Unit 5

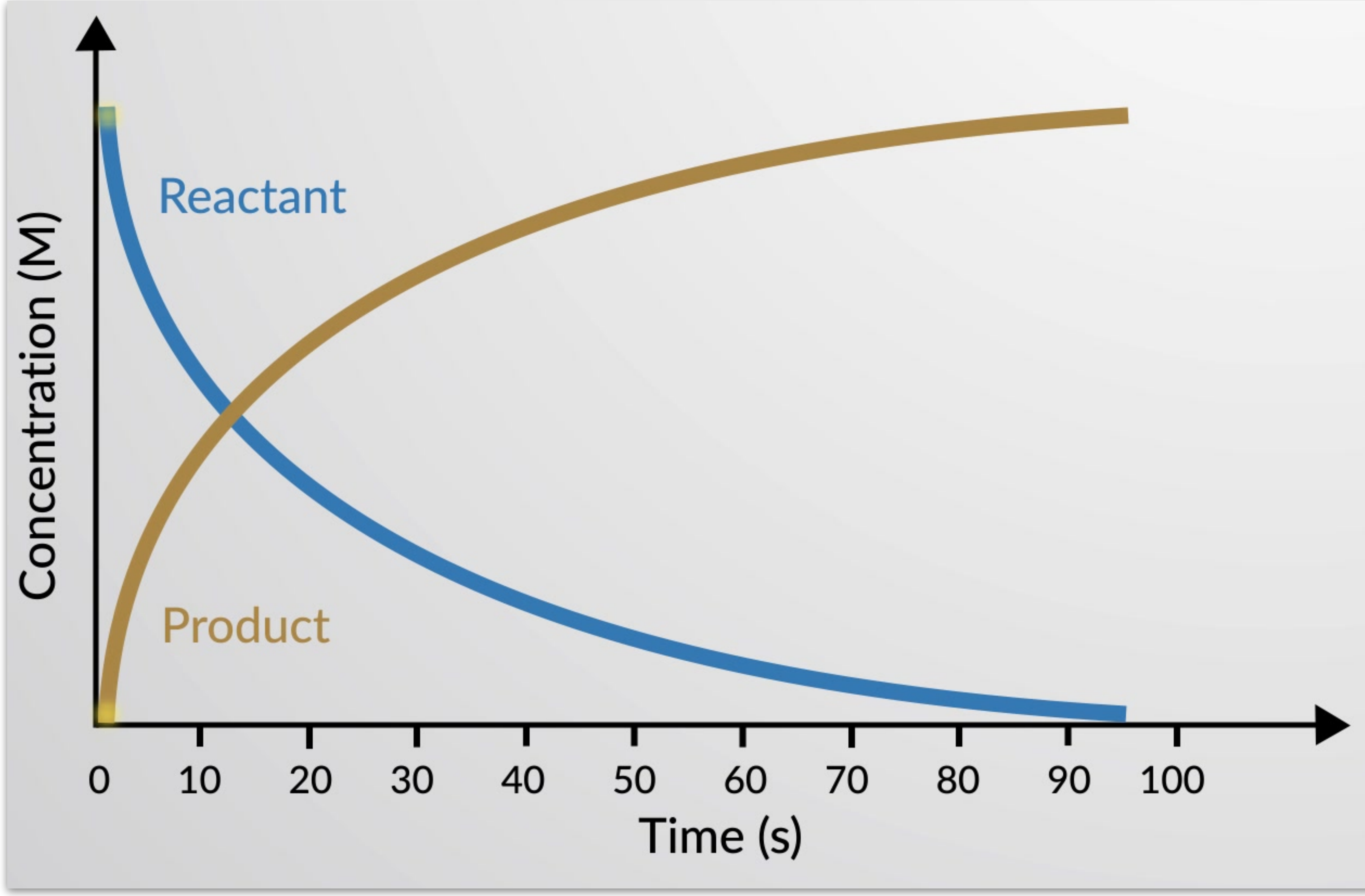
Kinetics

5.1 Reaction Rates
5.2 Introduction to Rate Law

- Reaction Rates
- The Order of Reactions
- Rate Laws

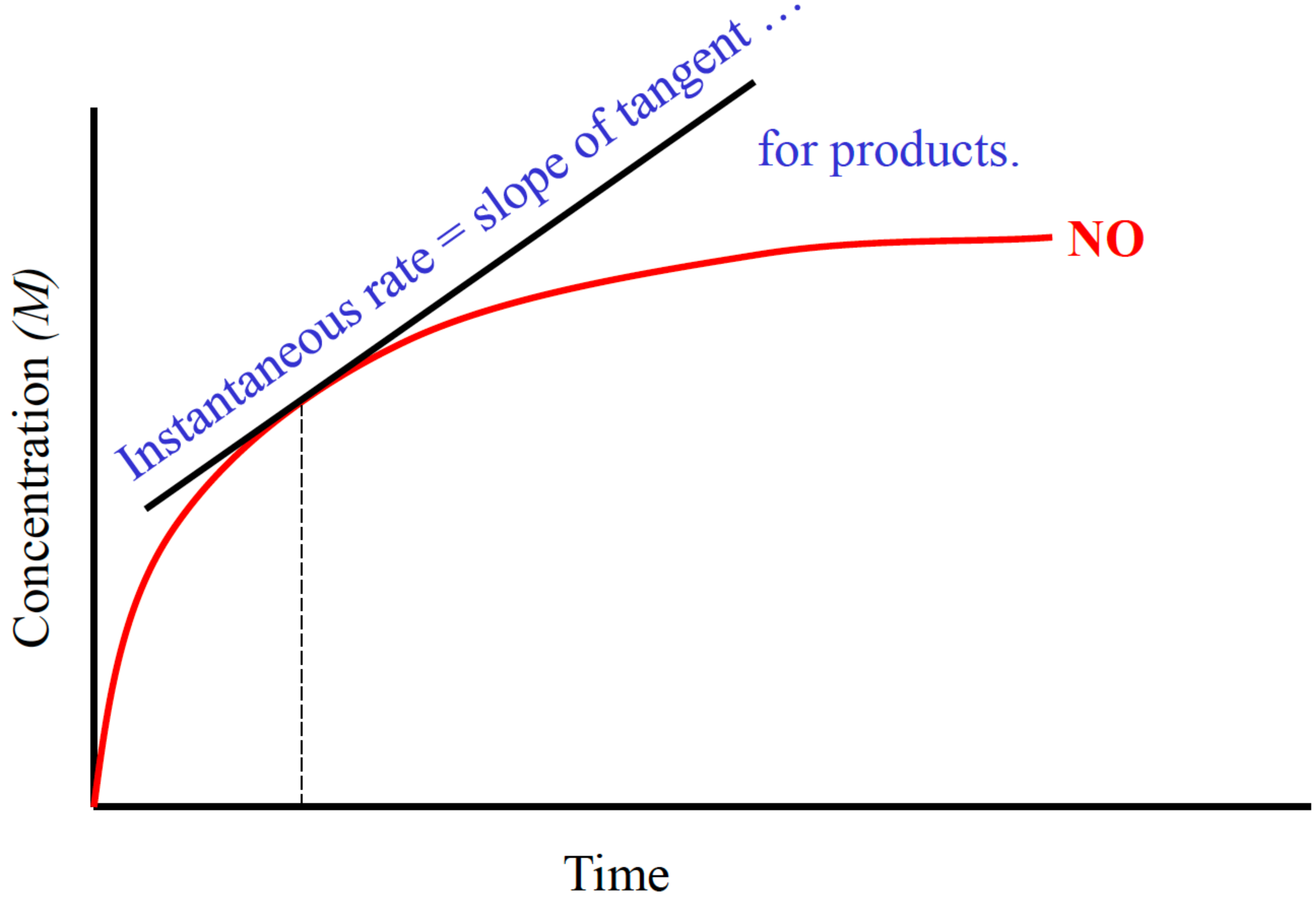
Kinetics - The Study of Reaction Rates

- The rate of a reaction can be viewed 3 ways:
  1. The rate of disappearance of a reactant.
  2. The rate of appearance of a product.
  3. The rate at which the overall reaction proceeds.



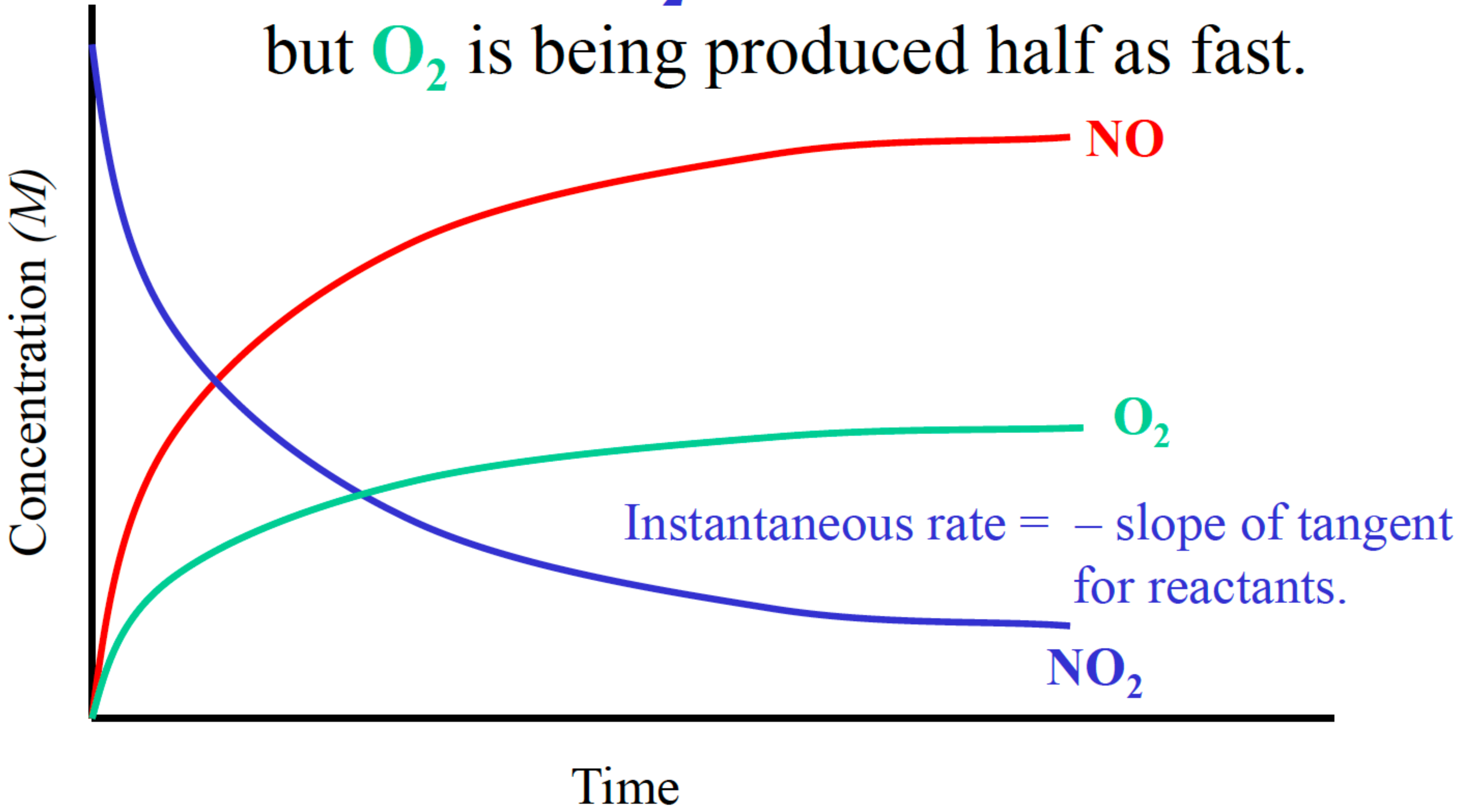
- All reaction rates are found by looking at the change in concentration over a period of time.
- Reaction rate is ALWAYS positive.

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



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

NO and **NO_2** share the same rate,
but **O_2** is being produced half as fast.



Instantaneous rate = – slope of tangent for reactants.

Rate Law

- The rate of the overall reaction

$$A + B \rightarrow C + D$$

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

Rate = rate of disappearance of reactants (concentration/time)

k = rate constant, or proportionality constant (temp dependent)

m = reaction order in terms of A

n = reaction order in terms of B

Reaction Order

- Reaction order CANNOT be predicted from the balanced equation. They can only be found experimentally.

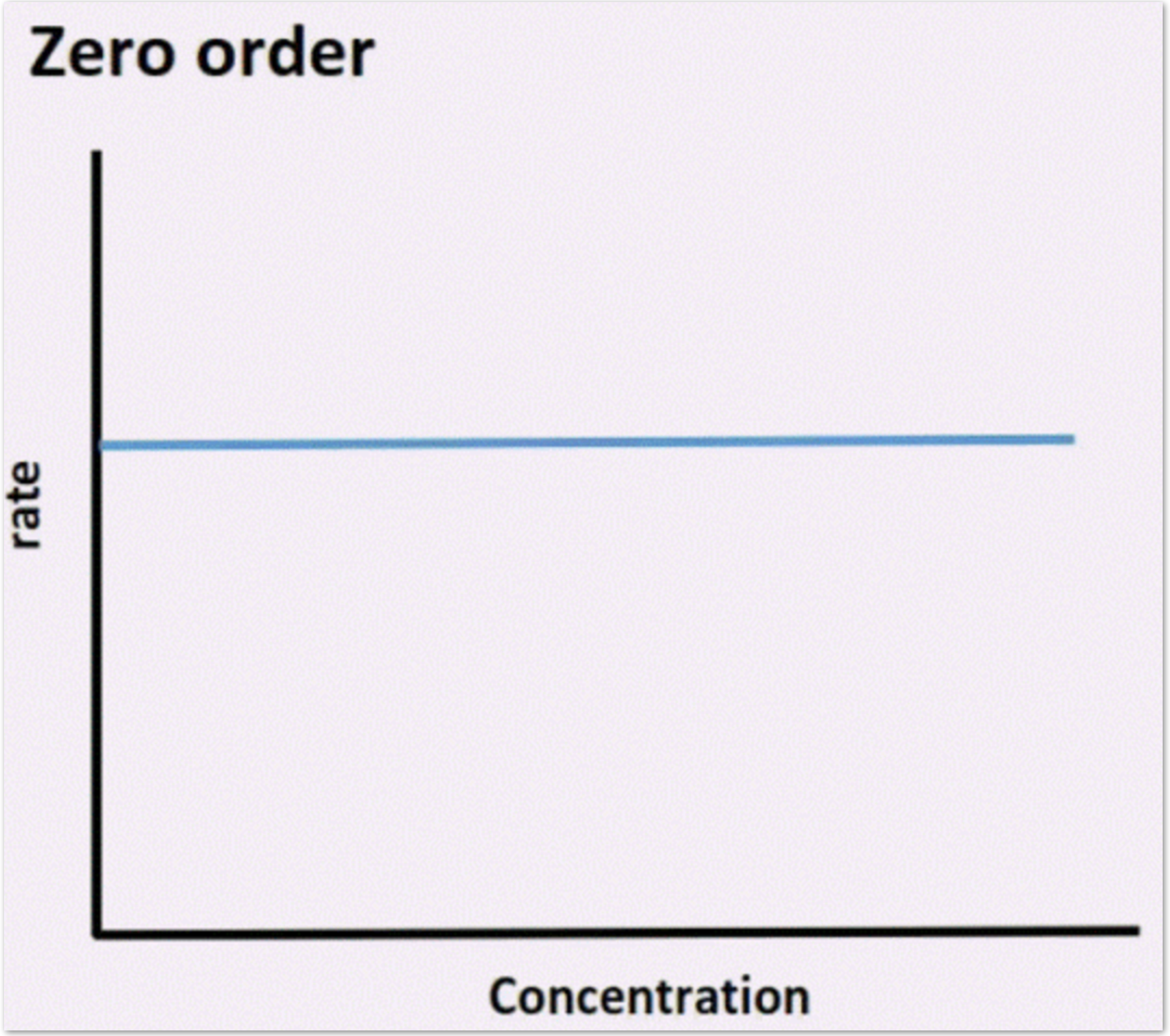
Reaction orders may be:

- Zero Order
- First Order
- Second Order

Zero Order Reactions

- Doubling the concentration of a reactant has no affect on the reaction rate.

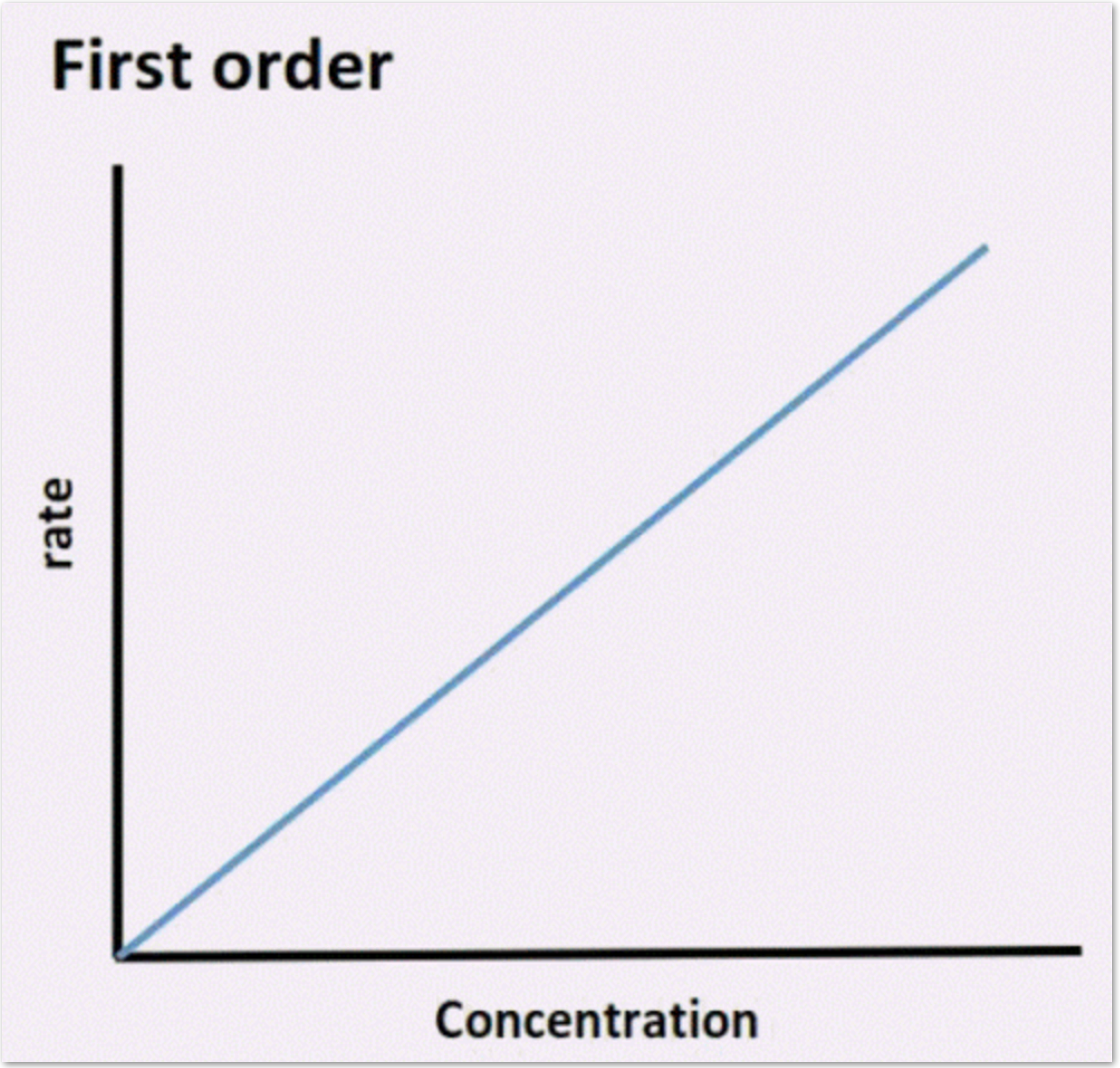
Rate = $k[A]^0$ or … Rate = k



First Order Reactions

- Doubling the concentration of that species doubles the reaction rate. (Changes in concentration result in proportional changes in rate.)

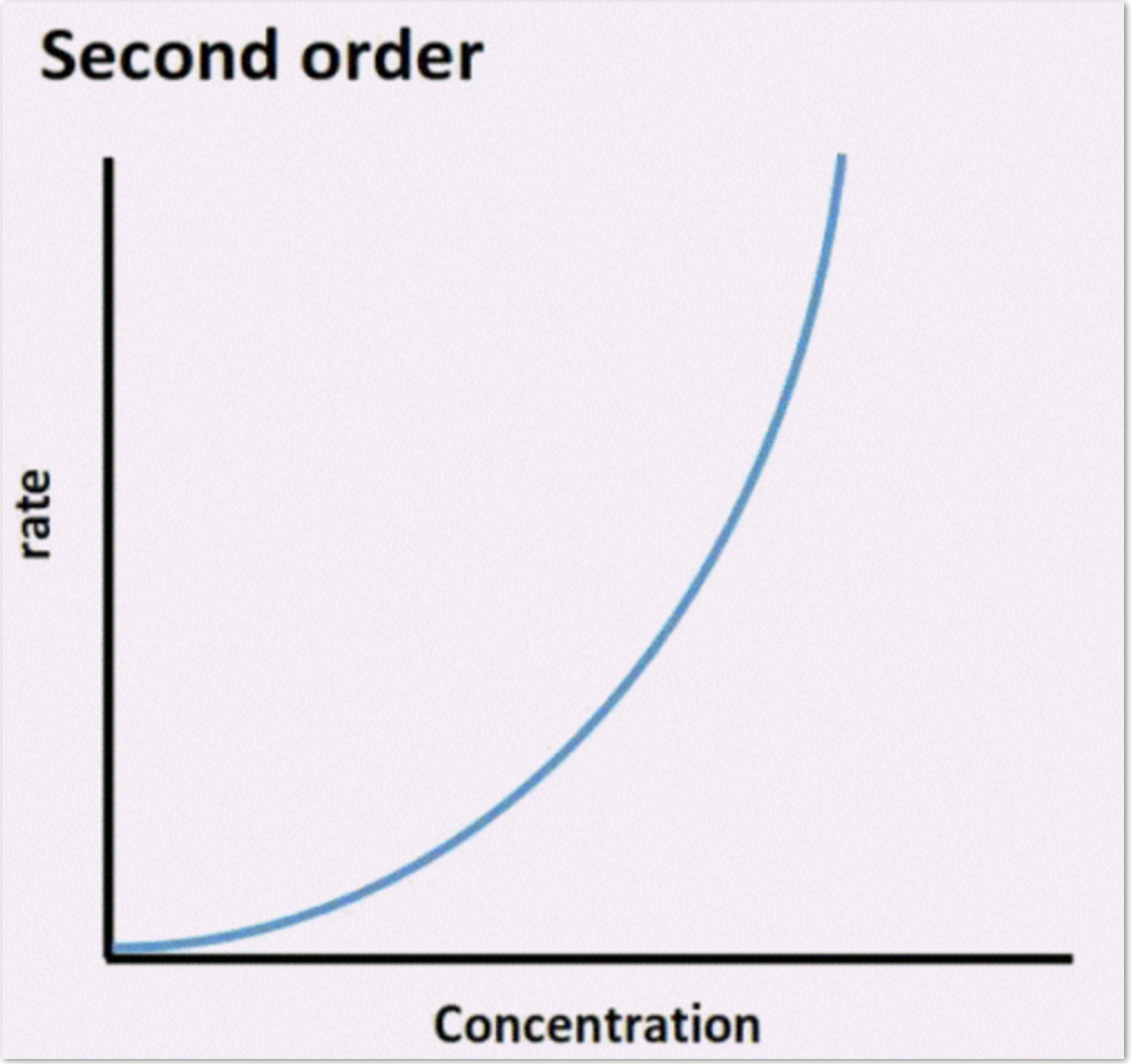
$$\text{Rate} = k[\text{A}]^1$$



Second Order Reactions

- Doubling the concentration of a reactant quadruples (squares) the reaction rate.

Rate = $k[A]^2$



Overall Order for a Reaction

- To find the overall order of a reaction you simply add the exponents in the rate law.

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

- Overall order of the reaction = m + n

Units for *k* - The Rate Constant

Order of Reaction	Basic Formula	Units for *k*
0	Rate = k	Ms^{-1}
1	Rate = $k[A]$	
2	Rate = $k[A]^2$	
3	Rate = $k[A]^3$	

To the board!!!

Example: Initial Rates Method

- Three experiments were conducted at a specific temperature for the following reaction. $2\ NO_{(g)} + 2\ H_{2(g)} \rightarrow N_{2(g)} + 2\ H_2O_{(g)}$

Experiment	$[NO]_{initial}$	$[H_2]_{initial}$	$Rate_{initial}$
1	0.20	0.30	0.0900
2	0.10	0.30	0.0225
3	0.10	0.20	0.0150

- Find the Rate Law, *k* and the overall order for the reaction.

Example 2: Initial Rates Method

$$\underset{\text{(colorless)}}{B_{(aq)}} + \underset{\text{(green)}}{C_{(aq)}} \rightarrow \underset{\text{(colorless)}}{D_{(aq)}} + \underset{\text{(colorless)}}{E_{(aq)}}$$

Experiment	$[B]_{initial}$	$[C]_{initial}$	$Rate_{initial}$
1	0.10	0.10	4.2×10^{-4}
2	0.10	0.20	8.3×10^{-4}
3	0.20	0.10	8.3×10^{-4}

- Find the Rate Law, *k* and the overall order for the reaction.

Reaction Rates Affected by Collisions & Catalysts

- Reaction rates increase in the presences of a catalyst (provide an alternate reaction pathway).
- Reaction rates increase when collision rates increase.
  - increase in concentration of liquid or gas reactants.
  - increases in the surface area of the reactants in the solid phase
  - temperature increases
    - when temperature increases, average kinetic energy increases ($KE = 1/2mv^2$)
    - collision rate increases as velocity increases.

5.3 Concentration Changes Over Time

- Integrated Rate Laws
- Half Life Reactions (1st order)

Zeroth Order Integrated Rate Law

This equation

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

can be integrated with calculus to produce…

$$[\text{A}]_t - [\text{A}]_o = - kt$$

$[\mathbf{A}]_o$ = the initial concentration (at $t = 0$s)

$[\mathbf{A}]_t$ = the concentration after some period of time

Zeroth Order Integrated Rate Law

$$[A]_t - [A]_o = - kt$$

can be rearranged to give…

$$\begin{array}{cccccc} {[A]_t} & = & (-k) & t & + & {[A]_o} \\ \uparrow & & \uparrow & \uparrow & & \uparrow \\ y & = & m & x & + & b \end{array}$$

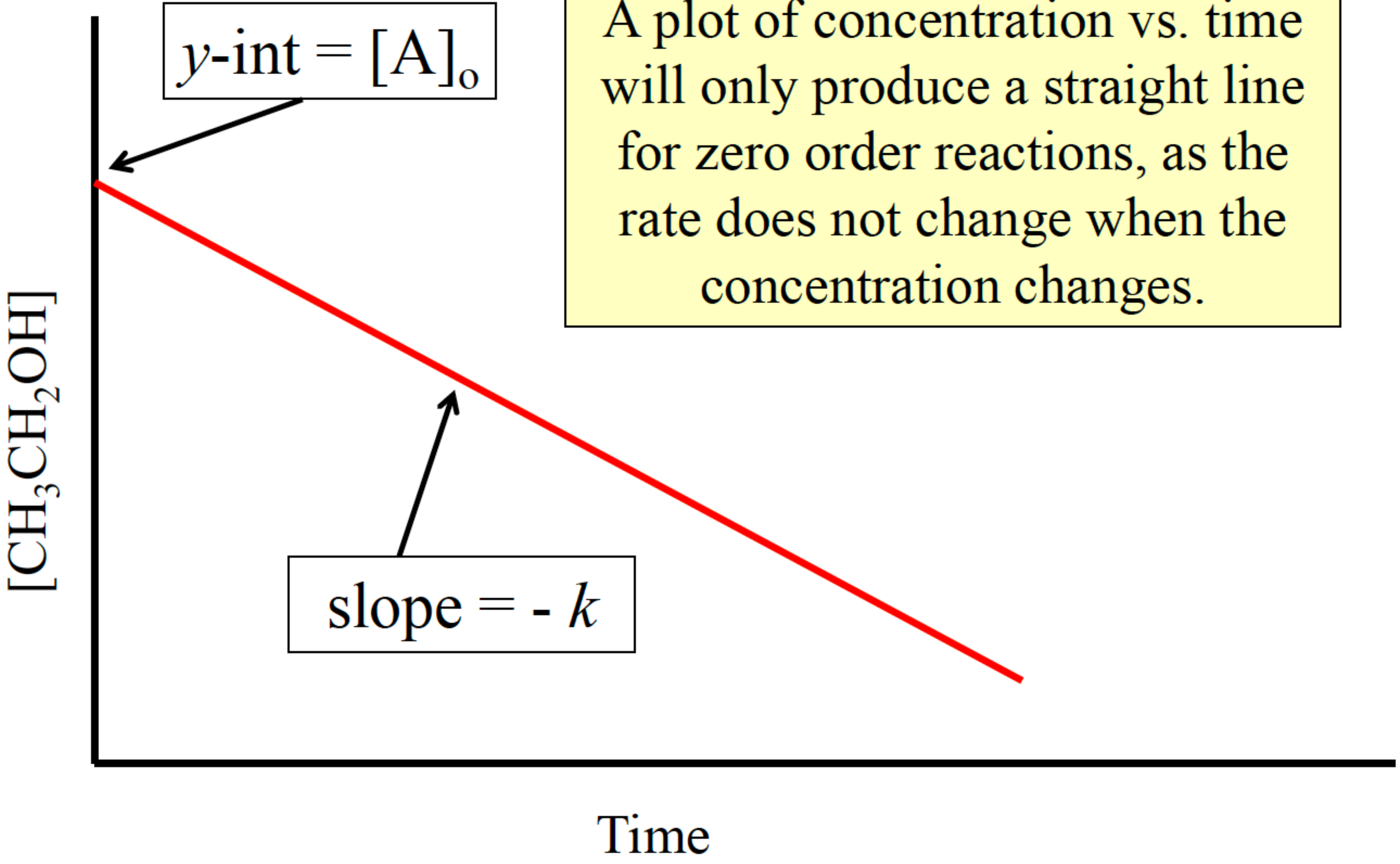
A plot of $\mathbf{[A]_t}$ vs. $\boldsymbol{t}$ produces a straight line for 0th order reactions

This is used to determine if a reaction is zeroth order, as a straight line will only occur if the reaction is zeroth order.

$[A]_t$ vs. t for 0th Order Reactions

$CH_3CH_2OH_{(g)} \rightarrow CH_3CHO_{(g)} + H_{2(g)}$

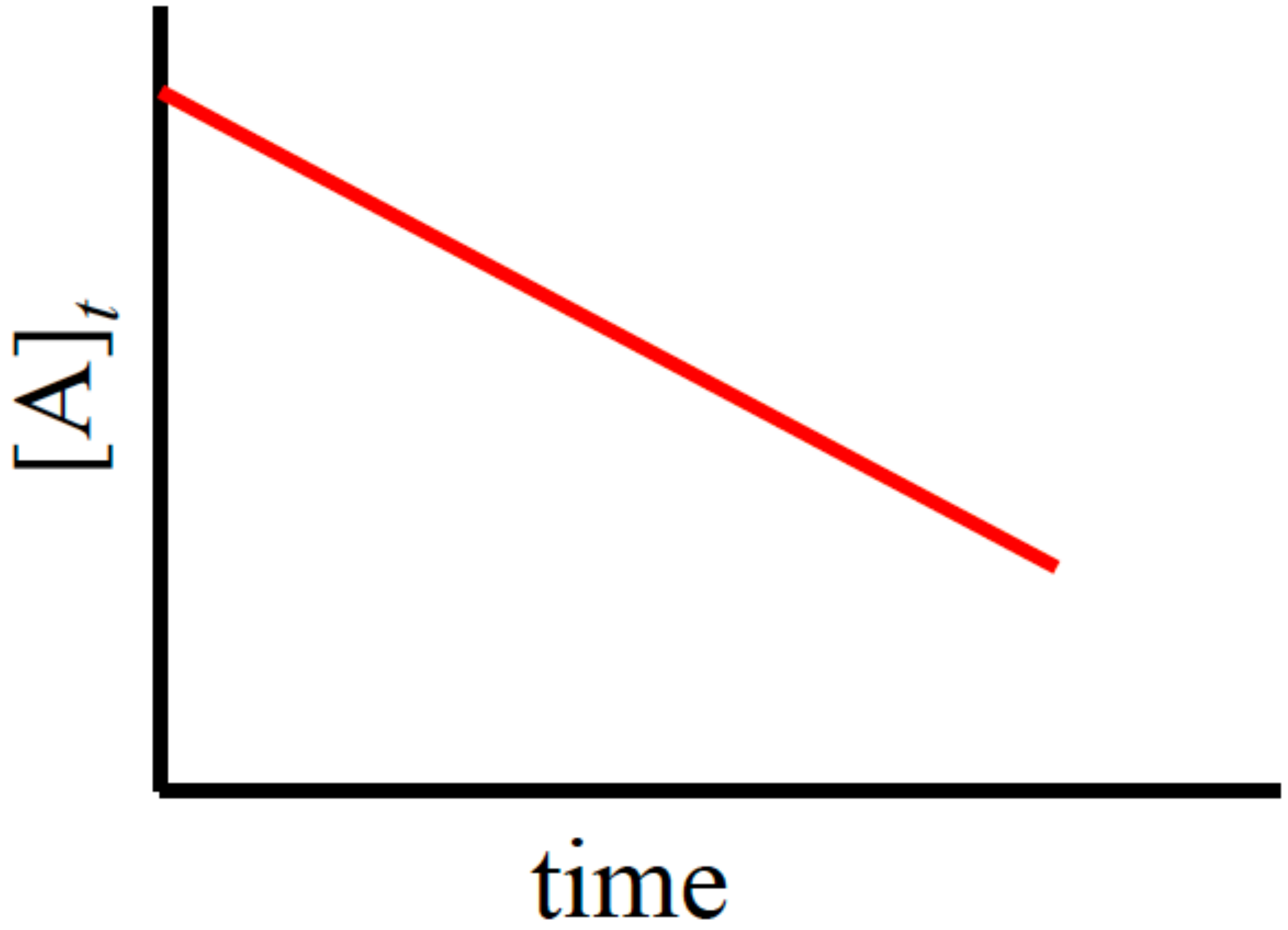
A plot of concentration vs. time will only produce a straight line for zero order reactions, as the rate does not change when the concentration changes.



Example: Zeroth Order Reactions

- Using the data provided, find the rate law and the rate constant.

Time (s)	[A] (*M*)
0.0	1.50
45.0	0.90



Example: Zeroth Order Reactions

- Rate law: We know it's a zeroth order reaction because the plot of $[A]_t$ vs. t gives a straight line.
- A → B + C tells us that A is the only reactant.

The Rate Law

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

$$\text{Rate} = k$$

Example: Zeroth Order Reactions

- To find k, use data at t = 0 and t = 45.0 s

$$-kt = [\mathrm{A}]_t - [\mathrm{A}]_\mathrm{o}$$

$$k = -\frac{[\mathrm{A}]_t - [\mathrm{A}]_\mathrm{o}}{t} = -\frac{0.90M - 1.50M}{45.0\ \mathrm{s}}$$

$$k = 1.33 \times 10^{-2}\ M/\mathrm{s}$$

First Order Integrated Rate Law

This equation

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

can be integrated with calculus to produce…

$$\ln[\text{A}]_{\text{t}} - \ln[\text{A}]_{\text{o}} = -\,kt$$

$\mathbf{[A]_o}$ = the initial concentration (at $t = 0\text{s}$)

$\mathbf{[A]}_{\boldsymbol{t}}$ = the concentration after some period of time

First Order Integrated Rate Law

$$\ln[\mathrm{A}]_t - \ln[\mathrm{A}]_\mathrm{o} = -\,kt$$

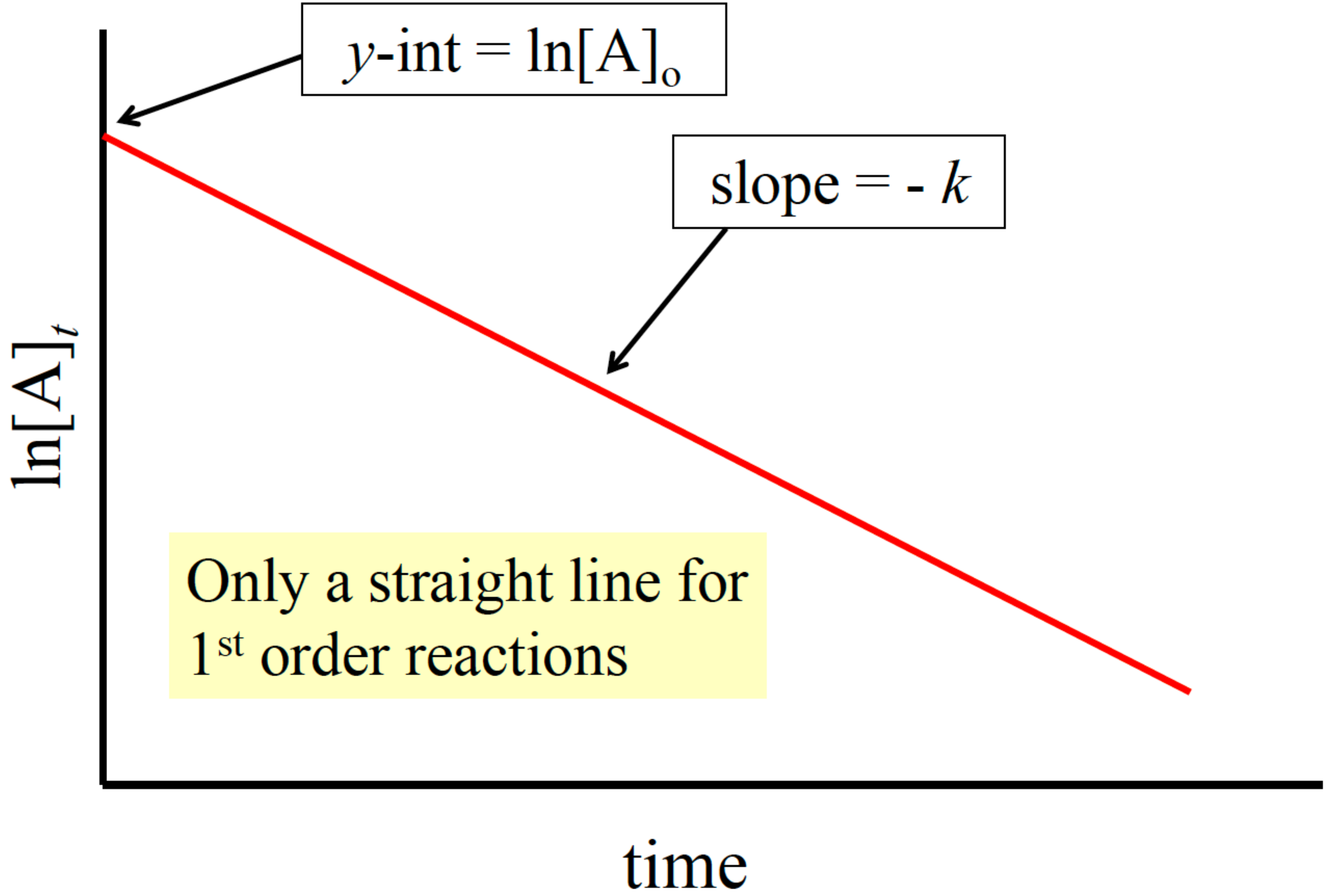
can be rearranged to give…

$$\begin{tikzcd}
\ln[\mathrm{A}]_t & = & (-k) & t & + & \ln[\mathrm{A}]_\mathrm{o} \\
y \arrow[u] & = & m \arrow[u] & x \arrow[u] & + & b \arrow[u]
\end{tikzcd}$$

A plot of $\mathbf{ln[A]_t}$ vs. $\boldsymbol{t}$ produces a straight line for 1st order reactions.

This is used to determine if a reaction is 1st order, as a straight line will only occur if the reaction is 1st order.

$\ln[A]_t$ vs. t for 1st Order Reactions



Only a straight line for 1st order reactions

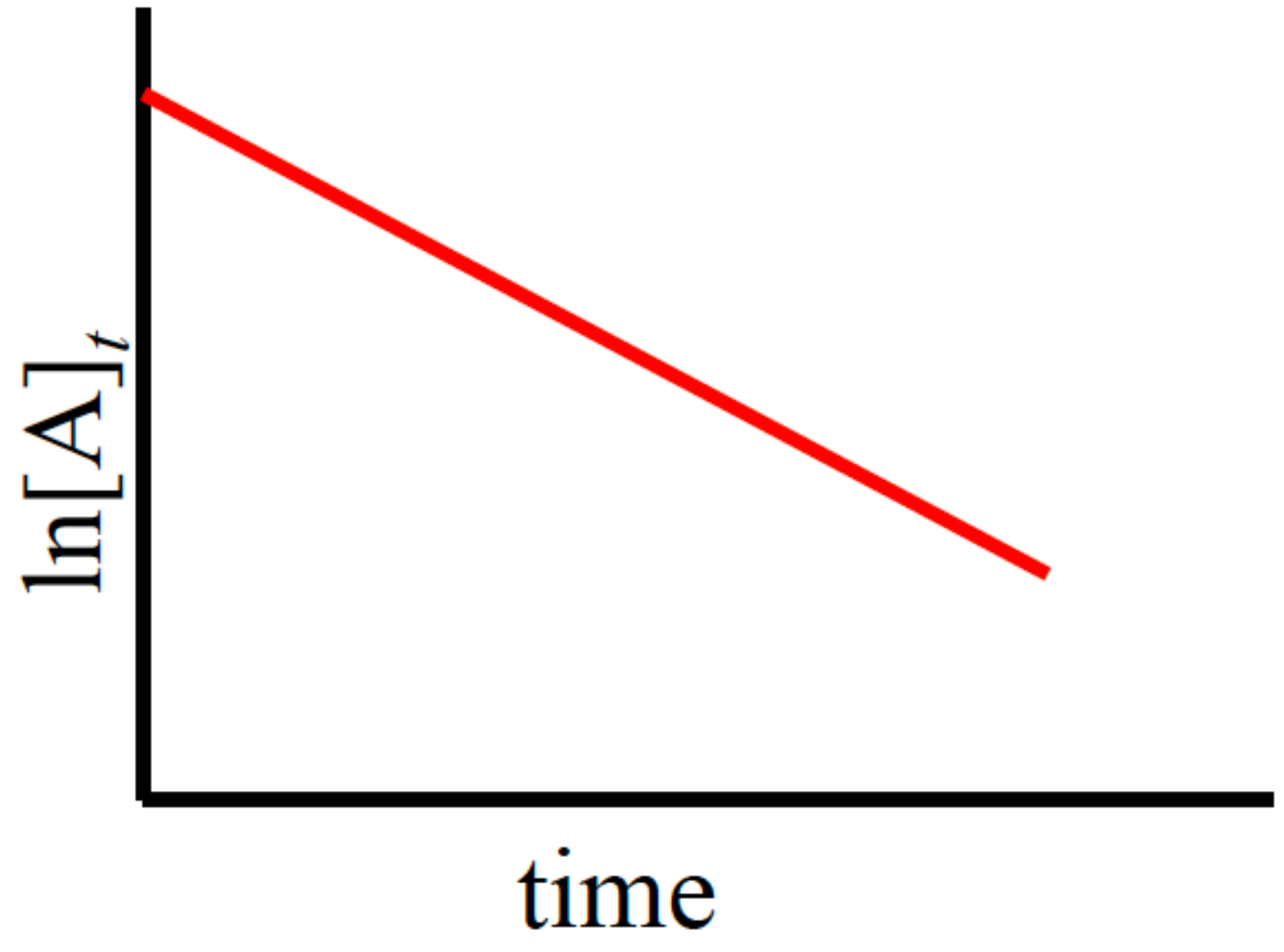
Example: First Order Reactions

$$A \rightarrow B + 2\,D$$

Ex1) Using the data provided, find:

a) The rate law.
b) The rate constant.
c) [A] at time = 5.0 x 10^2 s.

Time (s)	[A] (*M*)
0.0	0.020
5.0 x 10	0.017
1.0 x 10^2	0.014
1.5 x 10^2	0.012
2.0 x 10^2	0.010



Example: First Order Reactions

a) Find the rate law.

- ✓ We know it is a 1st order reaction, because a plot of **ln[A]$_t$** vs. ***t*** gives a straight line.
- ✓ A → B + 2 D tells us that A is the only reactant.

The Rate Law

$$\mathbf{Rate} = \boldsymbol{k}[\mathbf{A}]$$

Example: First Order Reactions

b) To find k, use data at $t = 0$ and some other time.

$$-kt = \ln[\mathrm{A}]_t - \ln[\mathrm{A}]_\mathrm{o}$$

$$k = -\frac{\ln[\mathrm{A}]_t - \ln[\mathrm{A}]_\mathrm{o}}{t} = -\frac{\ln 0.017 - \ln 0.020}{5.0 \times 10\ \mathrm{s}}$$

$$k = 3.3 \times 10^{-3}\,\mathrm{s}^{-1}$$

Example: First Order Reactions

c) To find [A] at 500 s, use data at $t = 0$

$$\ln[\mathrm{A}]_\mathrm{t} - \ln[\mathrm{A}]_\mathrm{o} = -kt$$

$$\ln[\mathrm{A}]_t = -kt + \ln[\mathrm{A}]_\mathrm{o}$$

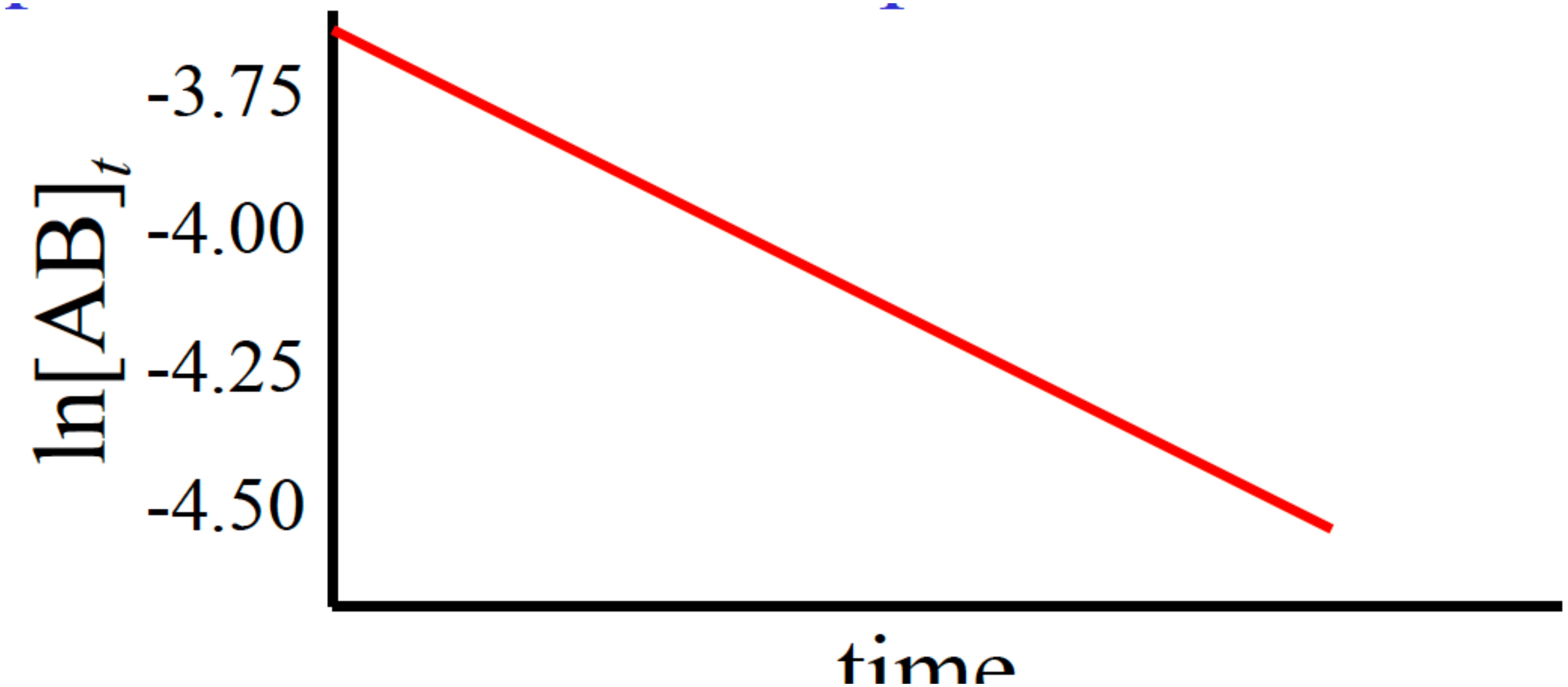
$$\ln[\mathrm{A}]_{500} = -0.0033\mathrm{s}^{-1}(5.0 \times 10^2\mathrm{s}) + \ln 0.020$$

$$[\mathrm{A}]_{500} = e^{(-0.0033 \times 500 + \ln 0.020)}$$

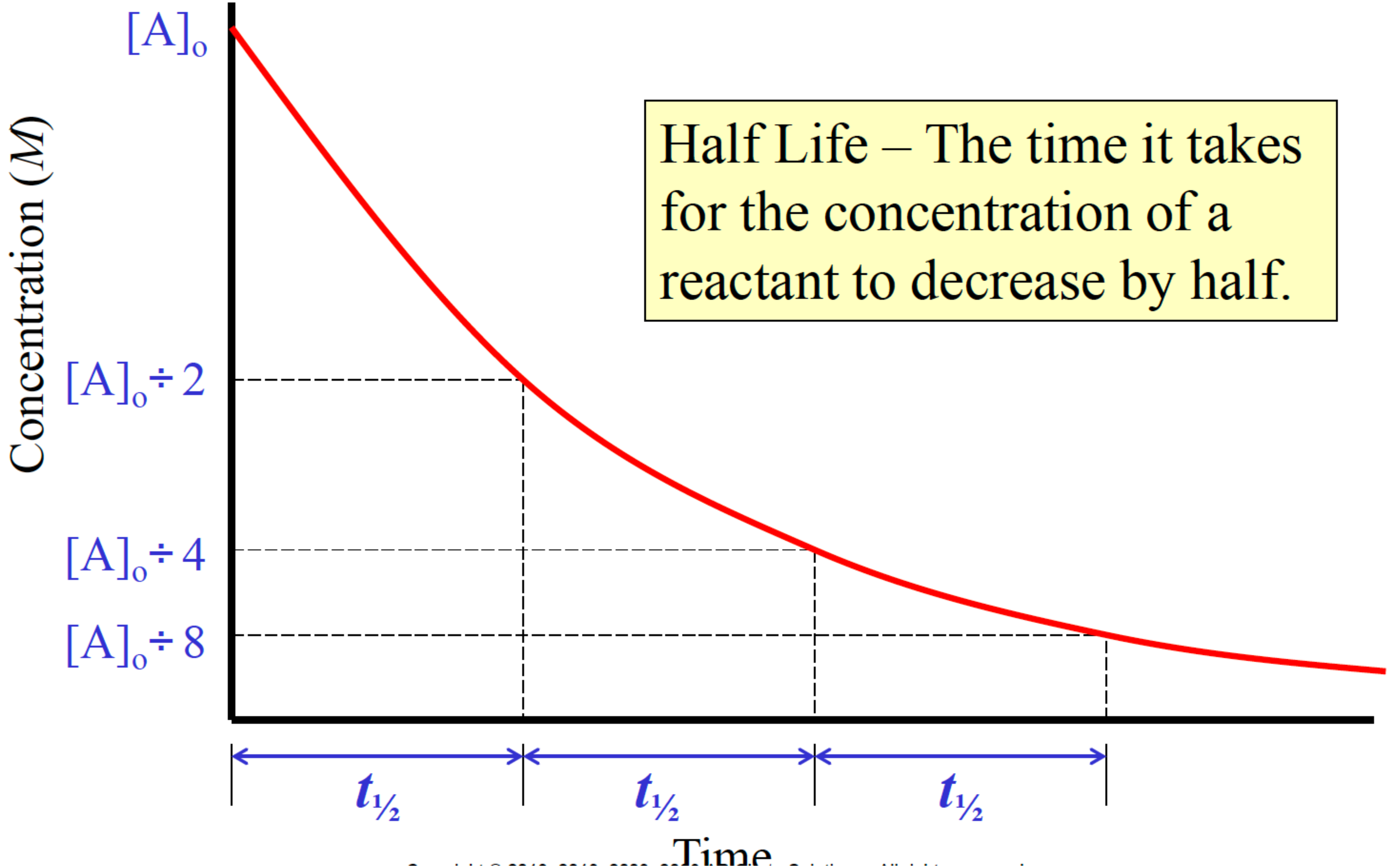
$$[\mathrm{A}]_{500} = 3.8 \times 10^{-3}\ M$$

Example #2: First Order Reactions

- Data from an experiment which examined the change in concentration over time for a first order process at 25°C was used to put the graph below. Sketch a line that shows the approximate results that would be expected if the same experiment was repeated at a lower temperature.



Half Life for 1st Order Reactions

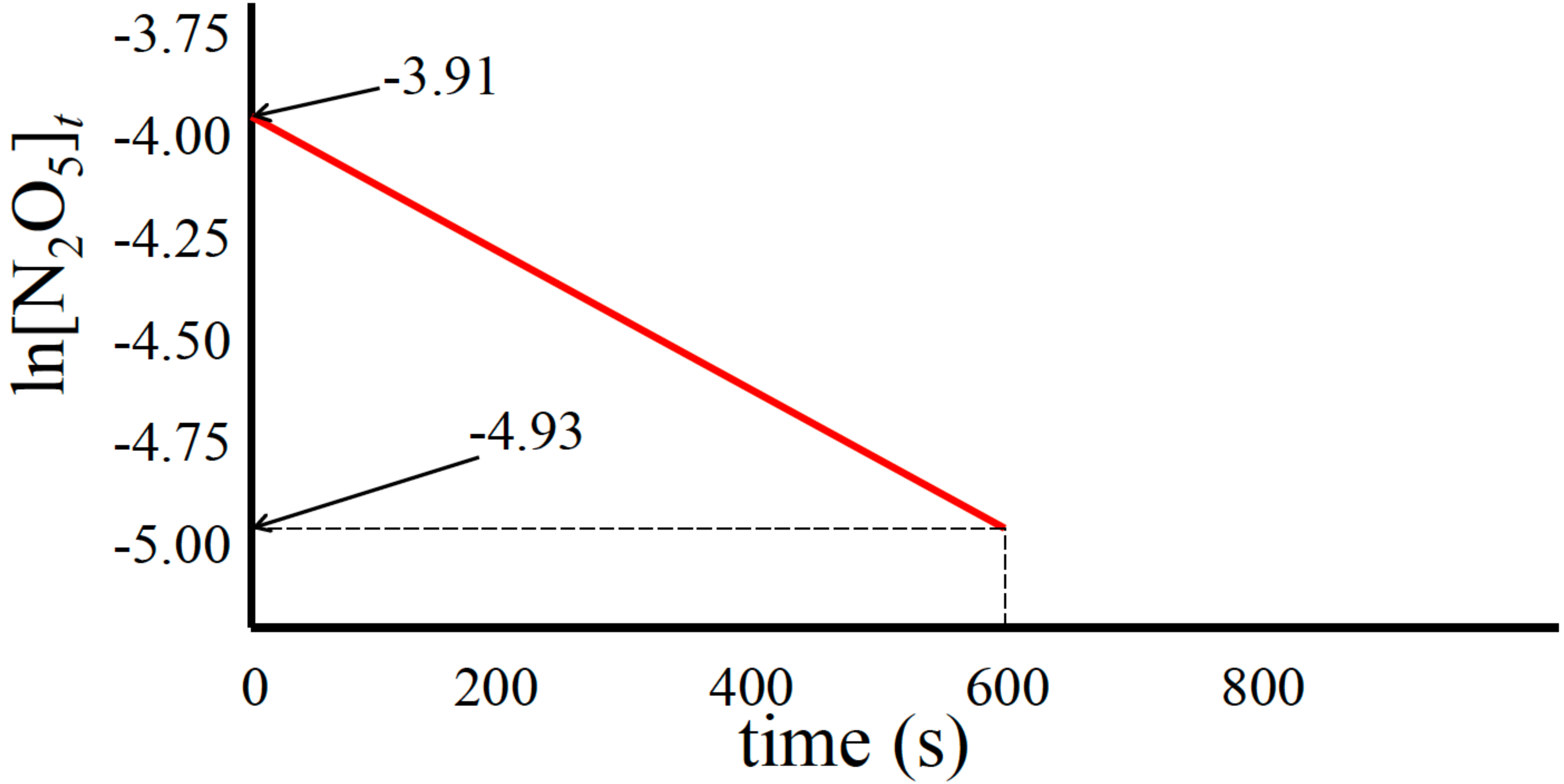


Half Life – The time it takes for the concentration of a reactant to decrease by half.

Example: Half Life for 1st Order Reactions

Ex1) Find the half life for the following reaction.

$$2\ N_2O_{5(g)} \rightarrow 4\ NO_{2(g)} + O_{2(g)}$$



Example: Half Life for 1st Order Reactions

Step 1. Find *k*

$$\text{slope} = \frac{\Delta y}{\Delta x} = \frac{-4.93-(-3.91)}{600\text{s}-0\text{s}} = \frac{-1.02}{600\text{s}}$$

$$= -1.70\times10^{-3}\,\text{s}^{-1}$$

$$k = -\text{slope} = 1.70\times10^{-3}\,\text{s}^{-1}$$

Example: Half Life for 1st Order Reactions

Step 2. Find the half life

$$-kt = \ln[\mathrm{A}]_t - \ln[\mathrm{A}]_{\mathrm{o}}$$

$$t = -\frac{\ln[\mathrm{A}]_t - \ln[\mathrm{A}]_{\mathrm{o}}}{k}$$

$$t_{1/2} = -\frac{\ln(0.5) - \ln(1)}{1.70 \times 10^{-3}\ \mathrm{s}^{-1}}$$

$$t_{1/2} = 408\ \mathrm{s}$$

For half-life problems, set the initial concentration to be 1 *M*, and the concentration after one half-life to be 0.5 *M*.

The half-life is inversely proportional to the rate constant, *k*.
If *k* is small, the rate is slow and the half-life is long.

Half Life for 1st Order Reactions

Deriving the half-life equation for first order processes

$$t_{1/2} = -\frac{\ln(0.5) - \ln(1)}{k}$$

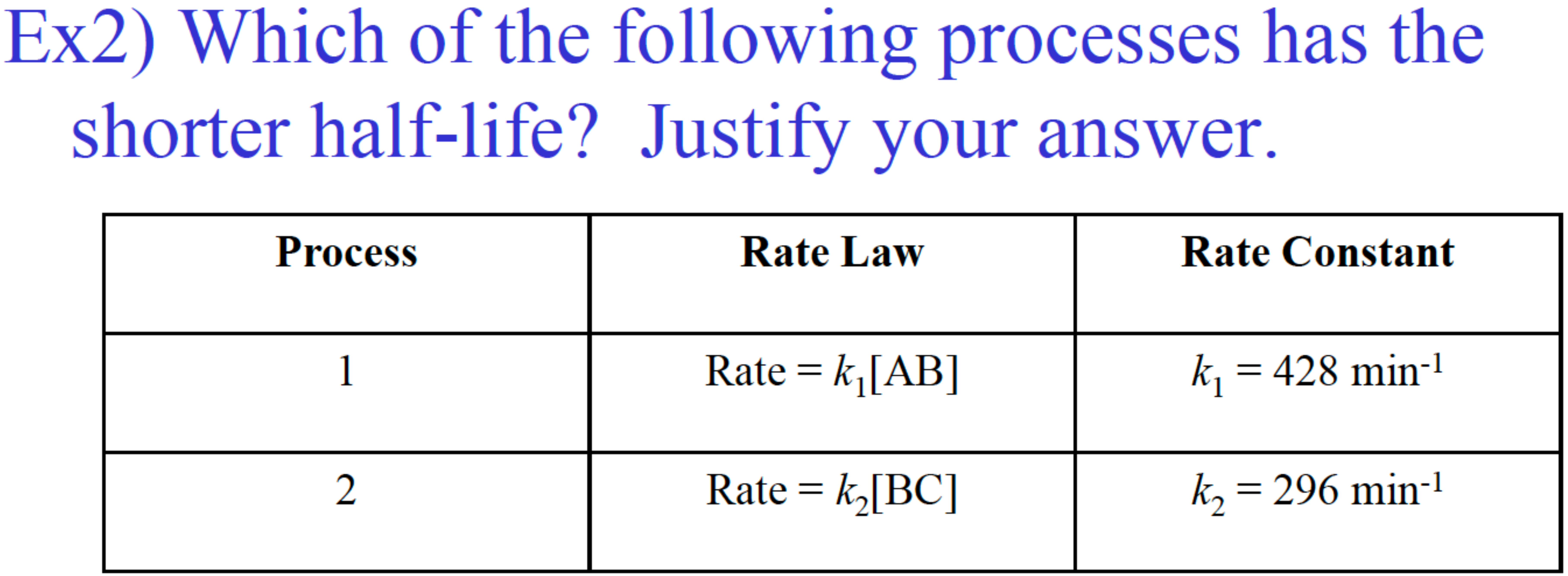
$$t_{1/2} = -\frac{(-0.693)}{k}$$

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

1st order half-life problems can be solved with this or this.

These equations can also be used for any radioactive decay problems, as those processes are always 1st order.

Example 2: Half Life for 1st Order Reactions



Ex2) Which of the following processes has the shorter half-life? Justify your answer.

Process	Rate Law	Rate Constant
1	Rate = k_1[AB]	$k_1 = 428\ \text{min}^{-1}$
2	Rate = k_2[BC]	$k_2 = 296\ \text{min}^{-1}$

- Process 1 has a shorter half-life.
  - both processes are first order
  - Process 1 occurs at a faster rate when both systems share the same initial concentrations, as its rate constant has a larger magnitude.

2nd Order Integrated Rate Law

This equation →

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

can be integrated using calculus to give…

$$\frac{1}{[\text{A}]_t} - \frac{1}{[\text{A}]_o} = kt$$

$[\text{A}]_o$ = the initial concentration (at $t = 0\text{s}$)

$[\text{A}]_t$ = the concentration after some period of time

2nd Order Integrated Rate Law

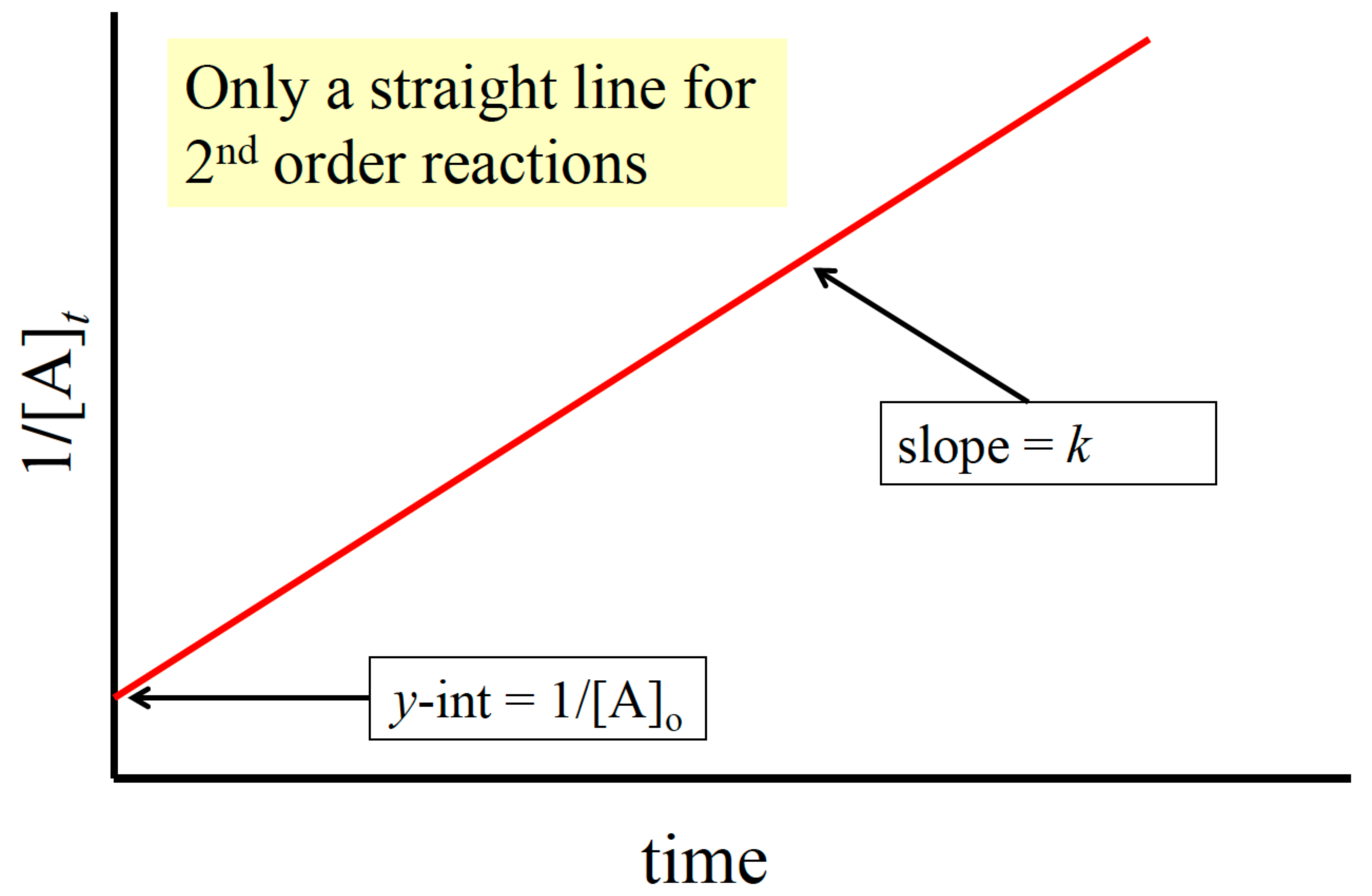
$$\frac{1}{[\mathrm{A}]_t} - \frac{1}{[\mathrm{A}]_o} = kt$$

$$\underset{\underset{\displaystyle y}{\uparrow}}{\frac{1}{[\mathrm{A}]_t}} \;\overset{}{=}\; \underset{\underset{\displaystyle m}{\uparrow}}{k}\,\underset{\underset{\displaystyle x}{\uparrow}}{t} + \underset{\underset{\displaystyle b}{\uparrow}}{\frac{1}{[\mathrm{A}]_o}}$$

$$y = mx + b$$

- A plot of **$1/[A]_t$** vs. ***t*** will give a straight line for 2nd order reactions. This is used to determine if a reaction is 2nd order, as a straight line will only occur if the reaction is 2nd order.

$1/[A]_t$ vs. t for 2^{nd} Order Reactions



Only a straight line for 2^{nd} order reactions

slope = k

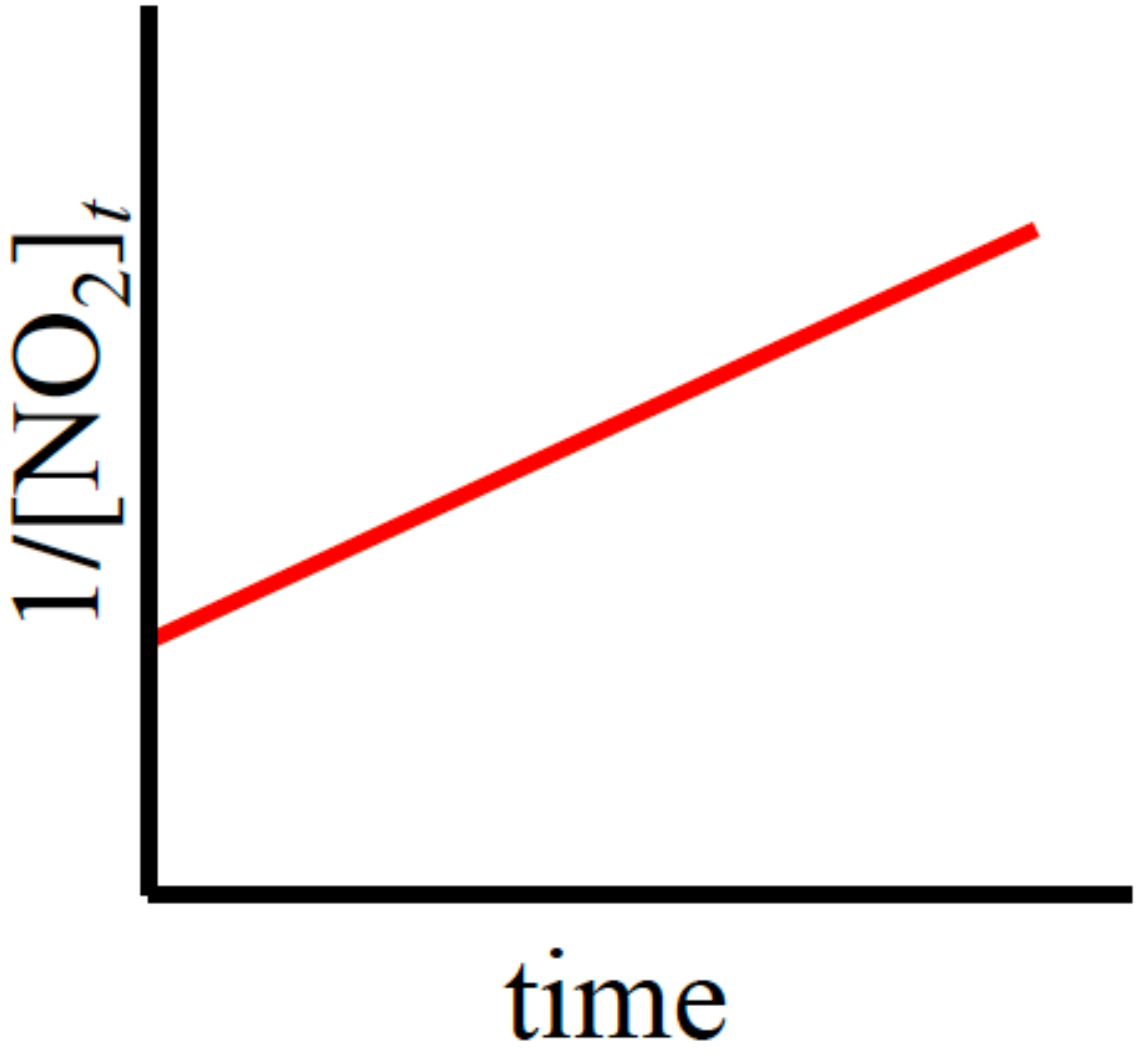
y-int = $1/[A]_o$

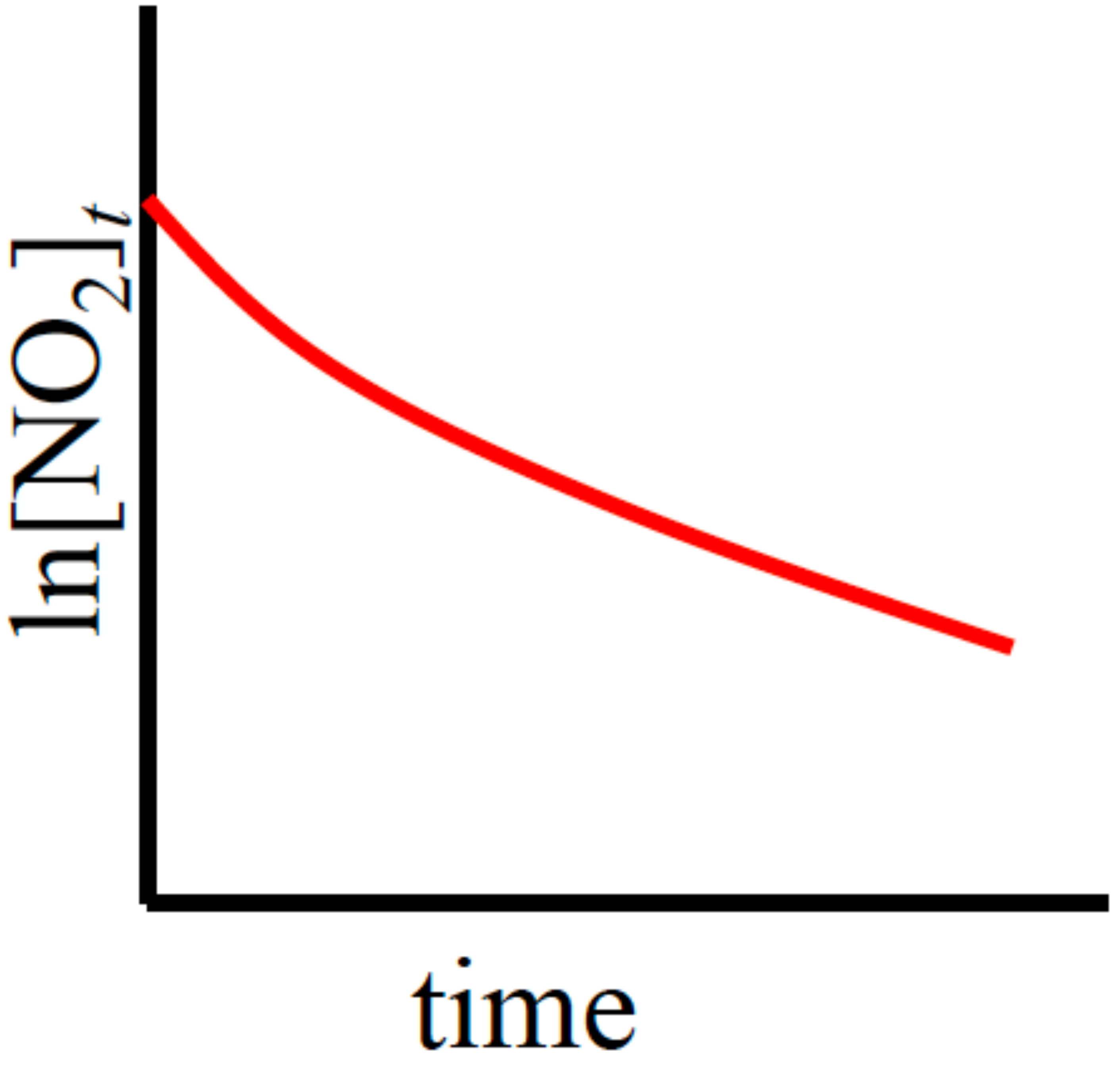
Example: Rate Laws

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

- Using the data provided, find the **rate law** and the **rate constant**

Time (s)	$[NO_2]$
0.0	0.070
1.0×10^2	0.015
2.0×10^2	0.0082
3.0×10^2	0.0057

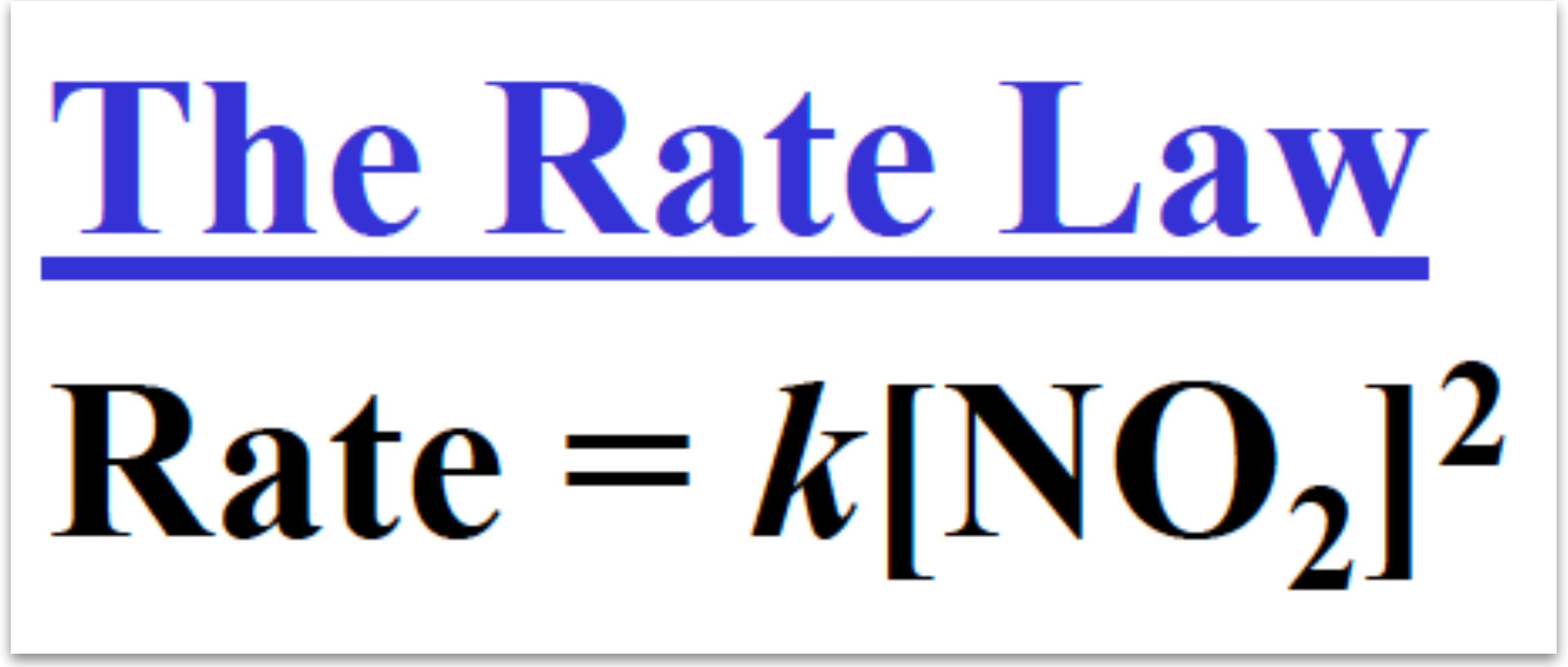




Example: Rate Laws

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

- Find the rate law:
  - We know it's a 2nd order reaction because a plot of **$1/[A]_t$** vs. ***t*** gives a straight line.
  - **$2NO_2(g) \rightarrow 2NO(g) + O_2(g)$** tells us that NO_2 is the only reactant.



The Rate Law

$$\text{Rate} = k[NO_2]^2$$

Example: Rate Laws

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

- To find *k*, use data for t = 0 and some other time.

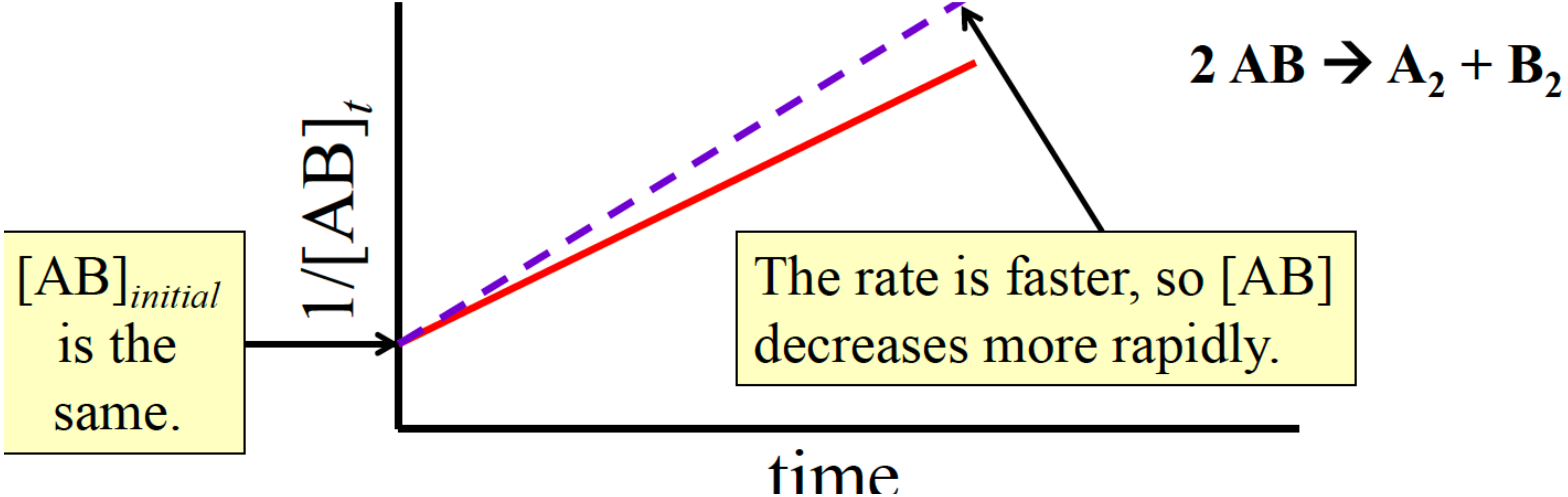
$$kt = \frac{1}{[A]_t} - \frac{1}{[A]_o} = \frac{1}{0.015M} - \frac{1}{0.070M}$$

$$k = \frac{\dfrac{1}{0.015M} - \dfrac{1}{0.070M}}{1.0\times10^2\,\mathrm{s}}$$

$$k = 0.52\ M^{-1}\mathrm{s}^{-1}$$

Example: 2nd Order Reactions

- Data from an experiment which examined the change in concentration over time for a second order process at 25°C was used to plot the graph below. Sketch a line that shows the approximate results that would be expected if the same experiment was repeated at a higher temperature.



$[AB]_{initial}$ is the same.

The rate is faster, so [AB] decreases more rapidly.

5.4 Elementary Reactions
5.7 Intro to Reaction Mechanisms
5.8 Reaction Mechanism & Rate Law
5.9 Steady-State Approximation

Reaction Mechanisms

- Most reactions **do not** happen in one step.

$2NO_{(g)} + O_{2(g)} \rightarrow 2NO_{2(g)}$

N_2O_2 is a reaction intermediate

Mechanism:

step 1: $NO_{(g)} + NO_{(g)} \rightarrow \cancel{N_2O_{2(g)}}$ fast

step 2: $\cancel{N_2O_{2(g)}} + O_{2(g)} \rightarrow 2NO_{2(g)}$ slow

$\mathbf{2NO_{(g)} + O_{2(g)} \rightarrow 2NO_{2(g)}}$

- Reaction mechanisms are the series of steps that sum to the overall reaction.

Determining a Rate Law

- The rate law for an overall reaction can only be found experimentally.
- Consider this overall reaction.

$$NO_{2(g)} + CO_{(g)} \rightarrow NO_{(g)} + CO_{2(g)}$$

$$\text{Rate} = k[NO_2]^2[CO]^0$$

$$\text{Rate} = k[NO_2]^2$$

Why????

Determining a Rate Law

$$NO_{2(g)} + CO_{(g)} \rightarrow NO_{(g)} + CO_{2(g)}$$

- But rate laws for elementary steps are predictable!

SLOW Step 1. $2NO_{2(g)} \rightarrow NO_{(g)} + NO_{3(g)}$

$$\text{Rate} = k_1[NO_2]^2$$

Same rate law as the overall reaction!

FAST Step 2. $NO_{3(g)} + CO_{(g)} \rightarrow NO_{2(g)} + CO_{2(g)}$

$$\text{Rate} = k_2[NO_3][CO]$$

NO_3 is consumed as soon as it is produced

Adding CO does not increase the rate, making it zero order in the overall reaction

For any elementary step…

$aA + bB \rightarrow dD + eE$ Rate = $k[A]^a[B]^b$

Determining a Rate Law

Overall Reaction: $2NO_{(g)} + O_{2(g)} \rightarrow 2NO_{2(g)}$

Step 1. $NO_{(g)} + O_{2(g)} \rightleftharpoons NO_{3(g)}$ **FAST, reversible**

$\mathbf{Rate_{(fwd)} = k_1[NO][O_2]}$ $\mathbf{Rate_{(rev)} = k_{-1}[NO_3]}$ ← **$rate_{forward} = rate_{reverse}$**

Step 2. $NO_{3(g)} + NO_{(g)} \rightarrow 2NO_{2(g)}$ **SLOW**

$\mathbf{Rate = k_2[NO_3][NO]}$

This reaction proceeds at the rate of the SLOW STEP, but NO_3 is an intermediate so its concentration is unknown. To solve this problem, the rate law must be modified.

Determining a Rate Law

Overall Reaction: $2NO_{(g)} + O_{2(g)} \rightarrow 2NO_{2(g)}$

Step 1. $NO_{(g)} + O_{2(g)} \rightleftharpoons NO_{3(g)}$ **FAST, reversible**

$k_1[NO][O_2] = k_{-1}[NO_3]$ ← **$\text{rate}_{\text{forward}} = \text{rate}_{\text{reverse}}$**

$[NO_3] = k_1/k_{-1}([NO][O_2])$

Step 2. $NO_{3(g)} + NO_{(g)} \rightarrow 2NO_{2(g)}$ **SLOW**

Rate = $k_2[NO_3][NO]$

Rate = $k_2(k_1/k_{-1}([NO][O_2]))[NO]$

Rate = $k_3[NO]^2[O_2]$ ← **this gives a rate law with no intermediates**

Determining a Rate Law

- Chemists determine the rate law through experimentation.
- They use the rate law to determine what the elementary steps are.
  - The rate law tells them what the slowest step is.
  - Then they try to determine the fast steps.
  - Though experimental detection of reaction intermediates, evidence is built to support proposed mechanisms.

Rate Laws of Elementary Steps

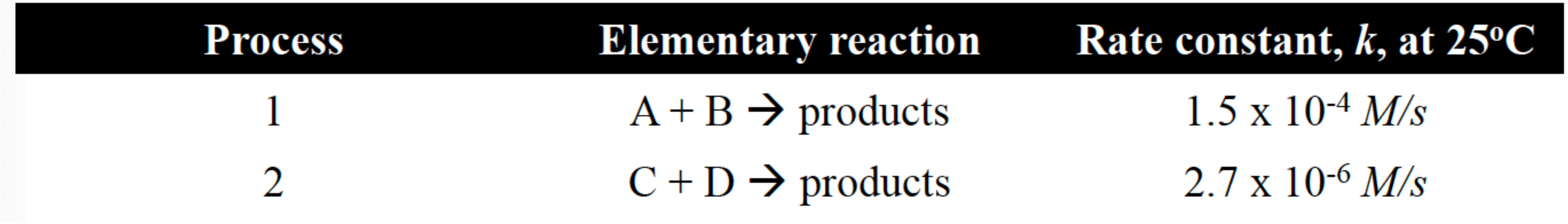
Molecularity	**Elementary Reaction**	**Rate Law**	**Order**
*Uni*molecular	A → products	Rate = $k[A]$	First order
*Bi*molecular	A + A → products	Rate = $k[A]^2$	Second order
*Bi*molecular	A + B → products	Rate = $k[A][B]$	Second order
*Ter*molecular	A + A + A → products	Rate = $k[A]^3$	Third order
*Ter*molecular	A + A + B → products	Rate = $k[A]^2[B]$	Third order
*Ter*molecular	A + B + C → products	Rate = $k[A][B][C]$	Third order

Termolecular elementary reactions are very rare.

The value of the rate constant, k, is temperature dependent.

Example: Rate Laws of Elementary Steps

The rate constants associated with the slowest elementary steps for two processes are given in the table below. Which process has the higher rate under standard conditions?



Process	Elementary reaction	Rate constant, k, at 25°C
1	A + B → products	$1.5 \text{ x } 10^{-4}$ *M/s*
2	C + D → products	$2.7 \text{ x } 10^{-6}$ *M/s*

Process 1 proceeds at a faster rate. Both are 2nd order and all reactants have 1.0 M concentrations. The rate constant for process 1 has a higher magnitude.

Example: Rate Laws of Elementary Steps

The rate laws associated with the slowest elementary steps for two processes are given below. Which process is most likely to proceed at a higher rate under standard conditions?

Process	Rate Law
1	Rate = $[A]^2[B]$
2	Rate = $[C][D]$

Process 2 is more likely to proceed at a faster rate. The slow step in Process 1 requires the simultaneous collision of three particles with sufficient energy and correct orientations.

5.5 Collision Model
5.6 Reaction Energy Profiles
5.10 Multistep Reaction Energy Profiles

- Factors Affecting Reaction Rates
- Activation Energy, E_a

Collision Rate

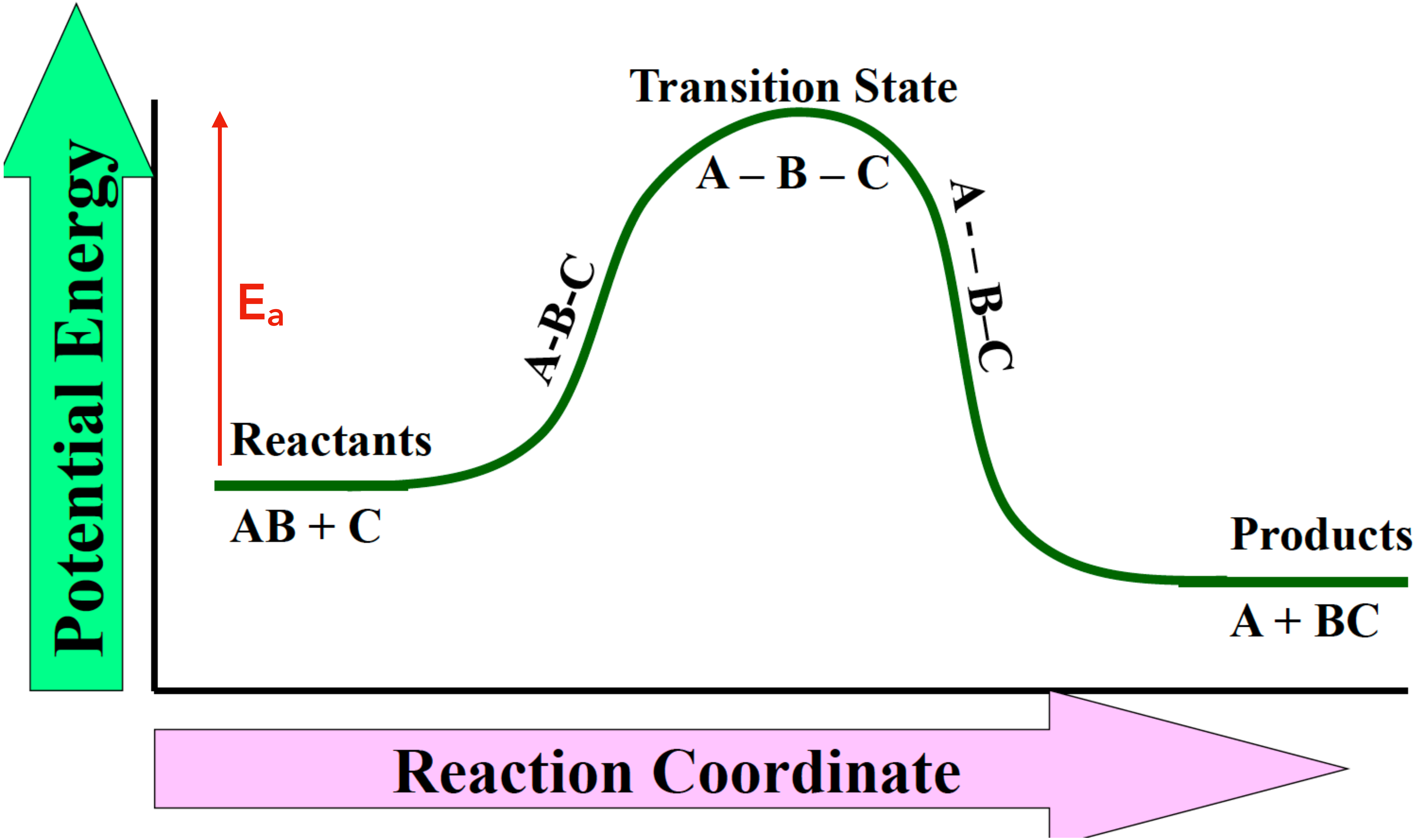
- Collision Rate Increases…*Poppers! Design of Experiment*
  1. As the concentration of reactants in the liquid or gas phase increases.
  2. As the surface area of reactants in the solid phase increases.
  3. As temperature increases.

Not every collision triggers a chemical reaction!

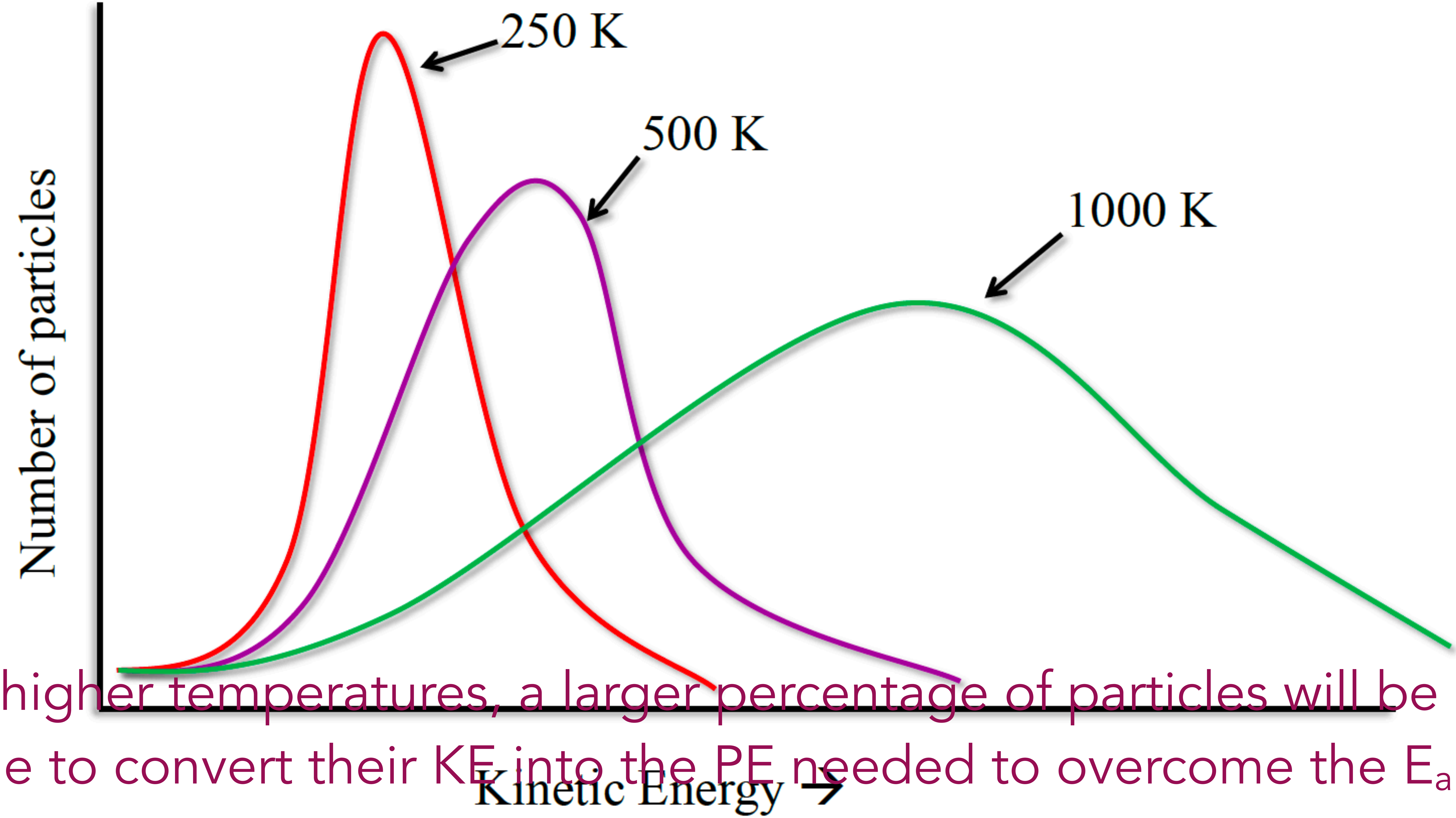
Molecules must collide with an orientation that can yield a reaction.

Reaction Energy Profile

$AB + C \rightarrow A + BC$



Maxwell-Boltzmann Distribution



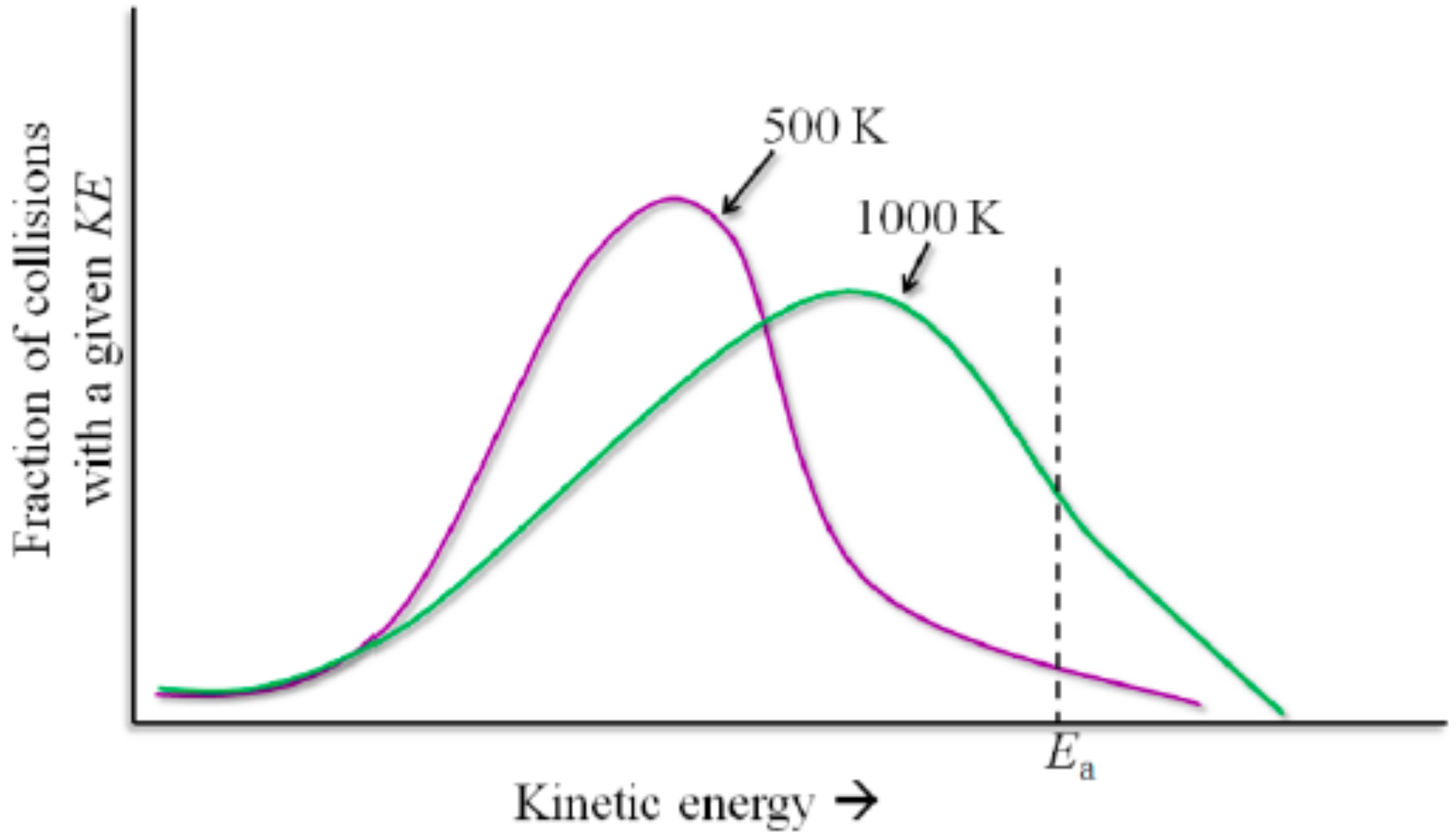
At higher temperatures, a larger percentage of particles will be able to convert their KE into the PE needed to overcome the E_a.

E_a for Unimolecular Decomposition Reactions

- The energy required to break the bonds in the reactant is obtained during the collision with a background or solvent particle.

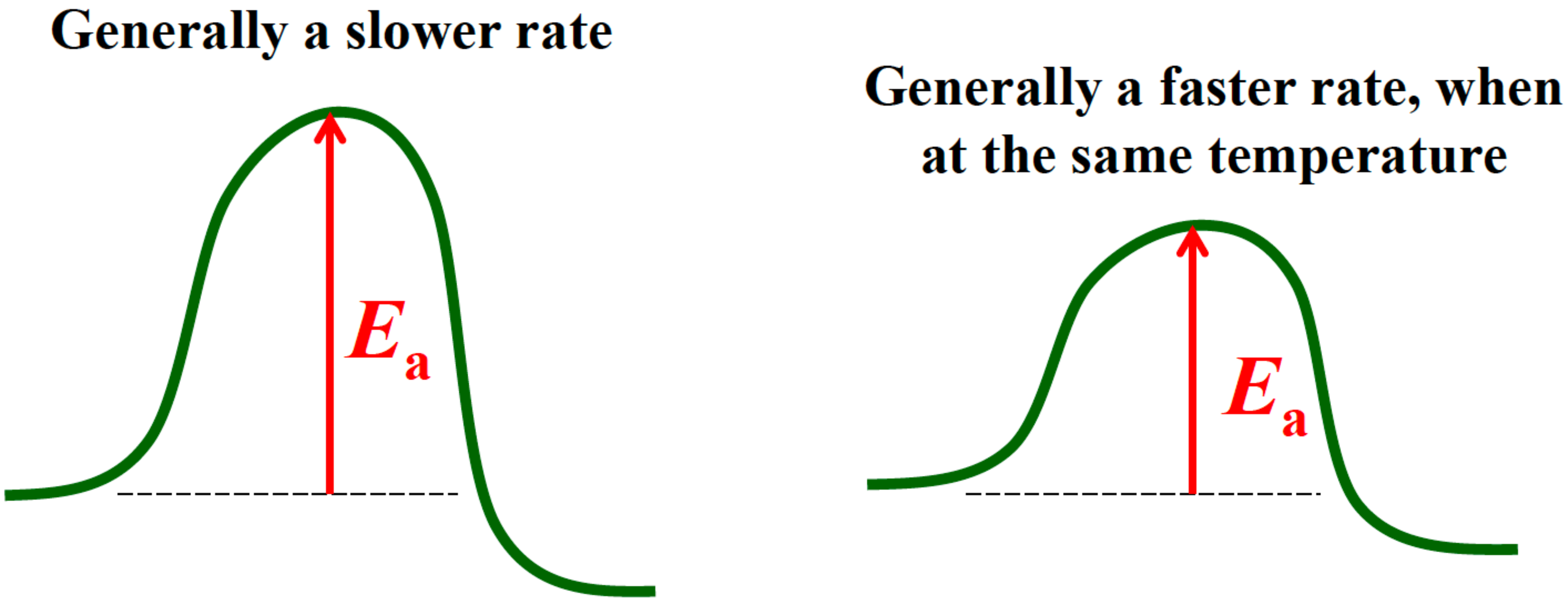
$$O_{3(g)} + M \rightarrow O_{2(g)} + O_{(g)} + M$$

  - For this reason, unimolecular decomposition rates increase as temperature increases.



Activation Energy (E_a)

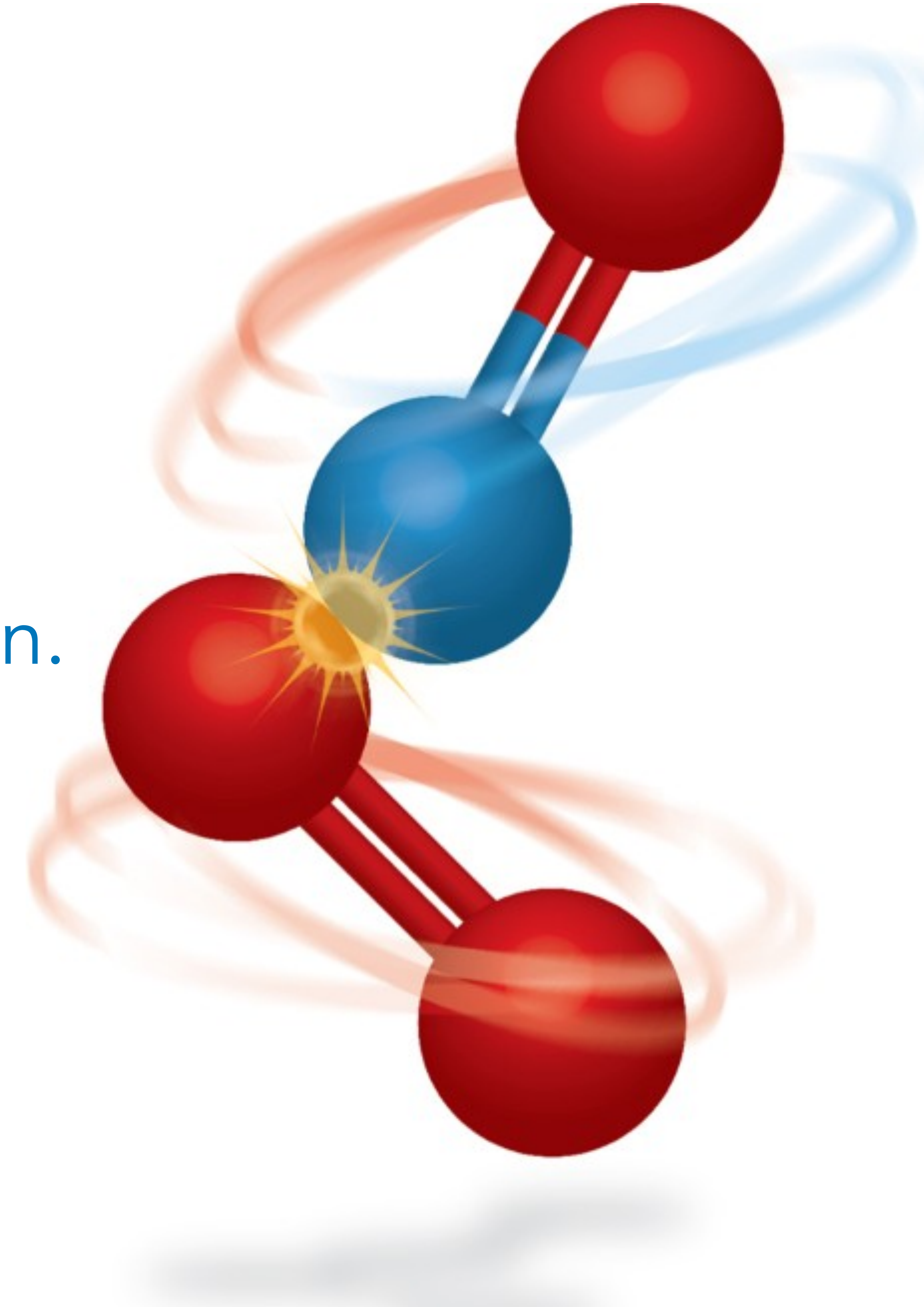
- Reaction rates depend on the magnitude of E_a.



Generally, if less energy is required to get over the hump, more reactants will collide with enough energy.

In Summary

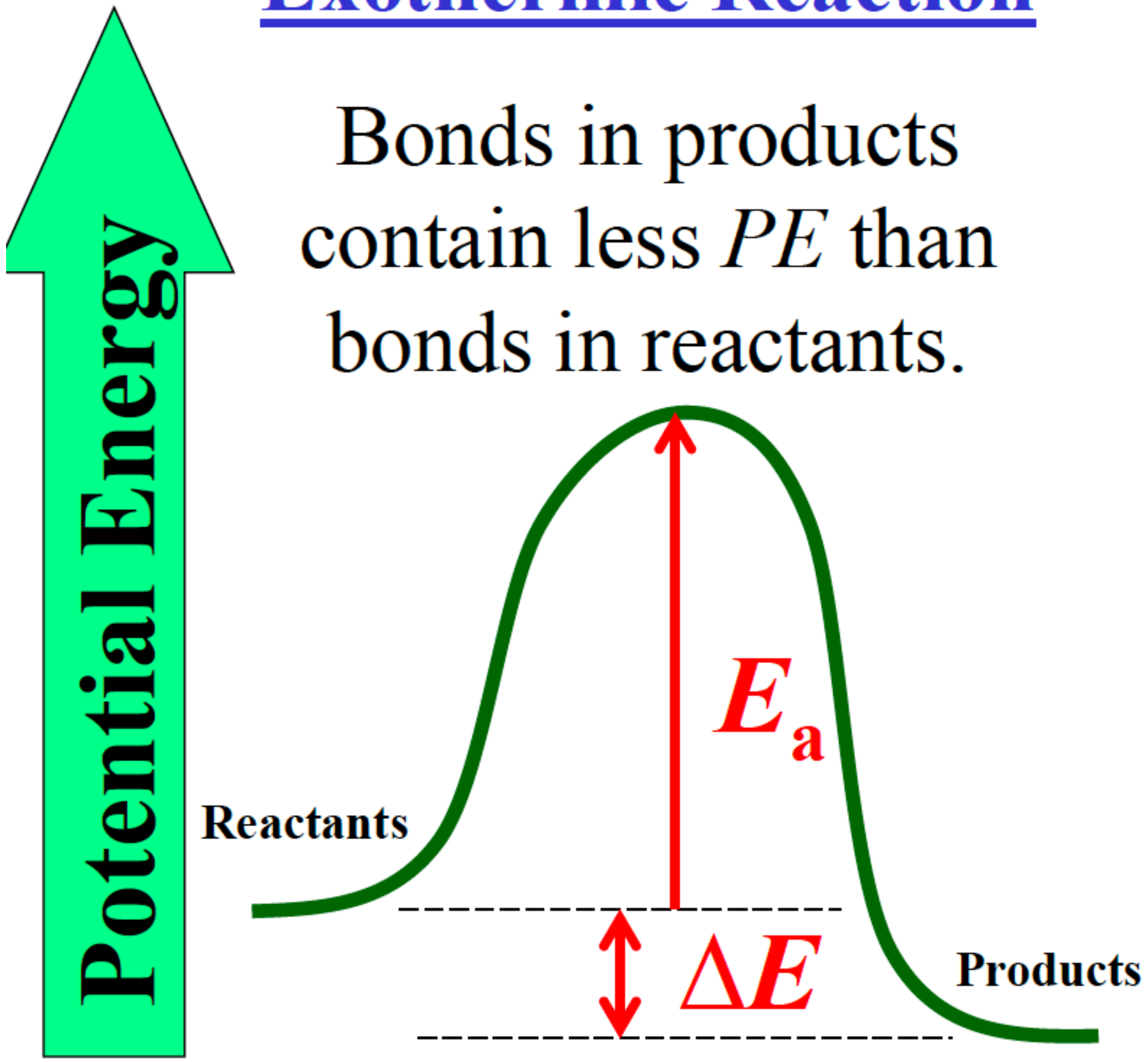
- All 3 of the following conditions must be met in order for a reaction to occur:
  1. There must be a collision.
  2. The collision must occur with an orientation that could cause a reaction.
  3. $E_{\text{collision}} \geq E_a$



Activation Energy (E_a)

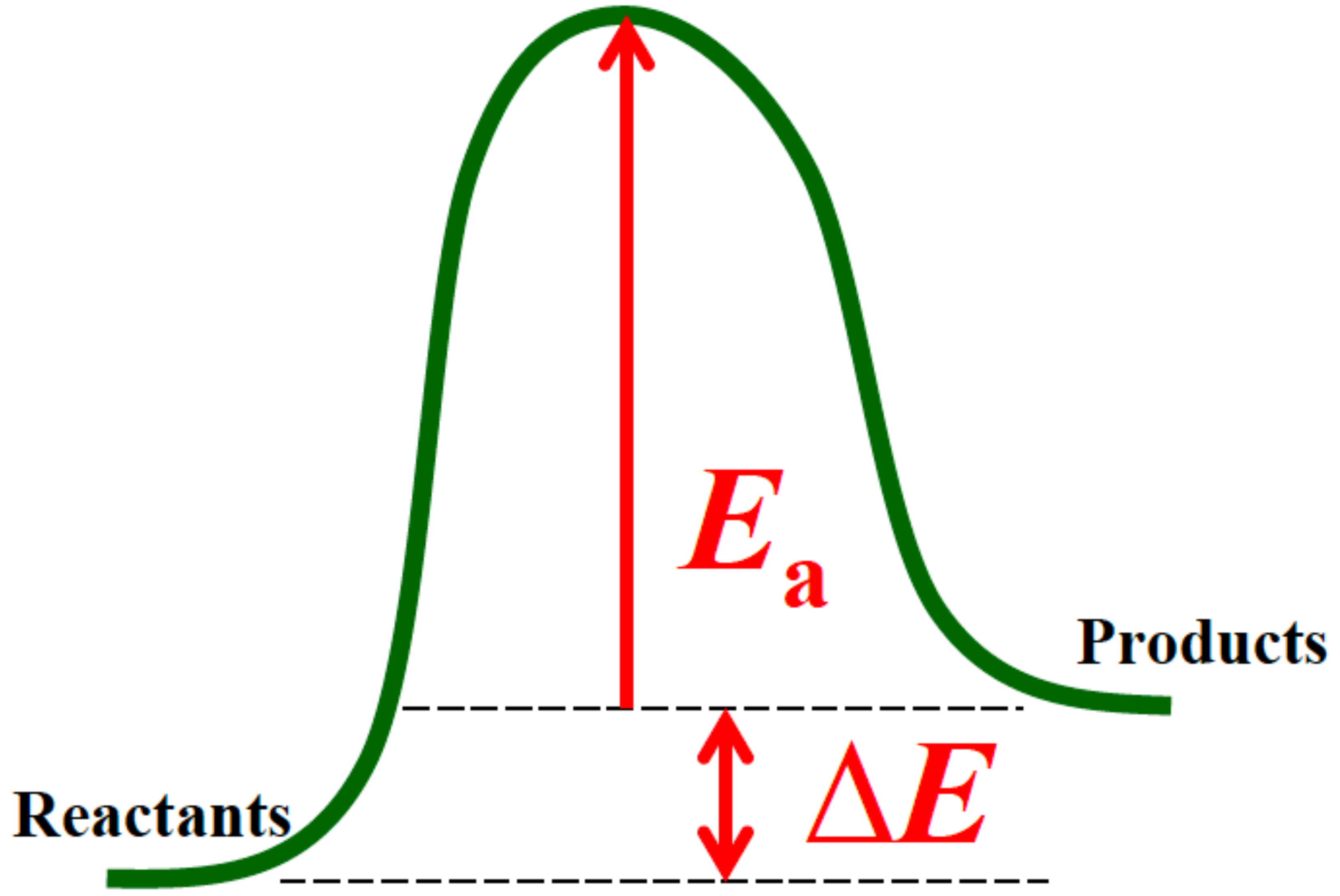
Exothermic Reaction

Bonds in products contain less *PE* than bonds in reactants.



Endothermic Reaction

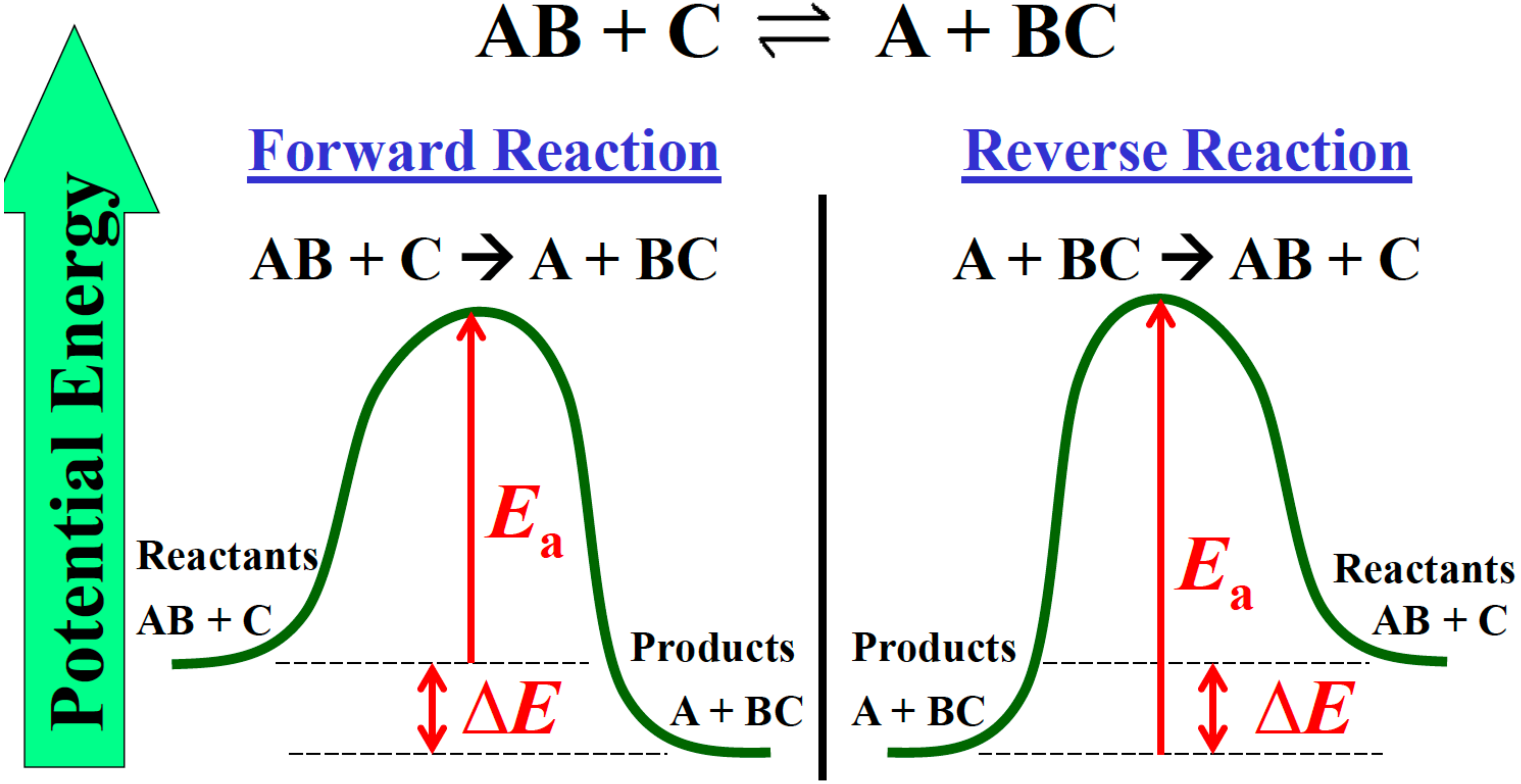
Bonds in products contain more *PE* than bonds in reactants.



ΔE is the energy lost or gained in a reaction. Also called the ΔH (enthalpy of reaction).

Activation Energy (E_a)

$$AB + C \rightleftharpoons A + BC$$



Potential Energy

Forward Reaction

$AB + C \rightarrow A + BC$

Reverse Reaction

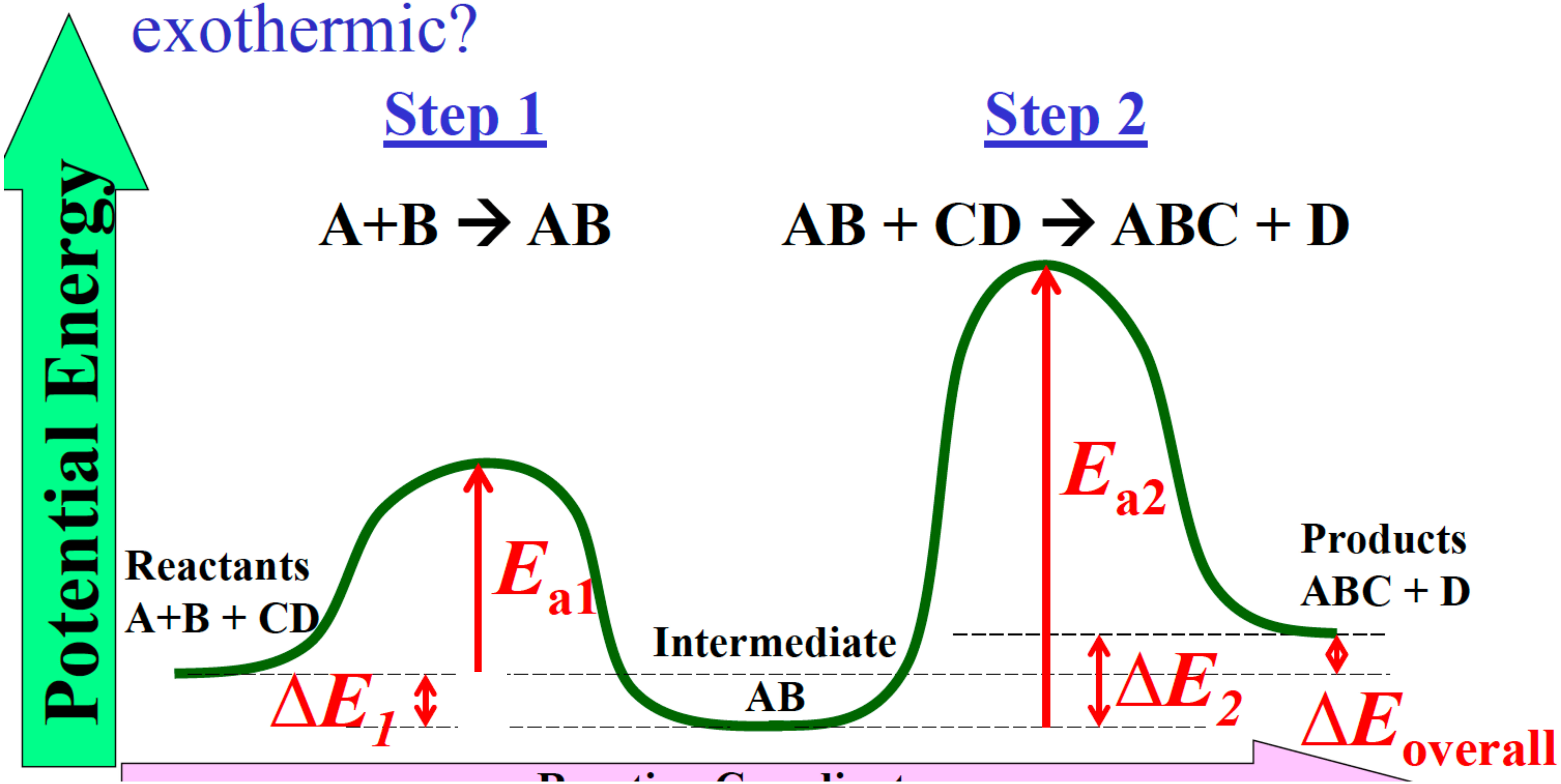
$A + BC \rightarrow AB + C$

The E_a value changes for the reverse reaction.

Example: Multistep Reaction Energy Profiles

1) Which step is the rate determining step?

2) Is the overall process endothermic or exothermic?



Step 1

A+B → AB

Step 2

AB + CD → ABC + D

The Arrhenius Equation

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

k = rate constant

E_a = activation energy (J)

R = 8.314 J/mol•K

T = absolute temperature (K)

A = a constant related to the frequency of collisions and the probability that the orientation could produce a reaction.

Svante Arrhenius won the Nobel Prize in 1903

The Arrhenius Equation

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

- The Arrhenius Equation shows that increasing the temperature increases the rate of a reaction.
  1. As the temperature increases, $-E_a/RT$ becomes less negative and the rate constant, k, increases.
  2. As the rate constant, k, increases, the rate increases.

Natural log time…

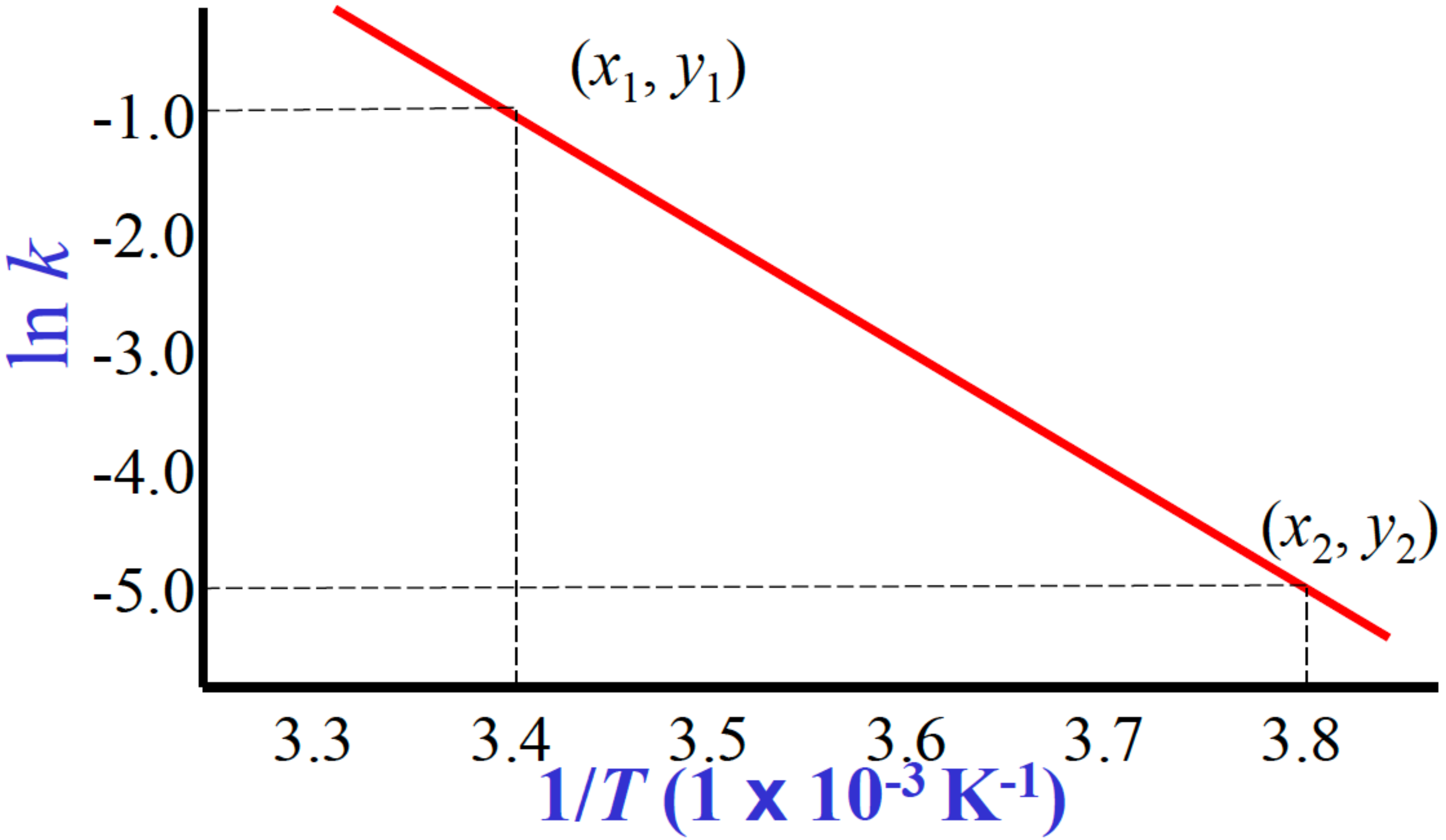
$$\begin{array}{cccccc} \ln k & = & \dfrac{-E_a}{R} & \left(\dfrac{1}{T}\right) & + & \ln A \\ \uparrow & & \uparrow & \uparrow & & \uparrow \\ y & = & m & x & + & b \end{array}$$

- A graph of ln[k] vs. 1/T produces a straight line.
- The activation energy, E_a, can be determined after calculating the slope of the line.

slope = $-E_a/R$

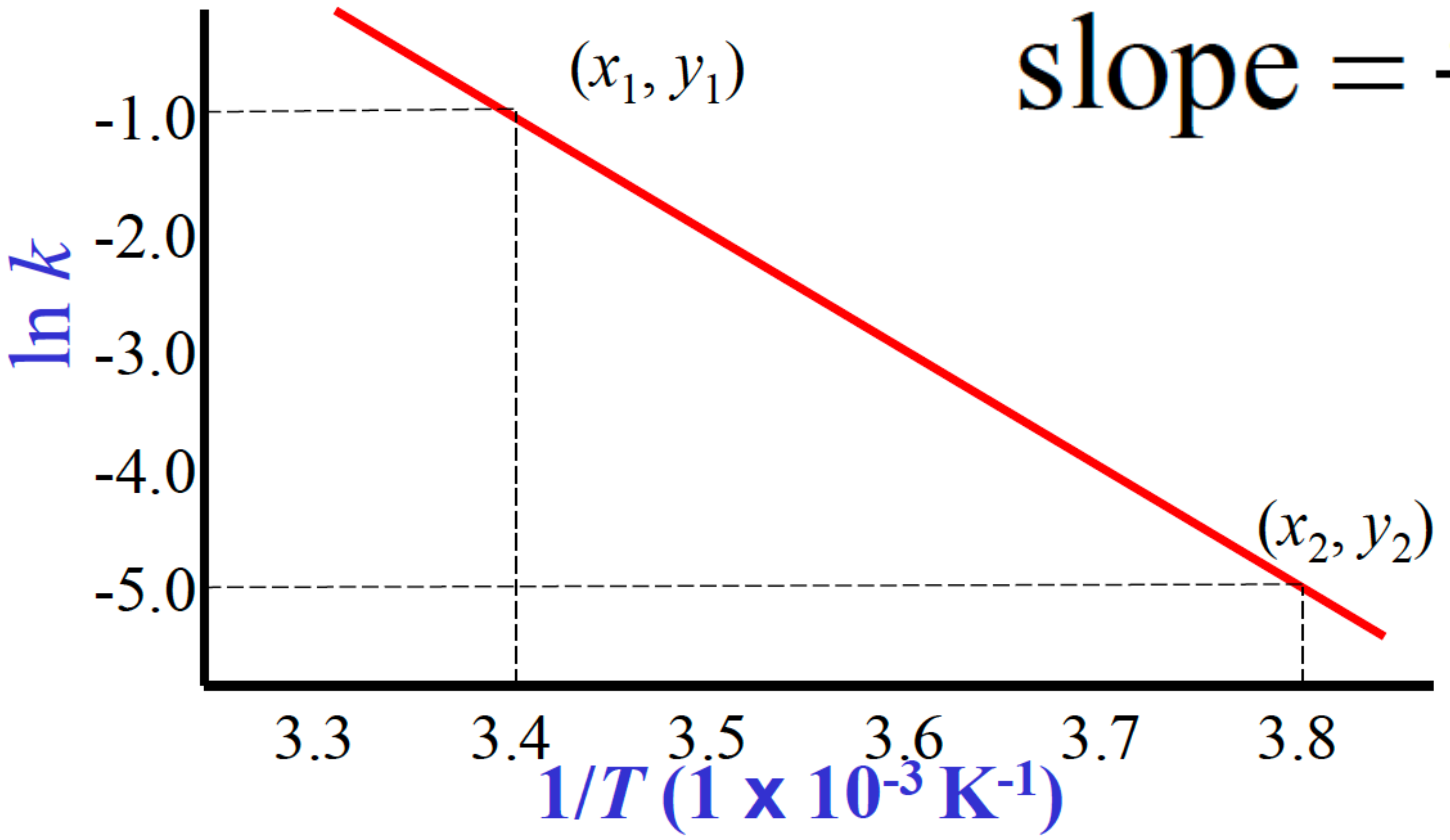
Example: Arrhenius Equation

- Data from a series of experiments conducted at different temperatures was used to produce the graph below. Find the activation energy for the reaction.



Example: Arrhenius Equation

- Find the slope of the line



$$\text{slope} = \frac{y_2 - y_1}{x_2 - x_1} = \frac{-5 - (-1)}{(3.8 \times 10^{-3}) - (3.4 \times 10^{-3})}$$

$$\boxed{\text{slope} = -1.0 \times 10^{4}\ \text{K}}$$

- Find E$_a$

$$\text{slope} = \frac{-E_a}{R}$$

$$\boxed{\begin{aligned} E_a &= -(-1.0 \times 10^{4}\,\text{K})(8.314\ \text{J} \cdot \text{K}^{-1}\text{mol}^{-1}) \\ E_a &= 83000\ \text{J/mol} = 83\ \text{kJ/mol} \end{aligned}}$$

$$\begin{array}{cccccc} \ln k & = & \dfrac{-E_a}{R} & \left(\dfrac{1}{T}\right) & + & \ln A \\ \uparrow & & \uparrow & \uparrow & & \uparrow \\ y & = & m & x & + & b \end{array}$$

$$E_a = -(\text{slope})(R)$$

5.11 Catalysis

- Acid-Base Catalysts
- Surface Catalysts
- Enzymes of Catalysts

Catalysis

- A catalyst increases the rate of a chemical reaction by providing an alternate reaction mechanism.
  - Lower activation energy and/or
  - Higher frequency of collisions with an orientation that could produce a reaction.
- Catalysts are added to the system.
  - There are there before the reaction starts and then they return when the reaction is complete.
  - The net concentration of the catalysts remains constant.

Catalysis - destruction of ozone

$CCl_2F_2 \rightarrow CClF_2\bullet + Cl\bullet$ *(weaker C-Cl bond breaks 1st)*

Cl• reacts with O_3

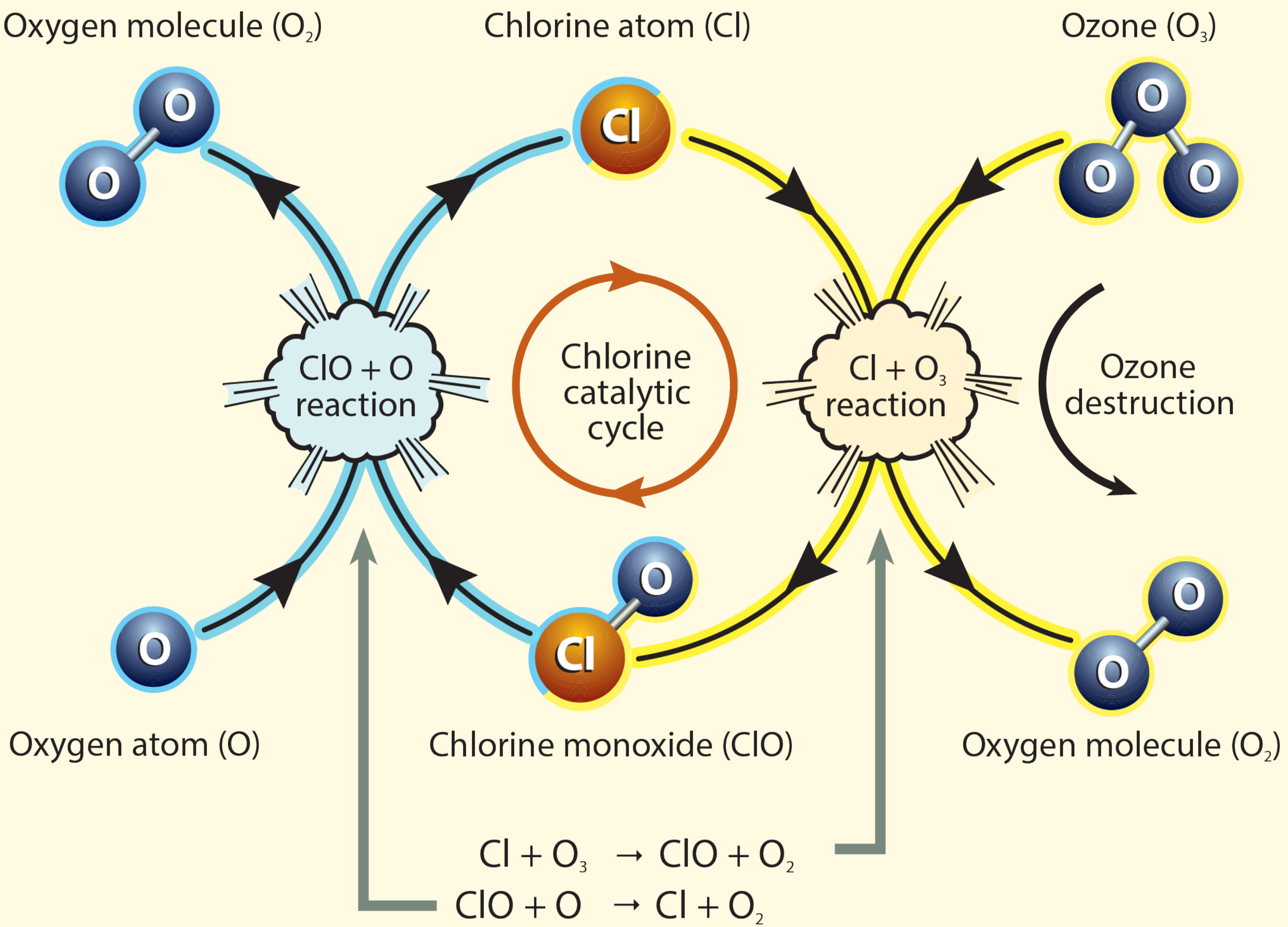
$Cl\bullet + O_3 \rightarrow O_2 + ClO\bullet$

$ClO\bullet + O\bullet \rightarrow O_2 + Cl\bullet$

$O_3 + O\bullet \xrightarrow{Cl} 2O_2$

Cl• is back to react with another O_3

Ozone Destruction Cycle 1



$$Cl + O_3 \rightarrow ClO + O_2$$

$$ClO + O \rightarrow Cl + O_2$$

$$\text{Net: } O + O_3 \rightarrow 2O_2$$

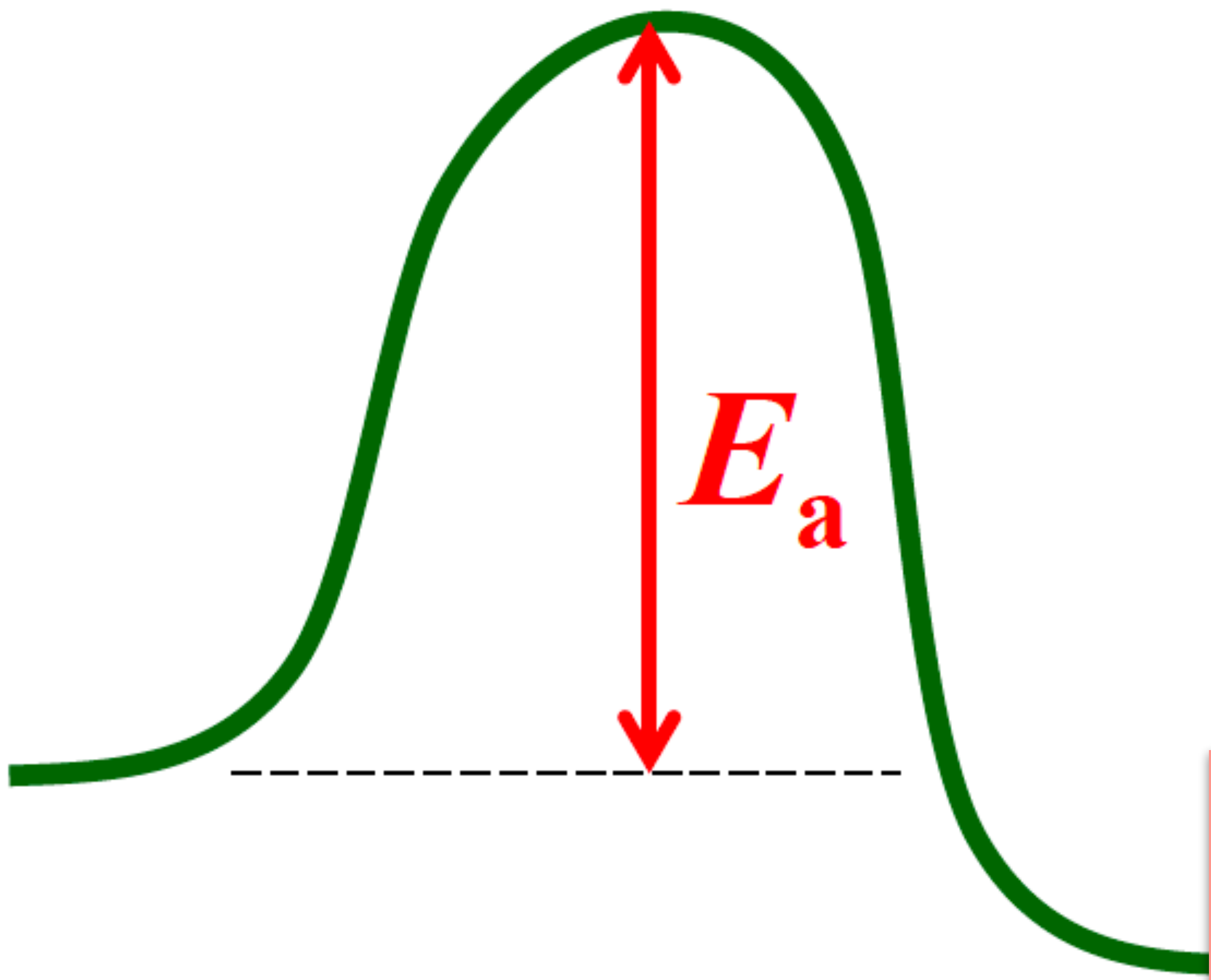
Catalysis and Activation Energy

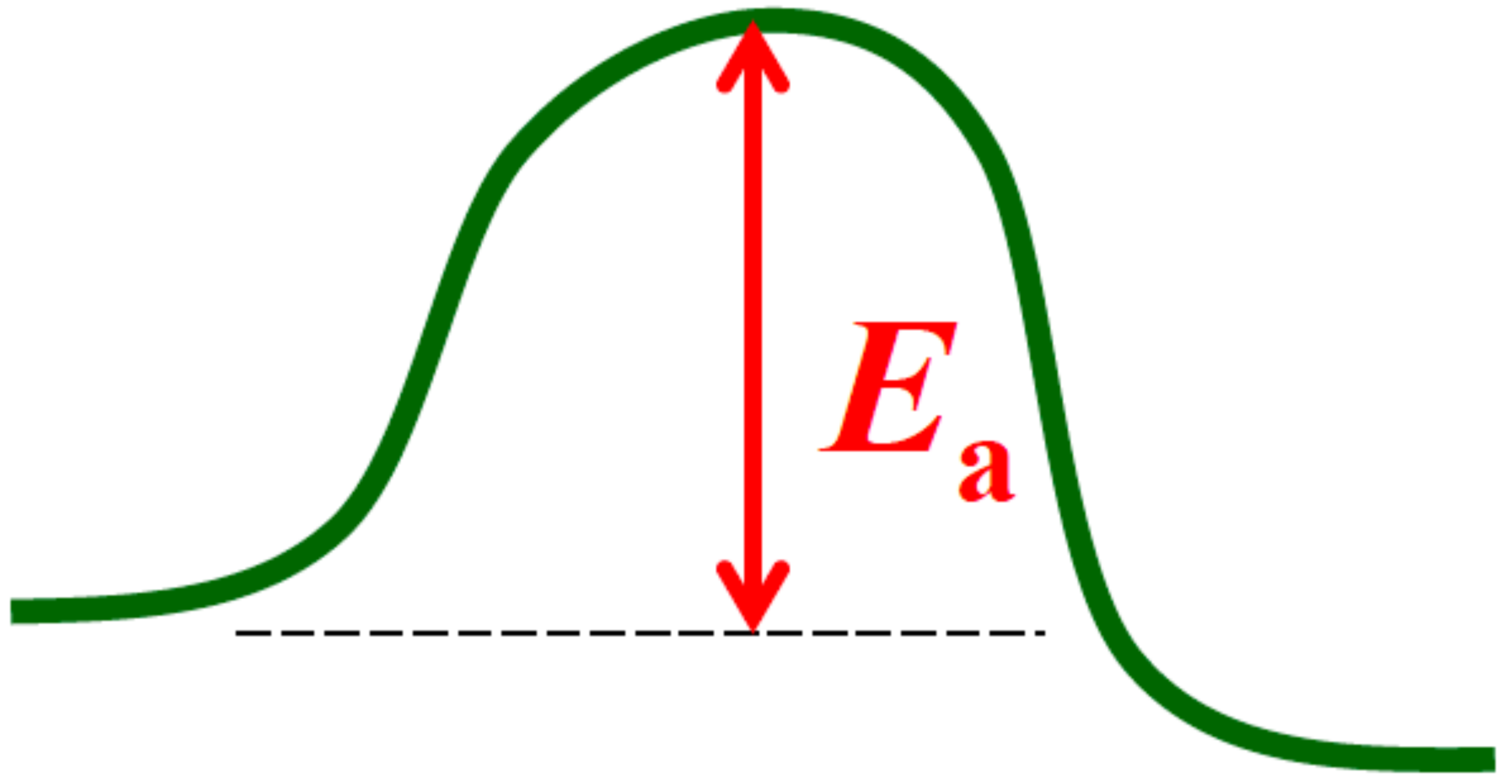
$O_3 + O\bullet \longrightarrow 2O_2$

no catalyst

$O_3 + Cl\bullet \longrightarrow ClO\bullet + O_2$

with a catalyst





E_a lowered for BOTH forward and reverse reactions. K_{eq} is the same at the same temperature, regardless of the presence of a catalyst.

Types of Catalysis (a few)

Acid-Base Catalysis

- A reactant gains or loses a proton (H^+), which forms a new intermediate.
  - *Acid-Catalyzed hydrolysis of esters*

Enzymes

- Enzyme binds to the reactant(s) to form a new reaction intermediate.

Surface Catalysis (heterogeneous)

- The catalyst binds to or forms covalent bonds with a surface, thereby forming a new intermediate.
  - *Catalytic Converters, hydrogenation of alkenes*