N_2O_5 in the gas phase is 1.66 L/mol/s at 650 K and 7.39 L/mol/s at 700 K. Assuming the kinetics of this reaction follow the Arrhenius equation, calculate the activation energy for this decomposition.

$$ln\left(\frac{K2}{K1}\right) = \frac{E_a}{R}\left(\frac{1}{T1} - \frac{1}{T2}\right)$$

$$\ln\left(\frac{7.39}{1.66}\right) = \frac{Ea}{8.314}\left(\frac{1}{650} - \frac{1}{700}\right)$$

$$\frac{1.4933}{9.136 \times 10^{-4}} = \boxed{Ea = 1634.48\ J/mol}$$

REACTION MECHANISM

A way of investigating how a chemical reaction occurs in detail.

Elementary Reaction/Process

The each step of the reaction such as breaking bonds, forming new bonds, or changing the position of the atoms.

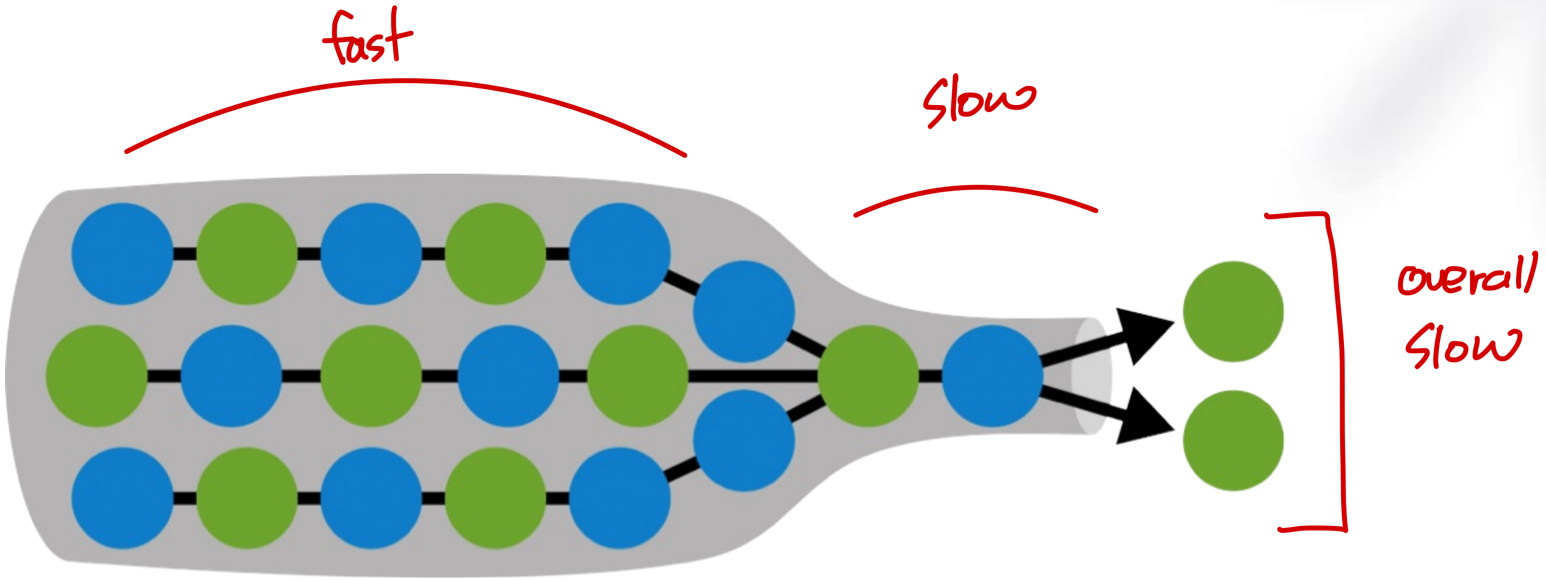
Intermediate

Species that are produced in one of the elementary steps, then are completely consumed in a ~~alter~~ step.

Later

RATE-DETERMINING STEP

During a reaction, one of the steps often takes place in a much slower manner than the other, and the slowest step then limits the rate for the entire reaction process. This slowest step is the rate-determining step.



$A + A \rightarrow X$ Rate = $k_1[A]^2$ (fast)

$X + B \rightarrow Y$ Rate = $k_2[X][B]$ (slow) ← Rate-determining Step

$Y + B \rightarrow D$ Rate = $k_3[Y][B]$ (fast)

$[A]^2$ replaces [X] since X is an intermediate.

Rate = $k_2(\overset{[X]}{K_1[A]^2})[B]$

Rate = $(K_2 \times K_1)\ [A]^2[B]$ Note: K_2 x K_1 becomes just K overall.

Rate = $K[A]^2[B]$

Ex)

$H_2 + IBr \leftrightarrow HI + HBr$ (fast) Forward (k1) Backward (k2)

$HI + Ibr \rightarrow I_2 + HBr$ (slow) Forward (k3)

- Overall rate law expression?
- Overall k calculation?

$$\text{rate} = k_1 [H_2][IBr]$$

$$\text{rate} = k_2 [HI][HBr]$$

$$\text{rate} : k_3 \underline{[HI]}[IBr]$$

$$K = \frac{k_3 \cdot k_1}{k_2}$$

$$\boxed{\frac{k_1 [H_2][IBr]}{k_2 [HBr]}} = \underline{[HI]}$$

$$\text{rate} = k_3 \left(\frac{k_1 [H_2][IBr]}{k_2 [HBr]} \right) [IBr]$$

$$\text{rate} \boxed{= \bigcirc\!\!\!\!\!K\ [H_2][HBr]^{-1}[IBr]^2}$$

CATALYST

- Catalysts provide an alternative reaction pathway with a lower activation energy, making it easier for reactants to convert into products.
- Catalysts are not consumed in the reaction and can be used repeatedly.