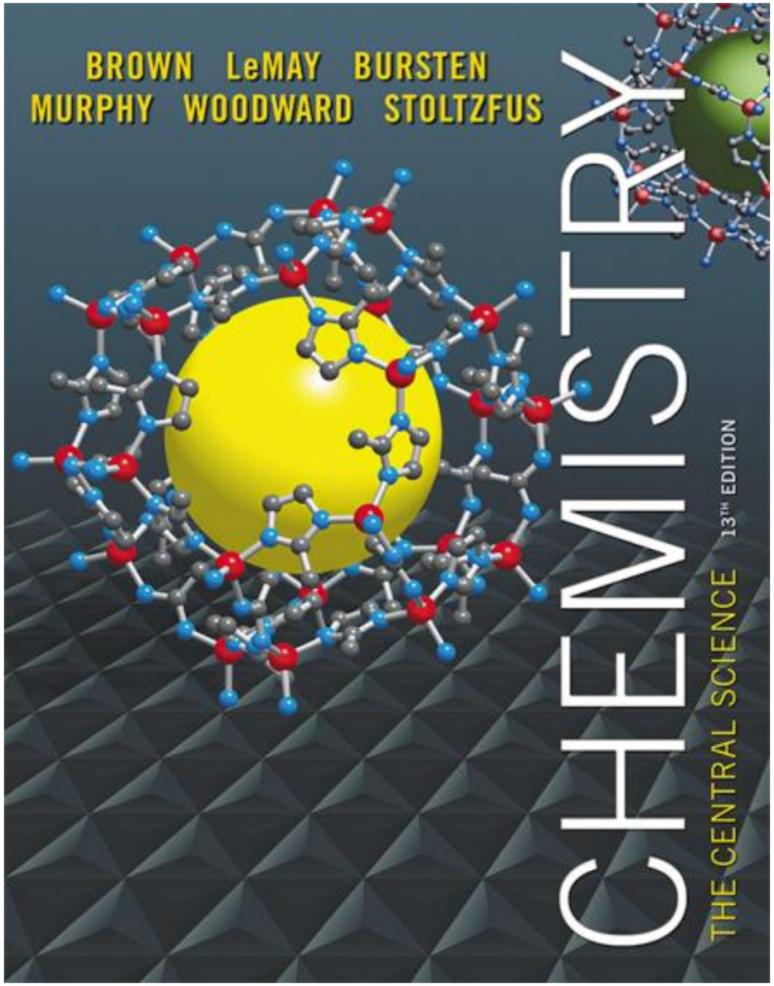
Chapter 14
Chemical Kinetics



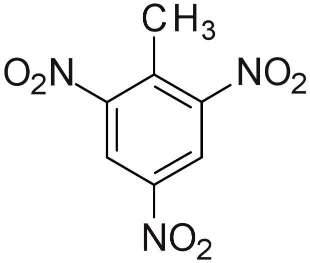
- How fast a reaction happens is absolutely essential.
  - Reactions can be so slow they take millions of years
  - Or so fast they can't be controlled.

- Kinetics is one of the few ways of seeing the ***mechanism*** of a reaction.

Some chemical reactions go fast

Explosion

Timescale: Fraction of a second



$$2\ C_7H_5N_3O_{6(s)} \rightarrow 3\ N_{2(g)} + 5\ H_{2(g)} + 12\ CO_{(g)} + 2\ C_{(g)}$$

TNT

soot

$$+\ 54.39\ \mathrm{kJ/mol}$$

(Heat)

Timescale: the time taken by a process or sequence of events. Widely used term in chemistry

Others are slow….

Corrosion (rusting)
Timescale: Years

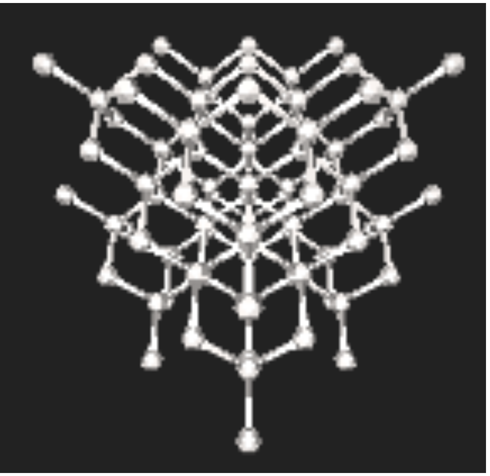
$$4Fe_{(s)} + 3O_{2(g)} + 6H_2O_{(l)} \rightarrow 4Fe(OH)_{3(s)}$$

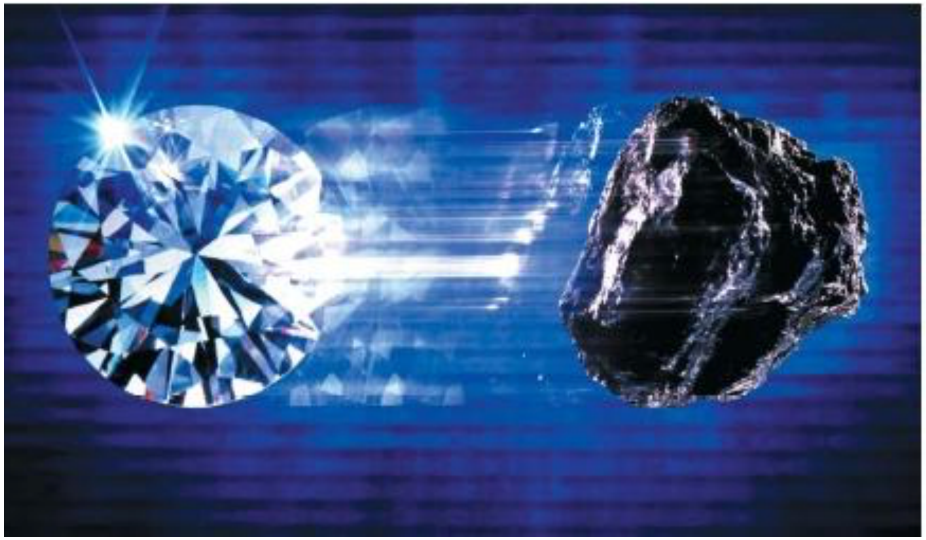
Iron (III) hydroxide

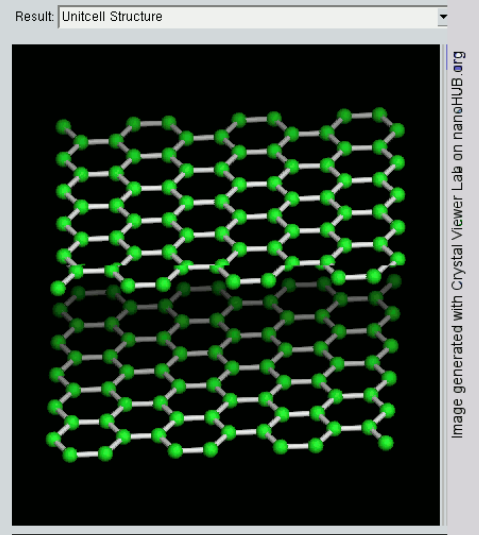
Ferrous (Fe^{2+})
Ferric (Fe^{3+})

Some are practically impossible to observe!

Conversion of diamond to graphite
Timescale: longer than the lifetime of the universe!







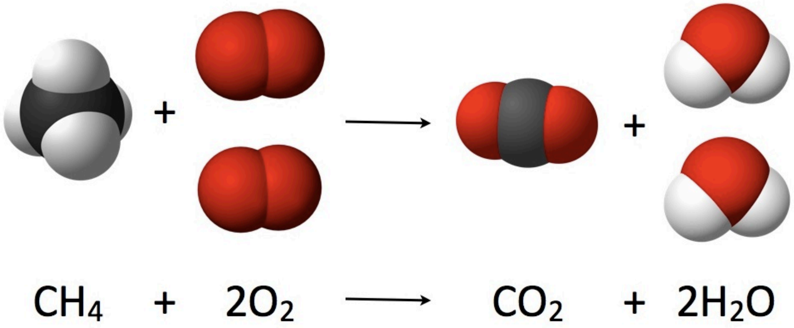
Carbon allotropes
(Covalent compounds)

Allotrope: each of two or more different physical forms in which an element can exist.

Finally, some reactions only occur once they are *"initiated"*.

Combustion
Fuel + Oxygen

Without ignition (spark or flame), the reactants will not react…



$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$

Chemical and Biological timescales: “fast” is relative

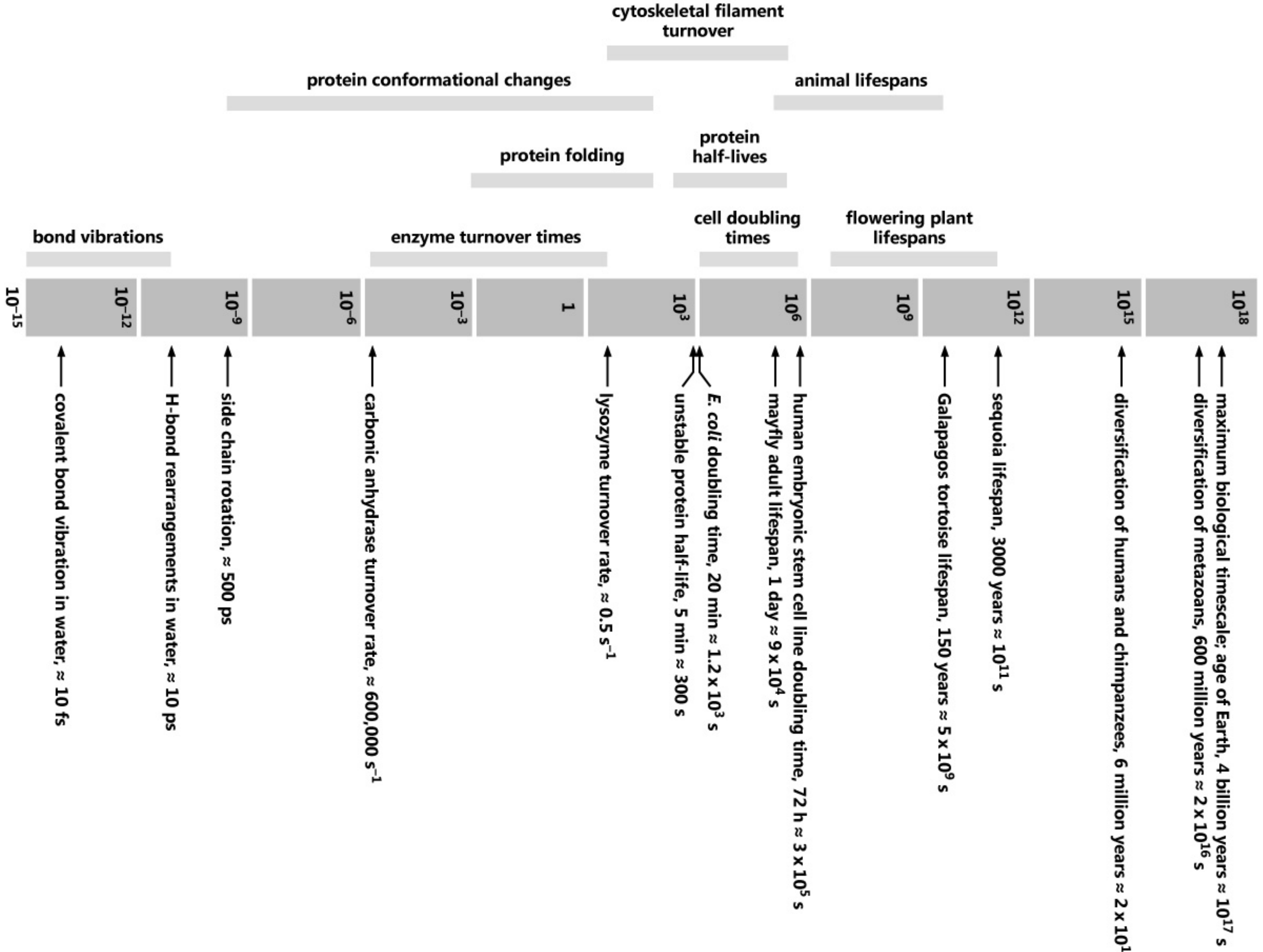
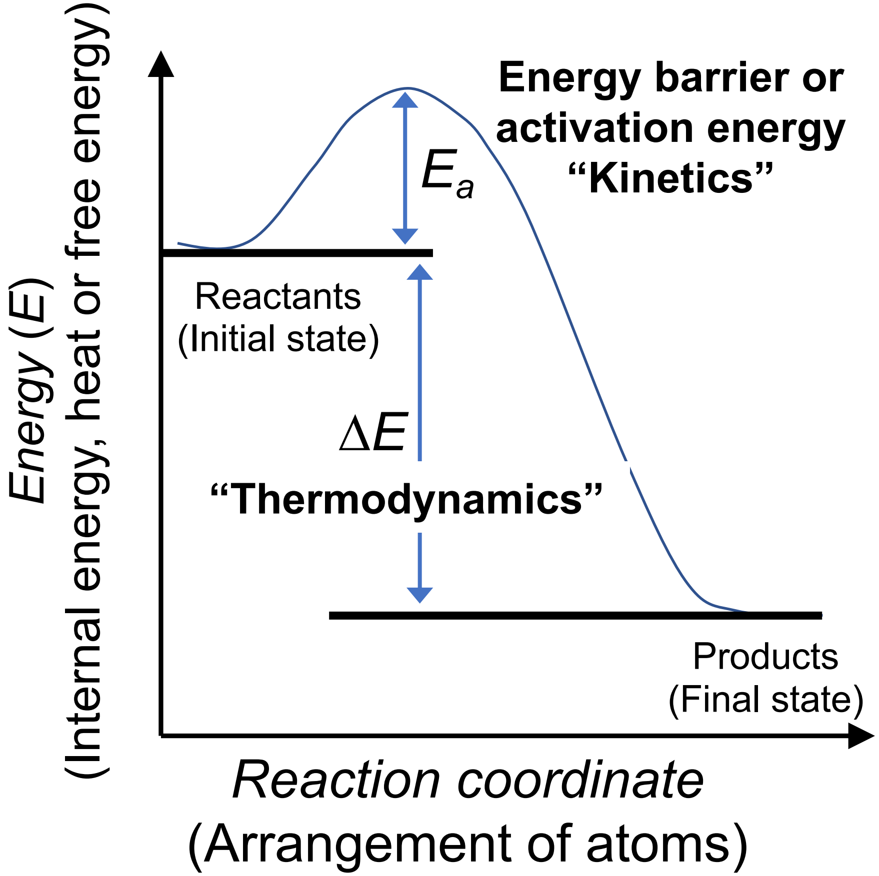


Figure 3.1 Physical Biology of the Cell (© Garland Science 2009)

Femtosec picosec. Microsec. Milisec. Sec. Min. Days years cent. Thous. Mill. billion

A chemical reaction is determined by thermodynamics and kinetics, and can be described by the “energy diagram”.



Thermodynamics

- Concerns the energy difference (ΔE) between the ”states”.
- Determines the relative population of the reactants and products after the reaction is finished.
- The state with a lower energy
  > likely to be more populated at equilibrium.

Kinetics

- Concerns the energy barrier (E_a).
- Determines the “rate” of a reaction, that is, how “fast” a reaction happens.

Thermodynamics and kinetics are two distinct areas in chemistry.

- In general, ΔE and E_a are not related.
- Reaction can happen in both directions depending on the energy barrier.

Factors that affect reaction rates

More collisions, faster reaction.

1) Physical state (phase- gas, liquid or solid) of the reactants

- **Homogeneous** reactions (reactants are in the same phase) are often **faster**.
- Heterogeneous reactions (gas with solid, etc.) are
  - faster if the surface area is increased (fine powder reacts faster than a pellet or tablet).

2) Reactant concentrations

- Increasing reactant concentration generally increases reaction rate.
  - more molecules, more collisions.

3) Reaction temperature

- Reaction rate generally increases with increased temperature.
  - higher T, higher K.E. collisions more energetic
  - Higher T, more collisions, molecules move faster.

4) Presence of catalyst

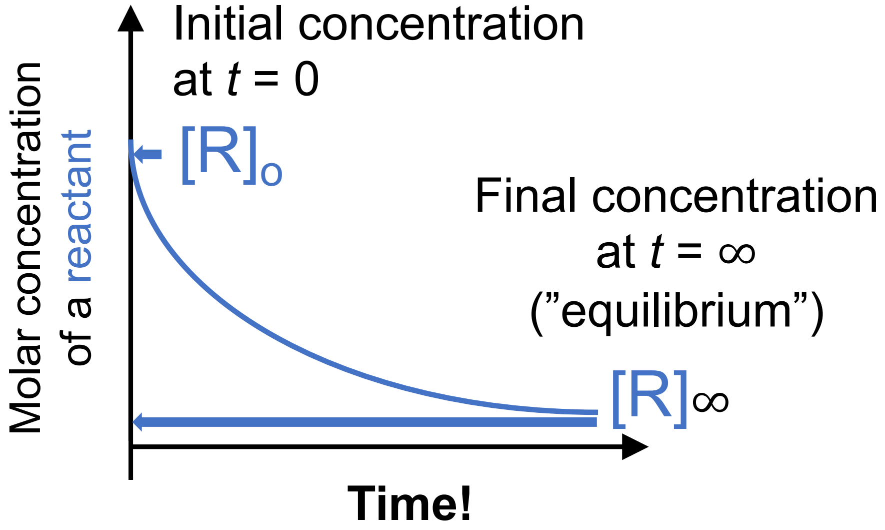
- Catalysts are not consumed in reaction.
  - They modify the reaction pathway in a way that lowers the energy barrier.

Kinetics of a reaction can be represented on a graph:

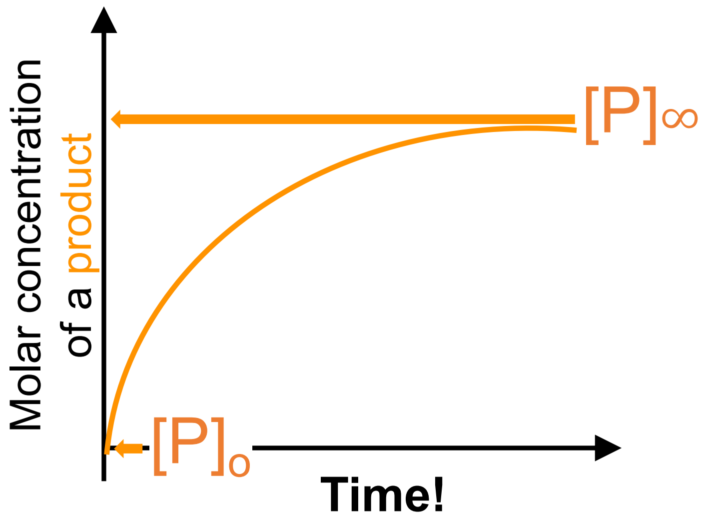
by monitoring a specific property that is characteristic of each species (absorbance, fluorescence, vibration, rotation, etc.)

Reactant (R) ⟶ **Product (P)**

Disappearance of a Reactant (Decay)



Appearance of a Product (Rise)



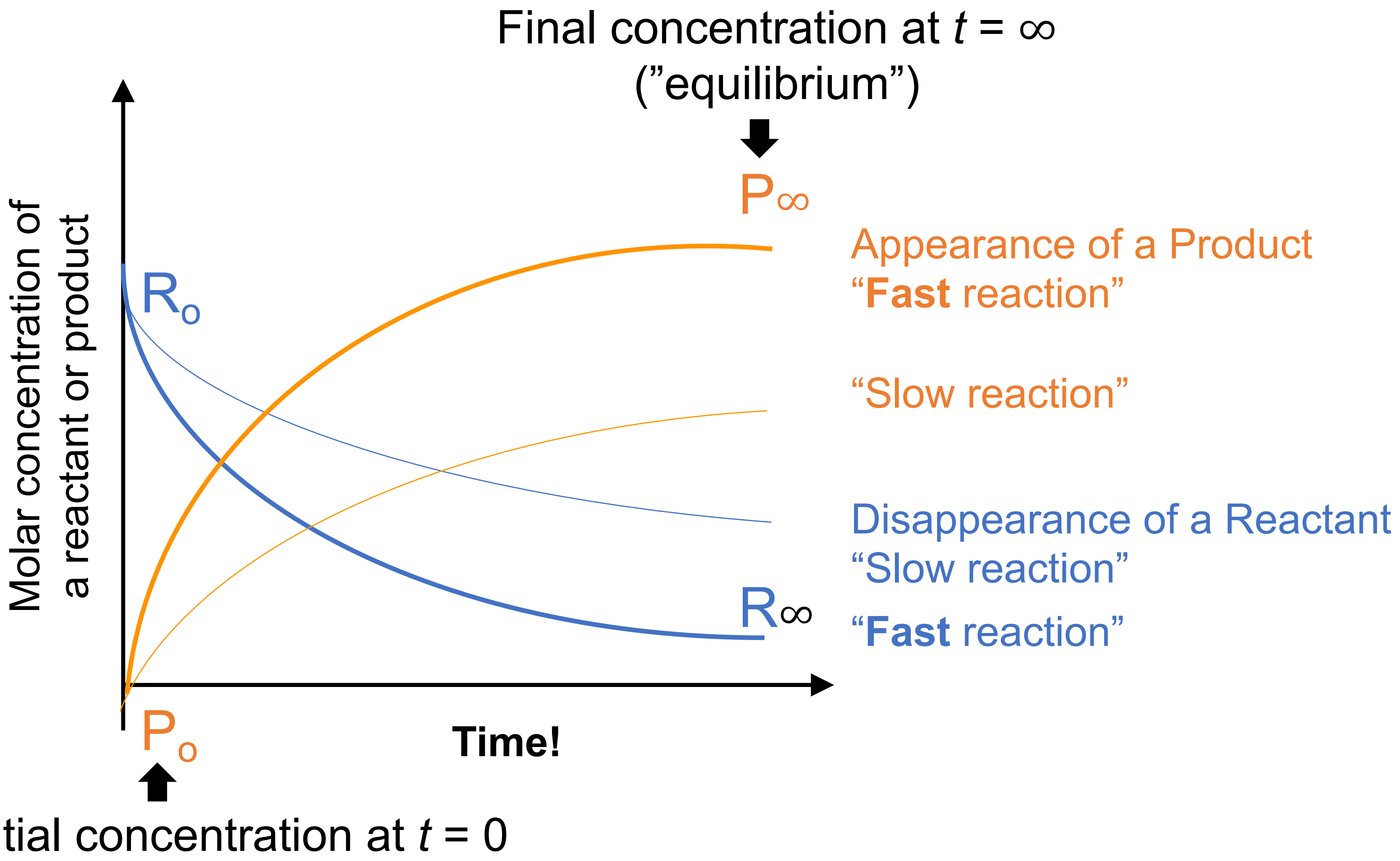
Information content of the "kinetic trace" (temporal change of concentration)

1) Is the compound a reactant or a product?
2) Initial amount of compound ("y" value at $t = 0$)
3) What is the final amount of the compound when the reaction is over?
4) How fast is the decay/rise of the compound? (how "steep" is the curve?)

Kinetics of a reaction can be represented on a graph:

by monitoring the amount of each species

Reactant (R) $\rightleftharpoons$ Product (P)



Definition of Reaction Rate

Reactant (R) ⟶ Product (P)

Rate is a change in concentration over a time period:

$$\Delta[A]/\Delta t$$

- Δ means “change”
- [A] means the molar concentration of a chemical species involved in a reaction (reactant or product).
- *t* represents time (sec, min, hour, day, etc).
- “Rate” is always POSITIVE.

Types of rates:

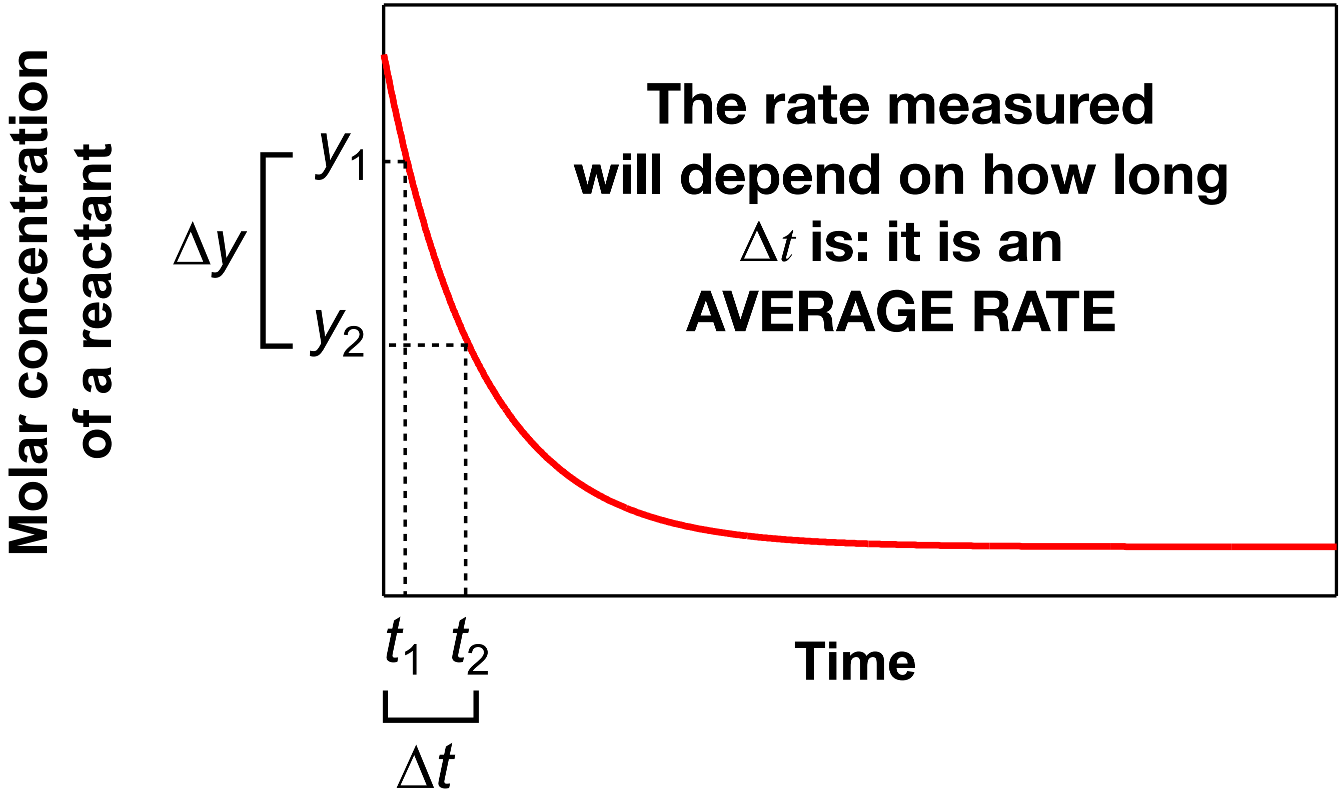
- Average rate
- Instantaneous rate
- Initial rate

Average rate

During a given time interval, how much product is made or how much reactant is consumed?

$$Average\ rate = \frac{|\Delta concentration|}{|\Delta time|} = \frac{|y_2 - y_1|}{|t_2 - t_1|} = \frac{\Delta y}{\Delta t}$$

Units: $mol \cdot L^{-1} \cdot s^{-1}$ or $M \cdot s^{-1}$

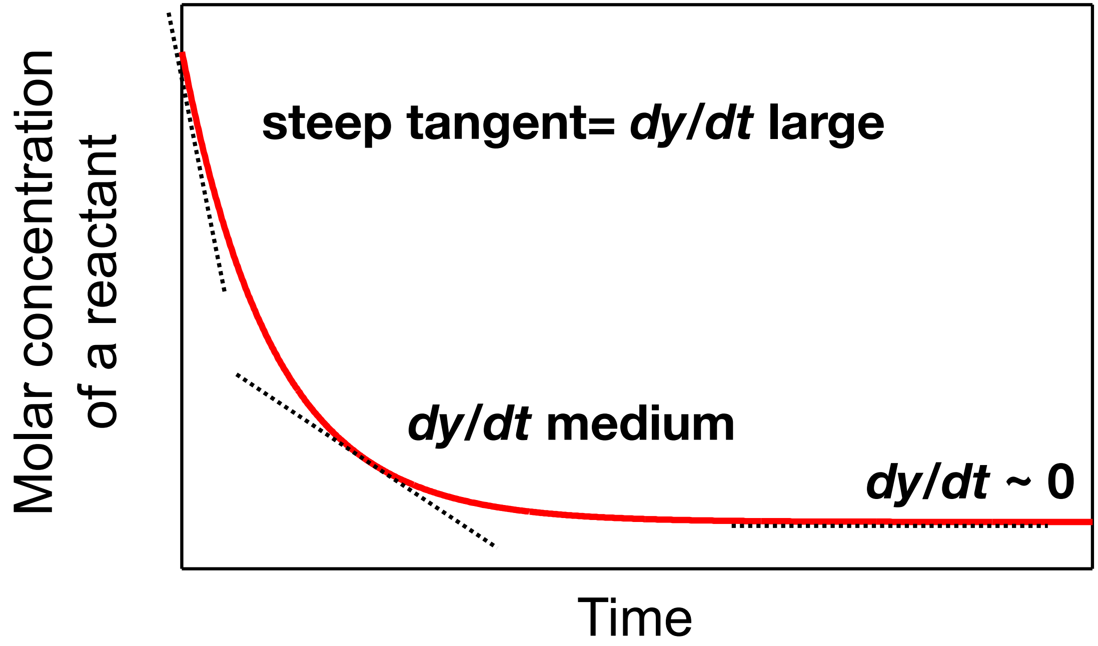


The rate measured will depend on how long Δt is: it is an AVERAGE RATE

Instantaneous rate

By taking the limit where Δt is infinitely small,
we can get the rate at a specific time,
which is the slope of the tangent of the curve at a certain time.

$$Instantaneous\ rate = \left|\lim_{t\to 0}\frac{\Delta concentration}{\Delta t}\right| = \left|\frac{d(concentration)}{dt}\right|$$



When we monitor the reactant concentration.

dy/dt = negative (conc. decreases)

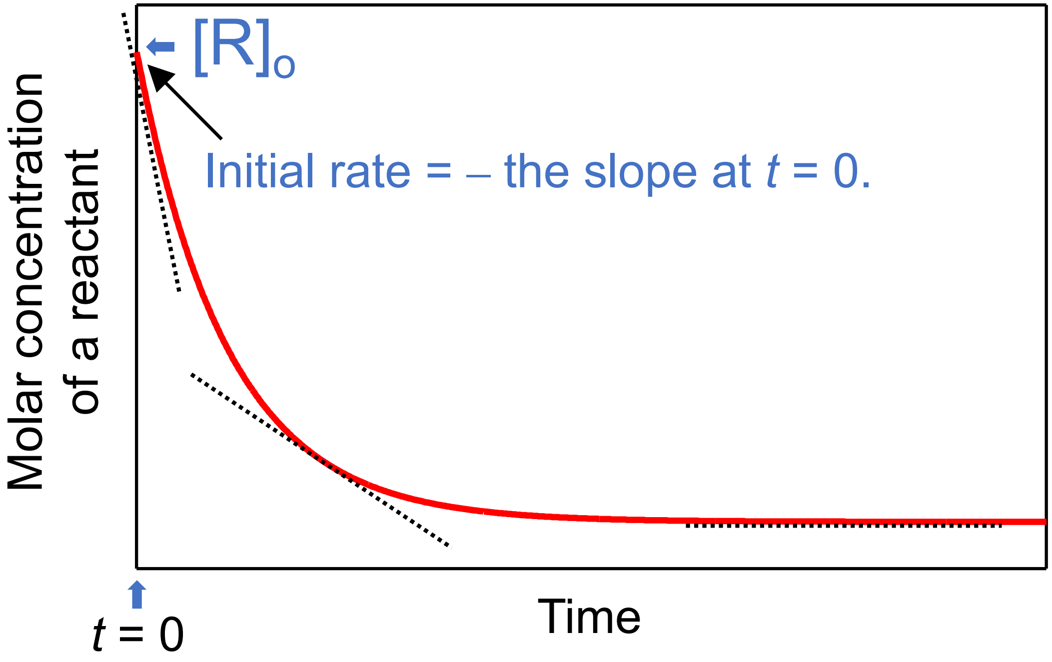
Rate = -dy/dt (positive)

NOTE: Rate is *changing* over time.
Why?

Initial rate

The instantaneous rate at the start of the reaction (i.e., the rate at *t* = 0).

$$Initial\ rate = \left|\lim_{t\to 0}\frac{\Delta(concentration)}{\Delta t}\right| = \Bigg|\Bigg|\left[\frac{d(concentration)}{dt}\right]_{t=0}\Bigg|$$



Importance of “initial rate”

- You know the concentrations of each reactant (the initial Conc’s).
- no product yet,
  - No reverse reaction
  - Rate only depends on *forward* process.
- **Initial rates** will be used to determine the **rate law**.

Normalized rates (or “relative” rates)

There is more than one way to describe the rate of a reaction, depending on which compound we choose to follow.

Example: synthesis of ammonia (Haber-Bosch reaction)

$$N_{2\,(g)} + 3\,H_{2\,(g)} \longrightarrow 2\,NH_{3\,(g)}$$

$$\frac{d[N_2]}{dt}$$

The rate of disappearance
of nitrogen gas
Sign: (–)

$$\frac{d[H_2]}{dt}$$

The rate of disappearance
for hydrogen gas
Sign: (–)

$$\frac{d[NH_3]}{dt}$$

The rate of appearance
for ammonia gas
Sign: (+)

Are these rates all the same?

Normalized rates (or “relative” rates)

$$N_{2\,(g)} + 3\,H_{2\,(g)} \longrightarrow 2\,NH_{3\,(g)}$$

$$\frac{d[N_2]}{dt}$$

Sign: (–)

$$\frac{d[H_2]}{dt}$$

Sign: (–)

$$\frac{d[NH_3]}{dt}$$

Sign: (+)

No!

When **one N_2** disappears
three H_2 disappear
two NH_3 appear.

We want to define one unique reaction rate for one specific reaction,

“Normalization of reaction rates”

Rule:

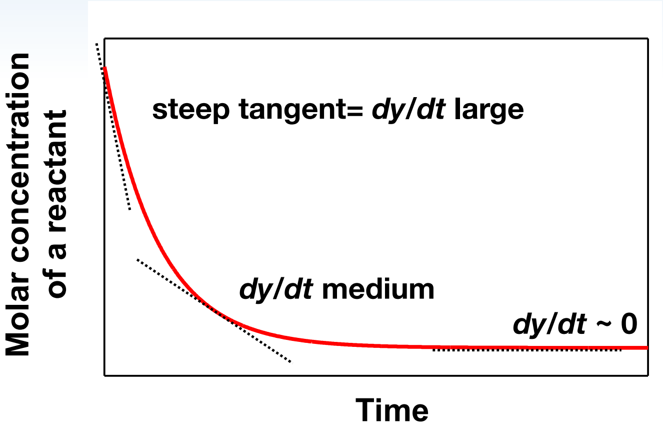
- Reaction rates are always positive quantities, no matter if a reactant consumed or a product is formed.
- We divide each rate by the stoichiometric factor of each compound in the balanced equation.

“Normalized rate”

$$\boxed{-\frac{d[N_2]}{dt} = -\frac{1}{3}\frac{d[H_2]}{dt} = \frac{1}{2}\frac{d[NH_3]}{dt}}$$

The Rate Law

- Why do reaction rates change with time?
    - Rates depend on the concentration of ***reacting*** species.
- But concentration changes with time,
    - so the rate must also change.
    - Almost always gets slower.



- "Rate Law"
    - Relates the rate to reactant concentrations.

$$\mathbf{Rate} = k\,[A]^n[B]^m \ldots.$$

"General form"

k**:** Rate constants (k is always a lower case)

[A], [B], … : Molar concentrations of reactants

n, m,… : Reaction orders (typically integer)

Some important definitions in the Rate Law

- We can define the "Rate Law", which links the rate to the concentration of the reactants.

$$\textbf{Rate} = d[A]/dt = k\,[A]^{n}[B]^{m} \ldots.$$

What is the "overall" reaction order?

n + m + … : sum of all exponents

What is the reaction order for the "individual" species?

n for A, m for B, … : the exponent for each species

What is the unit of the rate constant *k*?

It depends on the overall reaction order.

Whatever it needs to be for rate to be [conc]/sec

Usual units for rate: **M: molar Conc, s: time**

Units for k $= M \times M^{-n} \times M^{-m} \ldots \times s^{-1} = M^{1-(n+m+\ldots)} \times s^{-1}$

The unit of k

1st order : s^{-1}

2nd order: $M^{-1}\ s^{-1}$

Examples of Rate Laws

1) $2\ N_2O_5 \longrightarrow 4\ NO_2 + O_2$

$\text{Rate} = k[N_2O_5]$ *first order in N_2O_5, first order overall*

2) $2\ NO + Cl_2 \longrightarrow 2\ NOCl$

$\text{Rate} = k[NO]^2[Cl_2]$ *second order in NO, first order in Cl_2, third order overall*

3) $2\ NO + 2H_2 \longrightarrow N_2 + 2\ H_2O$

$\text{Rate} = k[NO]^2[H_2]$ *second order in NO, first order in H_2, third order overall*

4) $NO_2 + CO \longrightarrow NO + CO_2$

$\text{Rate} = k[NO_2]^3$ *third order in NO_2, zeroth order in CO, third order overall*

NOTE:

1) Rate laws do NOT depend on ***product*** concentrations.

2) NO link between the balanced reaction formula and the rate law.

3) NO link between stoichiometric coefficients and rate law.

Units of Rate Constant (*k*)

The units of the rate constant (*k*) depend on the overall order of the reaction:

OVERALL ORDER	EQUATION	UNITS of k
0th	$-\frac{d[R]}{dt} = k$	$M \cdot s^{-1}$
1st	$-\frac{d[R]}{dt} = k[R]$	s^{-1}
2nd	$-\frac{d[R]}{dt} = k[R]^2$	$M^{-1} \cdot s^{-1}$
3rd	$-\frac{d[R]}{dt} = k[R]^3$	$M^{-2} \cdot s^{-1}$

Units (convention):
LIQUID phase: CONCENTRATION works well (Molarity)
GAS phase: PRESSURE is a better quantity (atm, Torr, kPa)
SOLID phase: the MASS of the solid works better. (mg, g, kg, …)

In case of the reactants in the gas or solid phase, **change the unit in the table** for a unit of concentration, pressure (atm, Torr, kPa…) or mass.

Tricks for measuring the Rate Law
I. "The method of Initial Rate"

$$\underset{\text{ammonium cyanate}}{(NH_4)[OCN]} \longrightarrow \underset{\text{urea}}{(NH_2)_2CO}$$

Exp	$[NH_4OCN]$ (M)	initial rate ($M\cdot s^{-1}$)
1	0.250	0.162
2	0.500	0.651

"Initial concentrations"

$$\text{Rate} = k\,[A]^n[B]^m \;\ldots.$$

How can we find the reaction orders?

We can simply look at what happens to the rate when the initial concentration of the reactant is changed.

There is only one reactant.

$$\text{Rate} = k\,[A]^n[B]^m \;\ldots. \;\Rightarrow\; \text{Rate} = k\,[NH_4OCN]^n$$

Defining the Rate Law for a reaction "The method of Initial Rate"

$$(NH_4)[OCN] \longrightarrow (NH_2)_2CO$$

ammonium cyanate **urea**

Exp	$[NH_4OCN]$ (M)	initial rate ($M \cdot s^{-1}$)
1	0.250	0.162
2	0.500	0.651

"Initial concentrations"

$$\text{Rate} = k\,[NH_4OCN]^n$$

Goal: find the reaction order (n)

How does the rate change when the initial concentration of the reactant is changed.

$$\text{rate in Exp 1} \rightarrow R_1 = k[NH_4OCN]_1^{\,n} \leftarrow \text{concentration used in Exp 1}$$

$$\text{rate in Exp 2} \rightarrow R_2 = k[NH_4OCN]_2^{\,n} \leftarrow \text{concentration used in Exp 2}$$

Take the ratio of R_2 to R_1, then k is canceled out and *n* becomes the only unknown.

$$\frac{R_2}{R_1} = \frac{k[NH_4OCN]_2^{\,n}}{k[NH_4OCN]_1^{\,n}} = \left(\frac{[NH_4OCN]_2}{[NH_4OCN]_1}\right)^n$$

Defining the Rate Law for a reaction "The method of Initial Rate"

$$\underset{\textbf{ammonium cyanate}}{(NH_4)[OCN]} \longrightarrow \underset{\textbf{urea}}{(NH_2)_2CO}$$

Exp	$[NH_4OCN]$ (M)	initial rate ($M \cdot s^{-1}$)
1	0.250	0.162
2	0.500	0.651

Rate = *k* $[NH_4OCN]^n$

We want to isolate the order *n* from that equation:

$$\frac{R_2}{R_1} = \left(\frac{[NH_4OCN]_2}{[NH_4OCN]_1}\right)^{\boxed{n}}$$

This is done by taking the logarithm on both sides of the equation:

$$\log\left(\frac{R_2}{R_1}\right) = \log\left(\frac{[NH_4OCN]_2}{[NH_4OCN]_1}\right)^n$$

$$= n \times \log\left(\frac{[NH_4OCN]_2}{[NH_4OCN]_1}\right)$$

remember that:

$$\log\left(A^b\right) = b \cdot \log\left(A\right)$$

Defining the Rate Law for a reaction "The method of Initial Rate"

$(NH_4)[OCN] \longrightarrow (NH_2)_2CO$

ammonium cyanate → **urea**

Exp	$[NH_4OCN]$ (M)	initial rate ($M \cdot s^{-1}$)
1	0.250	0.162
2	0.500	0.651

Rate = *k* $[NH_4OCN]^2$

To get the order *n*, we simply plug in the rate and concentration values from the table above:

$\log (2)^2 = 2 \log (2)$

$$n = \frac{\log\left(\frac{R_2}{R_1}\right)}{\log\left(\frac{[NH_4OCN]_2}{[NH_4OCN]_1}\right)} = \frac{\log\left(\frac{0.651\ M\cdot s^{-1}}{0.162\ M\cdot s^{-1}}\right)}{\log\left(\frac{0.500\ M}{0.250\ M}\right)} = \frac{\log(4)}{\log(2)} = 2$$

Defining the Rate Law for a reaction
“The method of Initial Rate”

$$2\,NO\,(g) + 2\,H_2\,(g) \longrightarrow N_2\,(g) + 2\,H_2O\,(g)$$

Nitric oxide Hydrogen Nitrogen Water

Experiment	[NO] (M)	$[H_2]$ (M)	initial rate ($M \cdot s^{-1}$)
1	0.10	0.10	1.23×10^{-3}
2	0.10	0.20	2.46×10^{-3}
3	0.20	0.10	4.92×10^{-3}

“Initial concentrations”

Goals:

(a) Rate Law?

(b) Rate constant?

(c) Rate when [NO] = 0.050 M and $[H_2]$ = 0.150 M?

(a) Rate Law?

$$2\ \mathrm{NO}\ (g) + 2\ \mathrm{H_2}\ (g) \longrightarrow \mathrm{N_2}\ (g) + 2\ \mathrm{H_2O}\ (g)$$

Experiment	[NO] (M)	$[H_2]$ (M)	initial rate ($M \cdot s^{-1}$)
1	0.10	0.10	1.23×10^{-3}
2	0.10	0.20	2.46×10^{-3}
3	0.20	0.10	4.92×10^{-3}

Step 1) Setting the rate law

$$\text{Rate} = k\,[A]^m[B]^n \ \ldots\ldots = k\,[\mathrm{NO}]^m[\mathrm{H_2}]^n$$

Step 2) Determining the reaction order for NO.

$$\text{Rate1} = k\,[0.1]^m[0.1]^n = 1.23 \times 10^{-3}$$

$$\text{Rate2} = k\,[0.2]^m[0.1]^n = 4.92 \times 10^{-3}$$

When [NO] changes,
how does the rate change?

$$\text{Ratio} = \frac{\text{Rate2}}{\text{Rate1}} = \frac{4.92 \times 10^{-3}}{1.23 \times 10^{-3}} = 4 = \frac{k\,[0.2]^m[0.1]^n}{k\,[0.1]^m[0.1]^n} = 2^m = 4 \qquad \boldsymbol{m = 2}$$

(a) Rate Law?

$$2\,NO\,(g) + 2\,H_2\,(g) \longrightarrow N_2\,(g) + 2\,H_2O\,(g)$$

Experiment	[NO] (M)	$[H_2]$ (M)	initial rate ($M \cdot s^{-1}$)
1	0.10	0.10	1.23×10^{-3}
2	0.10	0.20	2.46×10^{-3}
3	0.20	0.10	4.92×10^{-3}

Step 3) Determining the reaction order for H_2.

Rate = $k\,[NO]^m[H_2]^n$

Rate1’ = $1.23 \times 10^{-3} = k\,[0.1]^m[0.1]^n$

Rate2’ = $2.46 \times 10^{-3} = k\,[0.1]^m[0.2]^n$

When $[H_2]$ changes,
how does the rate changes?

$$\text{Ratio} = \frac{\text{Rate2'}}{\text{Rate1'}} = \frac{2.46 \times 10^{-3}}{1.23 \times 10^{-3}} = 2 = \frac{k\,[0.1]^m[0.2]^n}{k\,[0.1]^m[0.1]^n} = 2^n = 2 \qquad \mathbf{n = 1}$$

Final rate law: Rate = $k\,[NO]^2[H_2]$

(b) Rate constant?

$$2\,NO\,(g) + 2\,H_2\,(g) \longrightarrow N_2\,(g) + 2\,H_2O\,(g)$$

Experiment	[NO] (M)	$[H_2]$ (M)	initial rate ($M \cdot s^{-1}$)
1	0.10	0.10	1.23×10^{-3} ⬅
2	0.10	0.20	2.46×10^{-3}
3	0.20	0.10	4.92×10^{-3}

What is the value of k?

Rate Law: Rate = $k\,[NO]^2[H_2]$

Rate1 = $k\,[NO]_1^2[H_2]_1 = k\,(0.1)^2(0.1) = 1.23 \times 10^{-3}$ **$k = 1.23$**

$1.23 \times 10^{-3}/(0.1)^3 = 1.23$

What is the unit of *k*?

$\mathbf{M \cdot s^{-1}} = \boldsymbol{k} \cdot M^2 \cdot M$ $\quad$ $k = \dfrac{M \cdot s^{-1}}{M^2 \cdot M} = M^{-2} \cdot s^{-1}$

⬇

Unit of rate is always Conc./time!

Final answer: $k = 1.23\ M^{-2} \cdot s^{-1}$

(c) Once we define the rate law, we can predict the rate at given reactant concentrations.

$$2\ NO\ (g) + 2\ H_2\ (g) \longrightarrow N_2\ (g) + 2\ H_2O\ (g)$$

Experiment	[NO] (M)	$[H_2]$ (M)	initial rate ($M \cdot s^{-1}$)
1	0.10	0.10	1.23×10^{-3}
2	0.10	0.20	2.46×10^{-3}
3	0.20	0.10	4.92×10^{-3}

(c) Rate when [NO] = 0.050 M and $[H_2]$ = 0.150 M?

$$\text{Rate} = k\,[NO]^2[H_2] = 1.23\ M^{-2} \cdot s^{-1}\ (0.05\ M)^2\ (0.150\ M)$$

$$= 4.61\ M \cdot s^{-1}$$

Rate Laws *vs* Integrated Rate Laws

Rate = $d[A]/dt = k\,[A]^n[B]^m$ …. “The form of time derivative”

Usually, we measure the **concentration** versus time:

The **RATE LAW** tells us how the rate changes as a function of reactant concentration. But how do you predict the actual ***amount*** of reactant or product at a given time?

$$[R] \quad vs. \quad t$$

INTEGRATED RATE LAW equation that gives [*R*] *vs. t*.

$$\text{Integrated Rate Law} = \int \text{Rate Law}$$

Integrated Rate Law of a First-Order Reaction

1st-order rate law:

$$\text{RATE} = -\frac{d[R]}{dt} = k[R]$$

minus sign because
R is a reactant

Step 1 Separate [R] from t:

$$\frac{d[R]}{[R]} = -kdt$$

Step 2 Integrate both sides:

$$\int_{[R]_0}^{[R]_t} \frac{1}{[R]} d[R] = -k\int_0^t dt$$

Integration range:
As time changes from 0 to *t*, reactant Conc. changes from $[R]_0$ to $[R]_t$.

$$\ln[R]_t - \ln[R]_0 = -k \cdot t$$

$$\ln\left([R]_t/[R]_0\right) = -k\cdot t$$

Integration law

$$\int \frac{1}{x} dx = lnx$$

Step 3 Finally, rearrange:

$$\boxed{[R]_t = [R]_0 \cdot e^{-k\cdot t}}$$

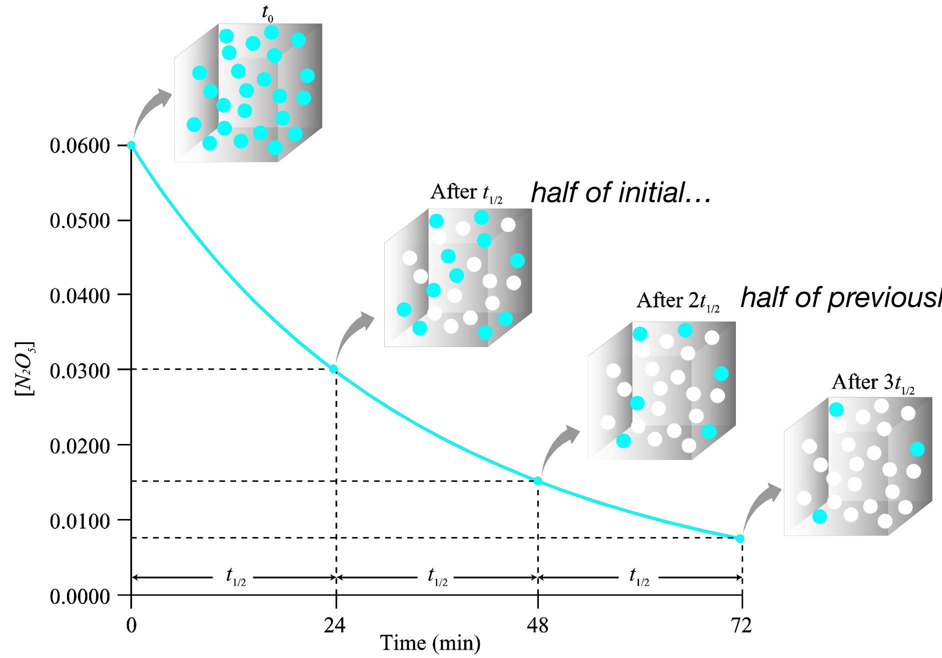
Integrated rate law for first-order reaction

Integrated Rate Law of a First-Order Reaction

This function is called an EXPONENTIAL DECAY (it's an exponential, it decays…) $[R]_0$ is the concentration at $t = 0$ (initial concentration of R) and $[R]_t$ is the concentration at time *t.*

INTEGRATED RATE LAW
OF A 1st-ORDER REACTION

$$\boxed{[R]_t = [R]_0 \cdot e^{-k \cdot t}}$$



half of initial…

half of previously…

half of previously…

equal $t_{1/2}$ throughout the whole decay…

Half-Life of a First-Order Reaction

Half-Life ($t_{1/2}$): the time needed to reduce the reactant concentration to half of what it is initially. It is one measure of how fast a reaction proceeds.

Integrated Rate Law:

$$[R]_t = [R]_0 \cdot e^{-k \cdot t}$$

$$\Rightarrow [R]_{t_{1/2}} = [R]_0 e^{-k \cdot t_{1/2}}$$

Replace $[R]_{t1/2}$ with $[R]_0/2$:

$$\frac{[R]_0}{2} = [R]_0 e^{-k \cdot t_{1/2}}$$

Divide by $[R]_0$ and take a log of both side:

$$\frac{[R]_0}{2[R]_0} = e^{-kt_{1/2}}$$

$$\frac{1}{2} = e^{-kt_{1/2}}$$

$$2 = e^{kt_{1/2}}$$

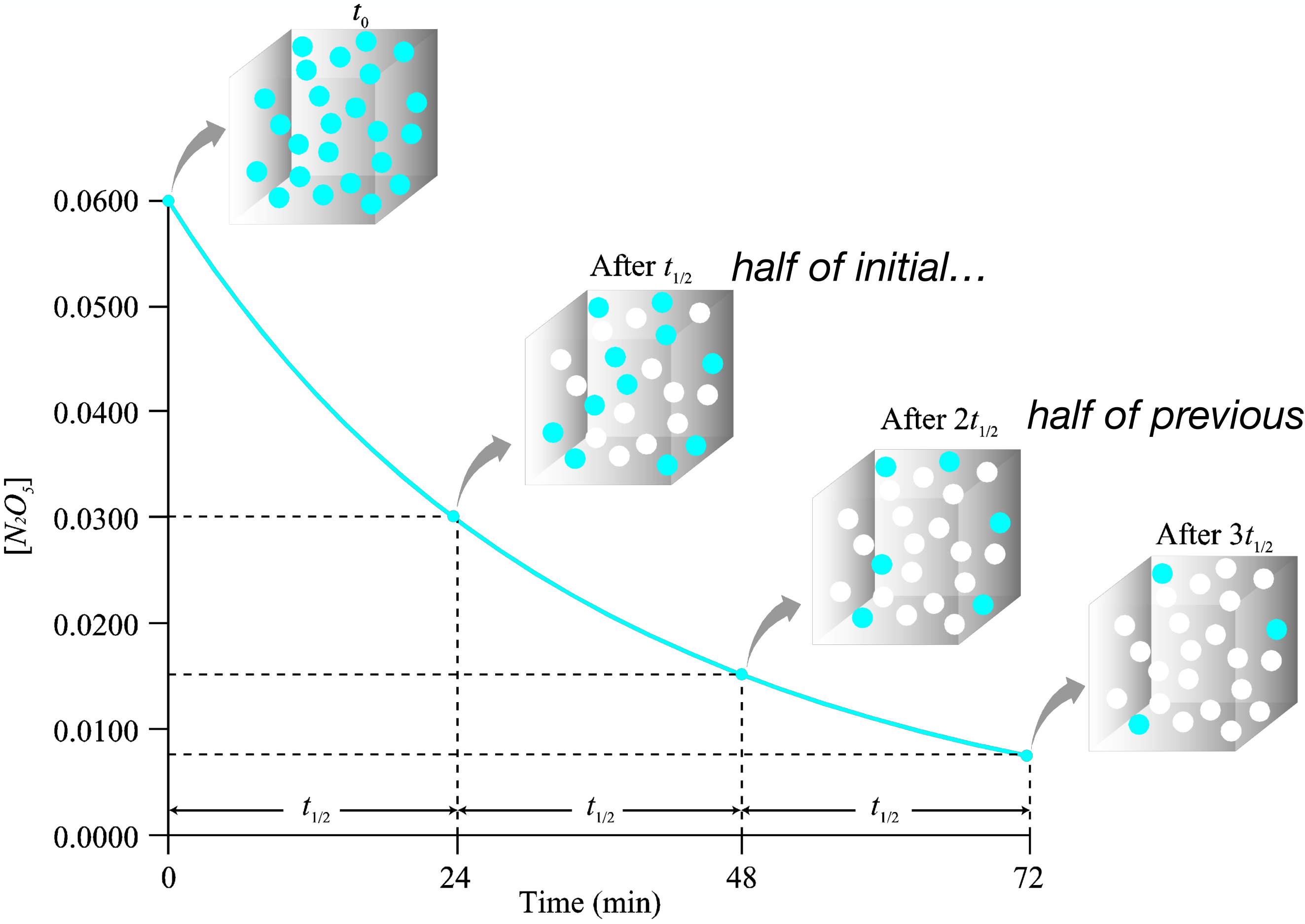
Take *ln*, rearrange:

$$\boxed{t_{1/2} = \frac{\ln 2}{k}}$$

Important characteristics of 1st-order reactions…

- The **half-life** of a first-order reaction depends only on the rate constant:
- independent of the initial reactant concentration.

Half-Life of a First-Order Reaction



half of initial…

half of previously…

half of previously…

equal $t_{1/2}$ throughout the whole decay…

Integrated Rate Law of a Second-Order Reaction

2nd-order rate law:

$$\text{RATE} = -\frac{d[R]}{dt} = k[R]^2$$

Step 1 separate [R] from t:

$$\frac{d[R]}{[R]^2} = -k \cdot dt$$

Step 2 integrate both sides:

$$\int_{[R]_0}^{[R]_t} \frac{1}{[R]^2}\, d[R] = -k \int_0^t dt$$

$$\frac{1}{[R]_t} - \frac{1}{[R]_0} = k \cdot t$$

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

$$\frac{1}{[R]_t} = \frac{1}{[R]_0} + kt\,\frac{[R]_0}{[R]_0}$$

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

Integration range:
As time changes from 0 to *t*, reactant Conc. changes from $[R]_0$ to $[R]_t$.

Integration law

Here, *n* = -2

$$\int x^n dx = \frac{x^{n+1}}{n+1} + C$$

Step 3 Finally, rearrange:

$$\boxed{[R]_t = \frac{[R]_0}{1 + [R]_0 \cdot k \cdot t}}$$

INTEGRATED RATE LAW of a 2nd-order reaction.

Half-Life of a Second-Order Reaction

Integrated Rate Law:

$$\boxed{[R]_t = \frac{[R]_0}{1+[R]_0 \cdot k \cdot t}}$$

➡

$$[R]_{t_{1/2}} = \frac{[R]_0}{1+[R]_0 \cdot k \cdot t_{1/2}}$$

Replace $[R]_{t1/2}$ with $[R]_0/2$:

$$\frac{[R]_0}{2} = \frac{[R]_0}{1+[R]_0 \cdot k \cdot t_{1/2}}$$

$$\frac{2}{[R]_0} = \frac{1+[R_O]kt_{1/2}}{[R_O]}$$

$$\frac{2R_O}{R_O} = 1+[R_O]kt_{1/2}$$

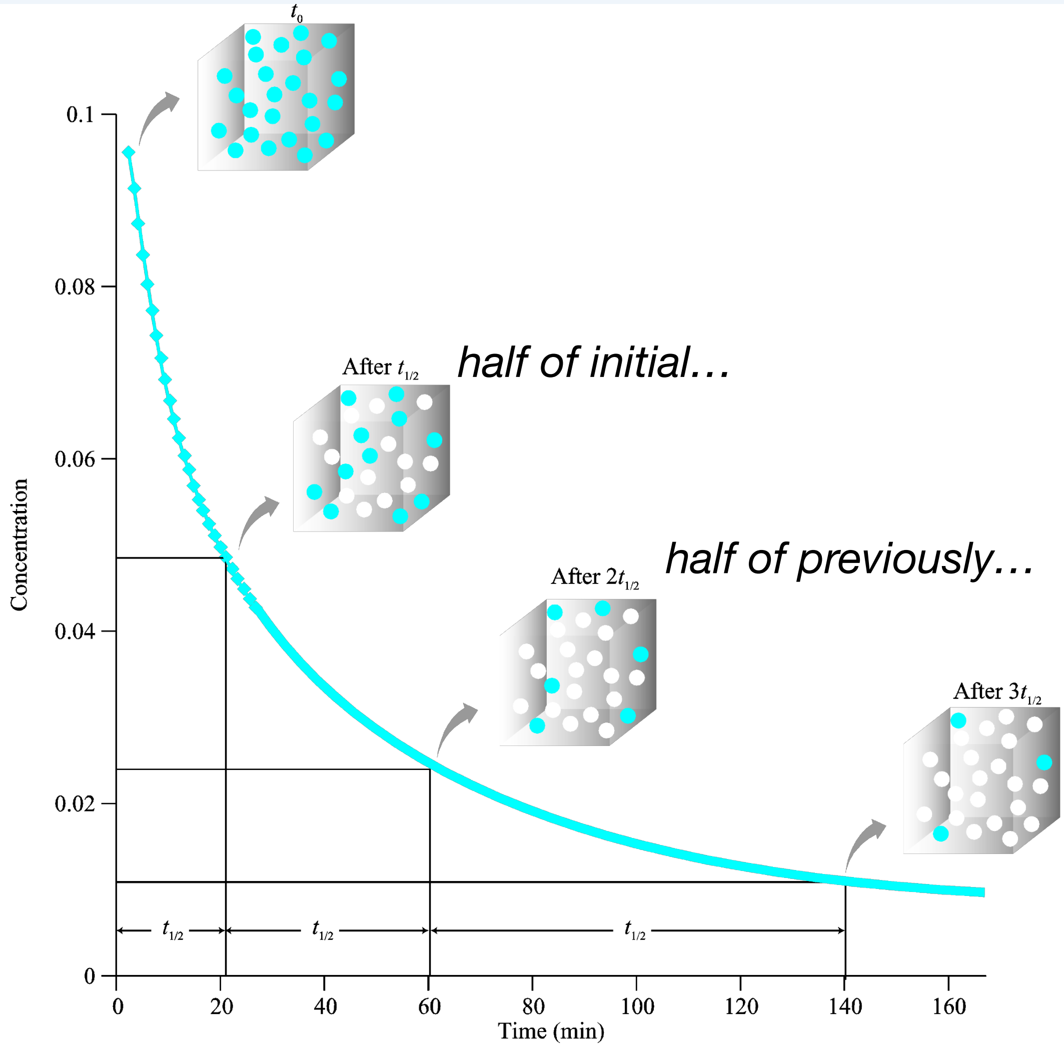
$$2-1 = 1 = [R_O]kt_{1/2}$$

Arrange:

$$\boxed{t_{1/2} = \frac{1}{k \cdot [R]_0}}$$

The half-life of a second-order reaction depends on the **initial reactant concentration:** the smaller $[R]_0$, the longer $t_{1/2}$ is…

Half-Life of a Second-Order Reaction



half of initial…

half of previously…

half of previously…

Note how $t_{1/2}$ *<u>increases</u>* as the reaction proceeds…

Integrated Rate Law of a Zeroth-Order Reaction

The 0th-order rate law: $$\text{RATE} = -\frac{d[R]}{dt} = k$$

Step 1 separate [R] from t: $$d[R] = -k \cdot dt$$

Step 2 integrate both sides: $$\int_{[R]_0}^{[R]_t} d[R] = -k \int_0^t dt$$

Integration range:
As time changes from 0 to *t*, reactant Conc. changes from $[R]_0$ to $[R]_t$.

Step 3 Finally, rearrange: $$[R]_t - [R]_0 = -k \cdot t$$

Integration law

$$\int 1 \cdot dx = x$$

$$\boxed{[R]_t = [R]_0 - k \cdot t}$$

INTEGRATED RATE LAW OF A 0th-ORDER REACTION

Half-Life of a Zeroth-Order Reaction

Integrated Rate Law:

$$\boxed{[R]_t = [R]_0 - k \cdot t}$$

Replace $[R]_t$ with $[R]_0$ / 2 :

$$\frac{[R]_0}{2} = [R]_0 - k \cdot t_{1/2}$$

$$\frac{[R]_0}{2} - [R]_0 = -kt_{1/2}$$

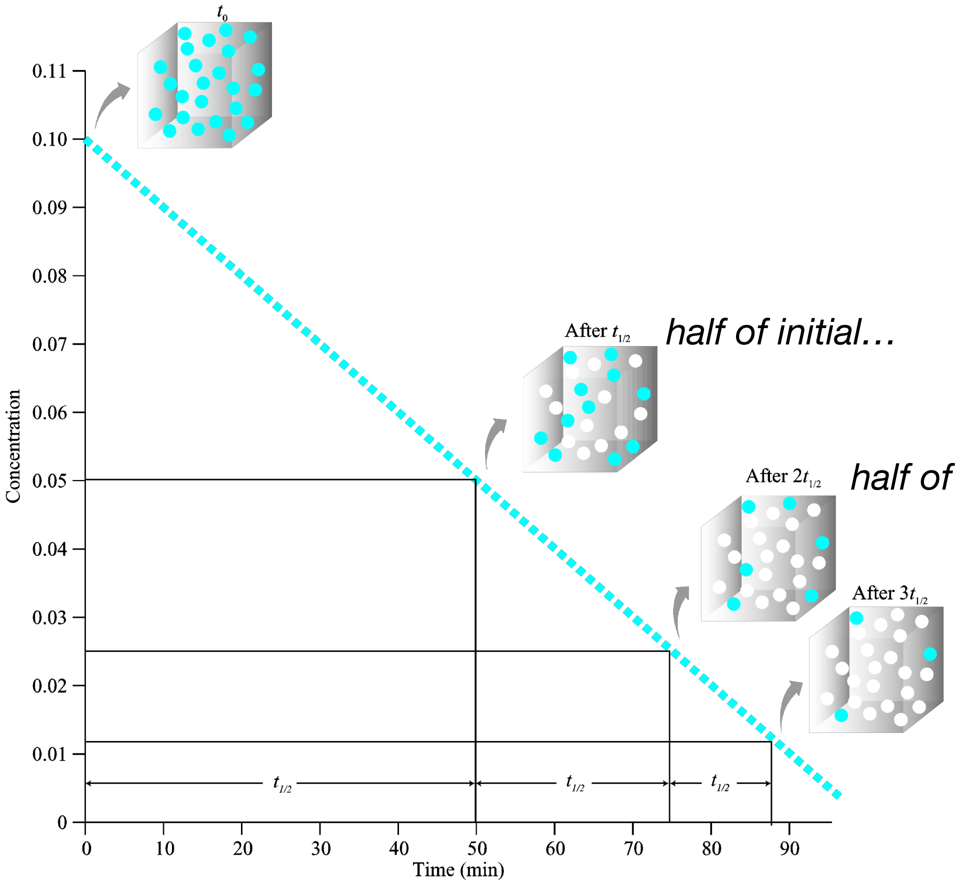
$$-\frac{[R]_0}{2} = -kt_{1/2}$$

Rearrange:

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

The half-life of a zeroth-order reaction depends on the **initial reactant concentration and *k*:** the smaller $[R]_0$, the smaller $t_{1/2}$ is…

Half-Life of a Zeroth-Order Reaction



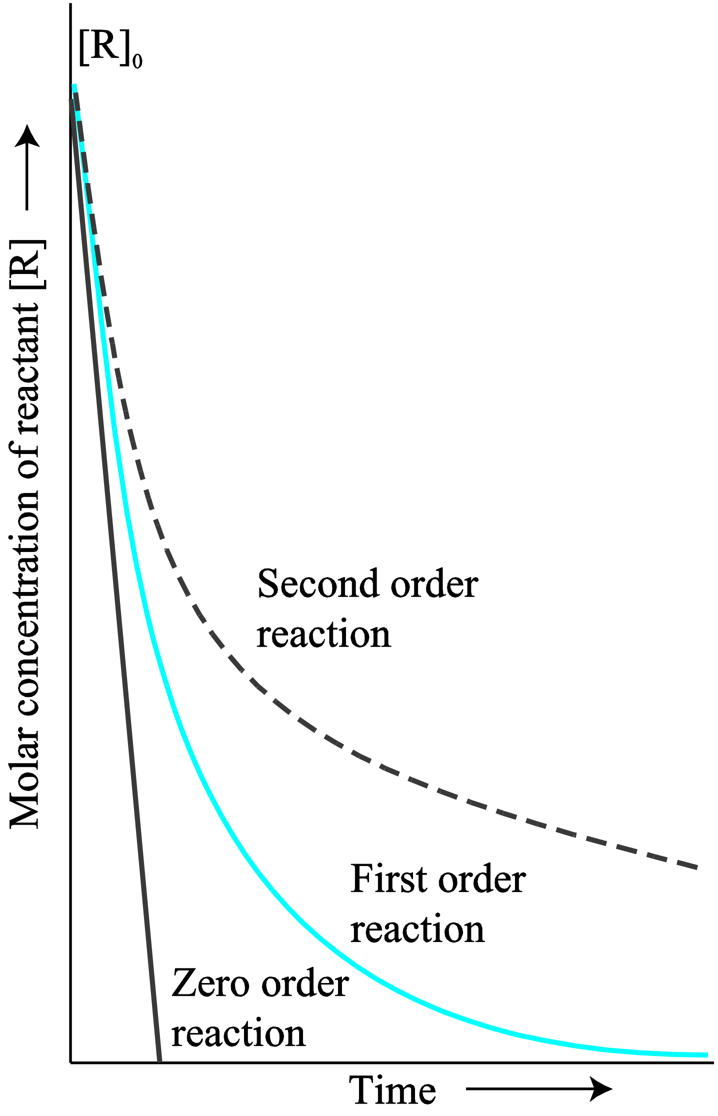
half of initial…

half of previously…

half of previously…

Note how $t_{1/2}$ *decreases* as the reaction proceeds…

Comparison of the Integrated Rate Laws



Half lives

First order

$$\boxed{t_{1/2} = \frac{\ln 2}{k}}$$

Second order

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

Zeroth order

$$\boxed{t_{1/2} = \frac{1}{k \cdot [R]_0}}$$

Example: Half-Life of a First-Order Reaction

Example: Gold-198 (^{198}Au) is a radioactive isotope of gold. It decays by a 1st-order process to become mercury, with a **half-life** of 2.697 days.
If you have 10.0 mg of gold-198 at the beginning of the week, how much is left by the end of the week?

- **What is the given information?** A half-life $t_{1/2}$ and the initial mass.
- **What can we get from the half-life?** Rate constant *k*!

$$t_{1/2} = \frac{\ln 2}{k} = 2.697 \text{ days}$$

$$k = \frac{\ln 2}{2.697 \text{ days}} \approx \frac{0.6931}{2.697 \text{ days}} = 0.2570 \text{ day}^{-1}$$

- If we know *k* and the initial mass, that is all we need to know to solve the problem for the first-order reaction. How?

Use the integrated rate law.

$$m_t = m_0 \cdot e^{-k \cdot t}$$

$$m_{7 \text{ day}} = 10.0 \text{ mg} \cdot e^{-0.2570 \text{ day}^{-1} \cdot 7 \text{ day}} \approx 1.7 \text{ mg}$$

because gold is a solid, we use mass instead of concentration…

Linearization of the integrated rate law

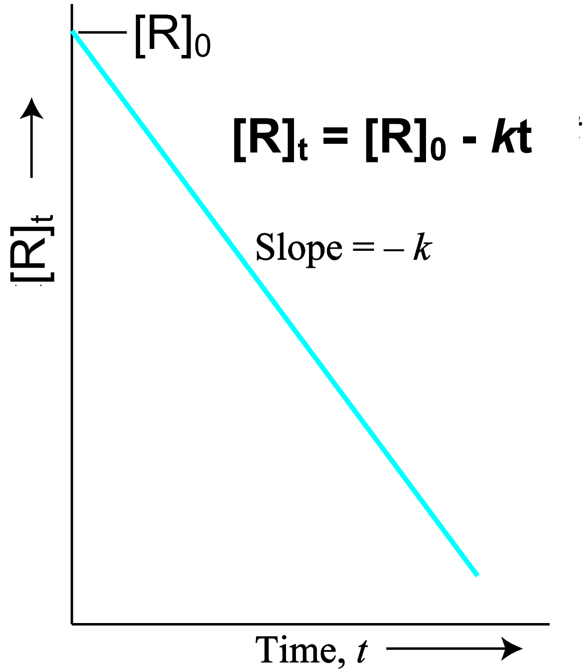
Each Integrated Rate Law can be *plotted on a graph* as a *line* ($Y = mX + b$), which is easier to visualize:

OVERALL ORDER	RATE LAW	INTEGRATED RATE LAW	PLOT "*Y vs. X*"	Linear Equation ($Y = a + b X$)	Slope (b)	Y-Intercept (a)
0th	RATE = k	$[R]_t = [R]_0 - k\,t$	$[R]_t$ vs. t	$[R]_t = [R]_0 - k\,t$	$-k$	$[R]_0$
		Linear as it is!				
1st	RATE = $k[R]$	$[R]_t = [R]_0 \cdot e^{-k \cdot t}$	$\ln([R]_t)$ vs. t	$\ln [R]_t = \ln [R]_0 - k\,t$	$-k$	$\ln [R]_0$
		Take natural log for both sides.				
2nd	RATE = $k[R]^2$	$[R]_t = \dfrac{[R]_0}{1 + [R]_0 \cdot k \cdot t}$	$1/[R]_t$ vs. t	$\dfrac{1}{[R]_t} = \dfrac{1}{[R]_0} + k \cdot t$	$+k$	$1/[R]_0$
		Take reciprocal for both sides.				

Linearization of the integrated rate law

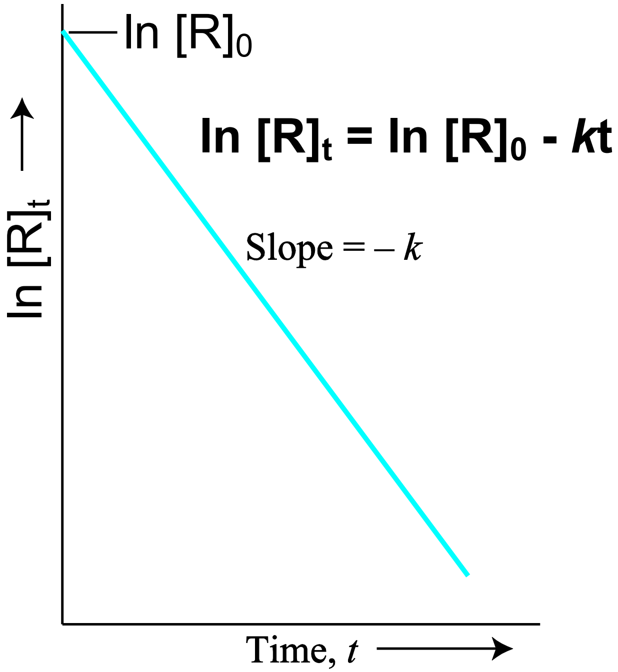
- Checking the linearity under each condition is a good test for defining the reaction order.
- We can easily obtain the rate constant (k) – directly related to the slope of the line.

Zeroth order



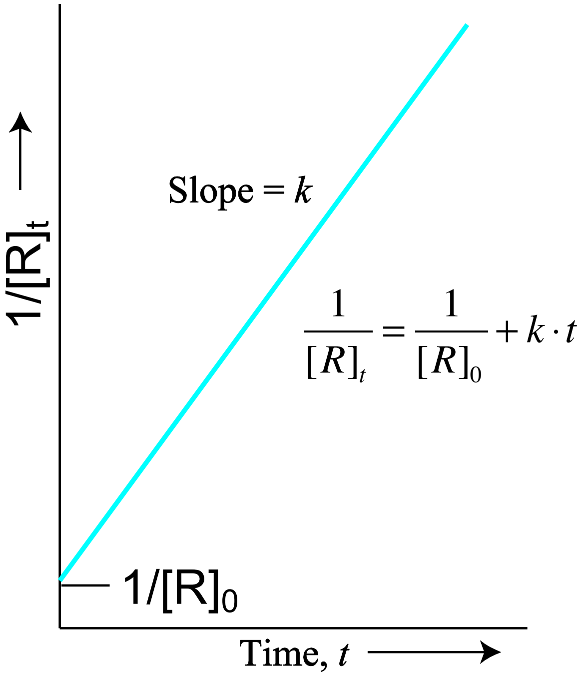
$$[R]_t = [R]_0 - kt$$

First order



$$\ln [R]_t = \ln [R]_0 - kt$$

Second order



$$\frac{1}{[R]_t} = \frac{1}{[R]_0} + k \cdot t$$

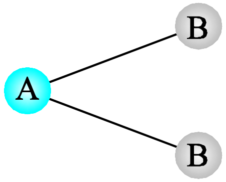
Collision Theory

How do we explain kinetics?
Chemical reaction: Old bonds break, new ones form.
How do they do that?

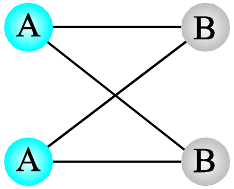
Molecules collide. more collisions, higher chance of reaction.

A + B → ***C*** : the collision between A and B is productive!

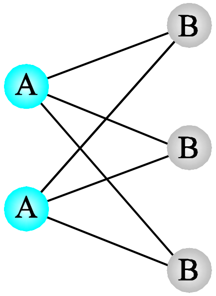
One molecule of A and two molecules of B
Only two collisions possible:



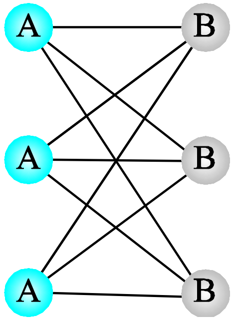
Two molecules of A and two molecules of B
Four collisions possible:



Two molecules of A and three molecules of B
Six collisions possible:



Three molecules of A and three molecules of B
Nine collisions possible:



But just a collision is not enough. What makes a *successful collision?*

Conditions for successful reaction:

- The orientation of the molecules matters.
- Collision must be hard enough, have enough energy to break and rearrange the bonds.

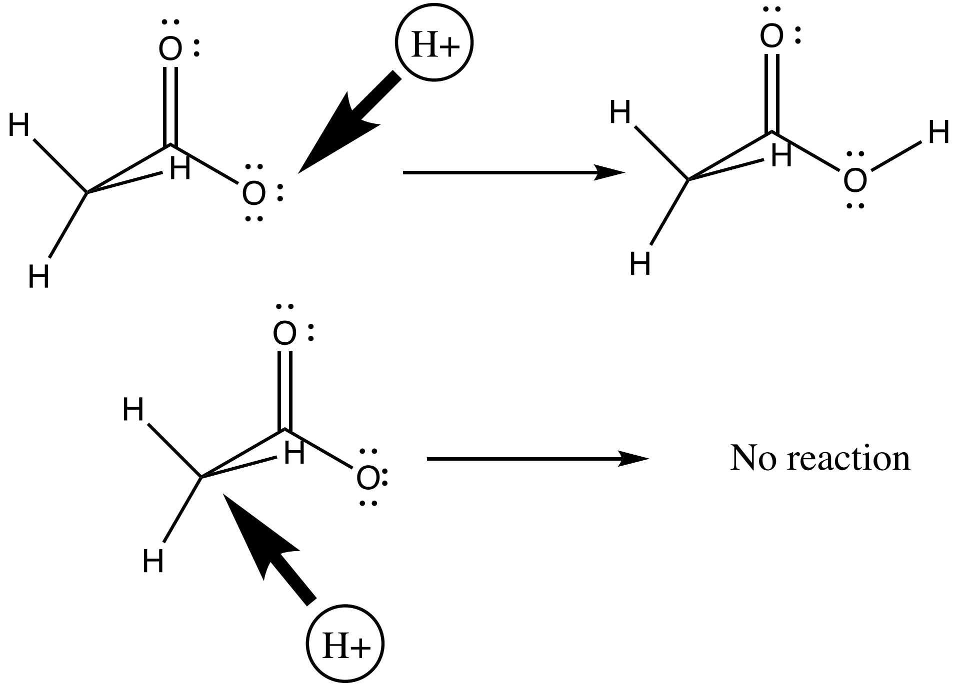
Example: Acid-base reaction

Protonation of acetic acid

$$CH_3COO^- + H^+ \rightleftarrows CH3COOH$$

Acetate Proton Acetic acid

Orientation matters.



Collision Theory: Arrhenius Theory

Definition of enthalpy (H):

Energy released upon reaction
in the form of "HEAT" (measurable) **at constant pressure**

$$H = E + PV$$

Enthalpy:
equivalent to "heat content" of the system

Internal energy

Pressure

Volume

All types of energy related to bonding and movement of particles (rotation, vibration and translation):

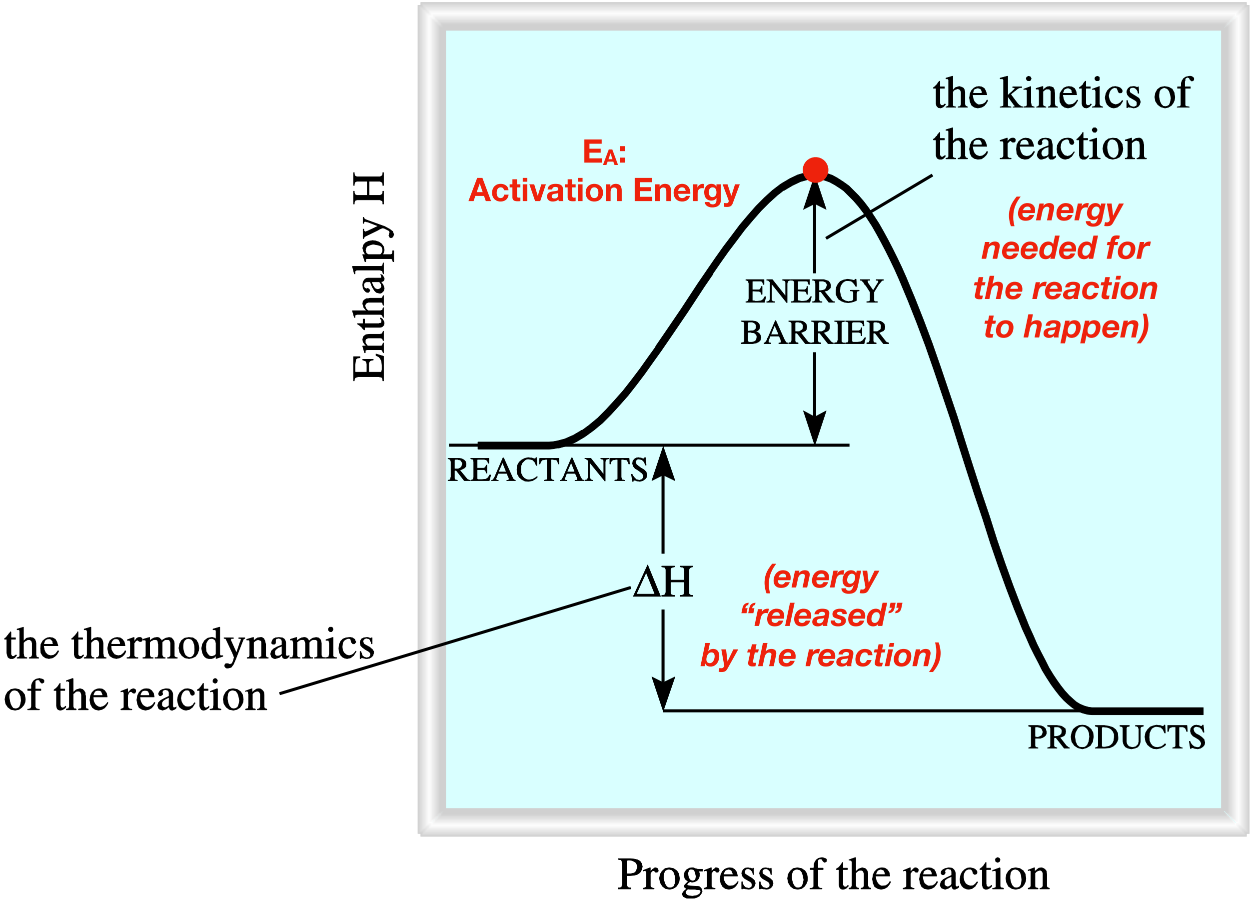
$$\Delta H = \Delta E + P\Delta V = q \text{ (heat)}$$

The first law of thermodynamics – energy conservation law:
For a given system, the change in the internal energy (ΔE) is converted to the change in the heat content ($q = \Delta H$) and the work done towards the environment ($-P\Delta V$) ***at constant pressure.***

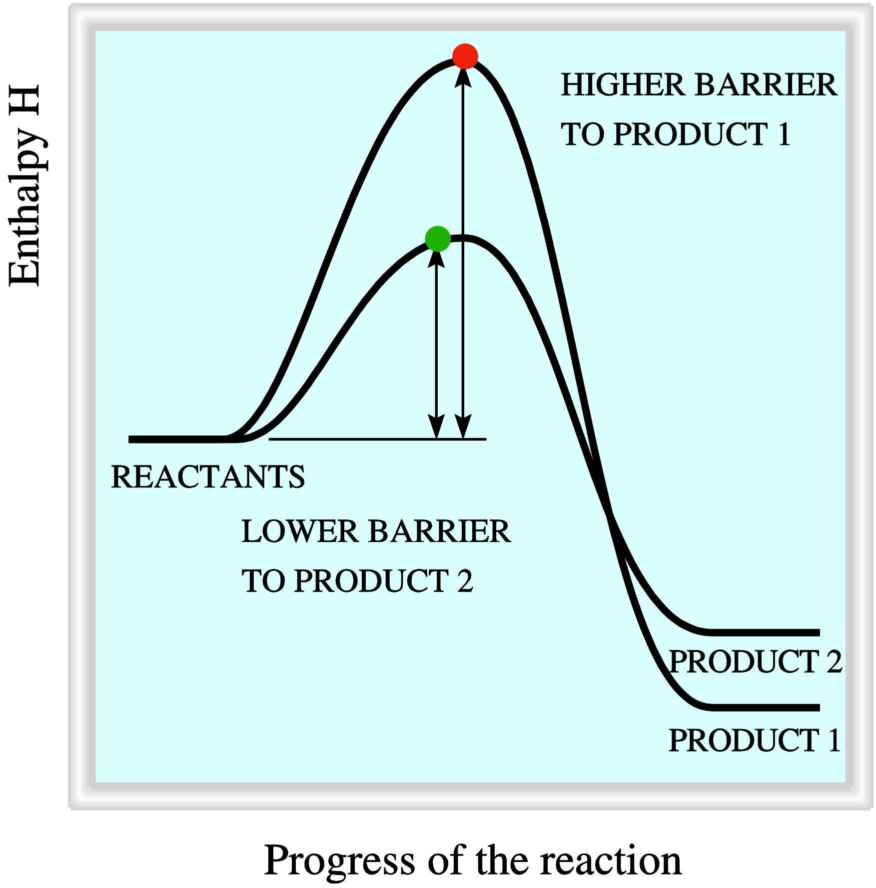
Heat can be measured by calorimetry.

Collision Theory: Arrhenius Theory

Now take the y-axis of energy diagram as “enthalpy”



Collision Theory: Arrhenius Theory



Which reaction do you think happens faster?

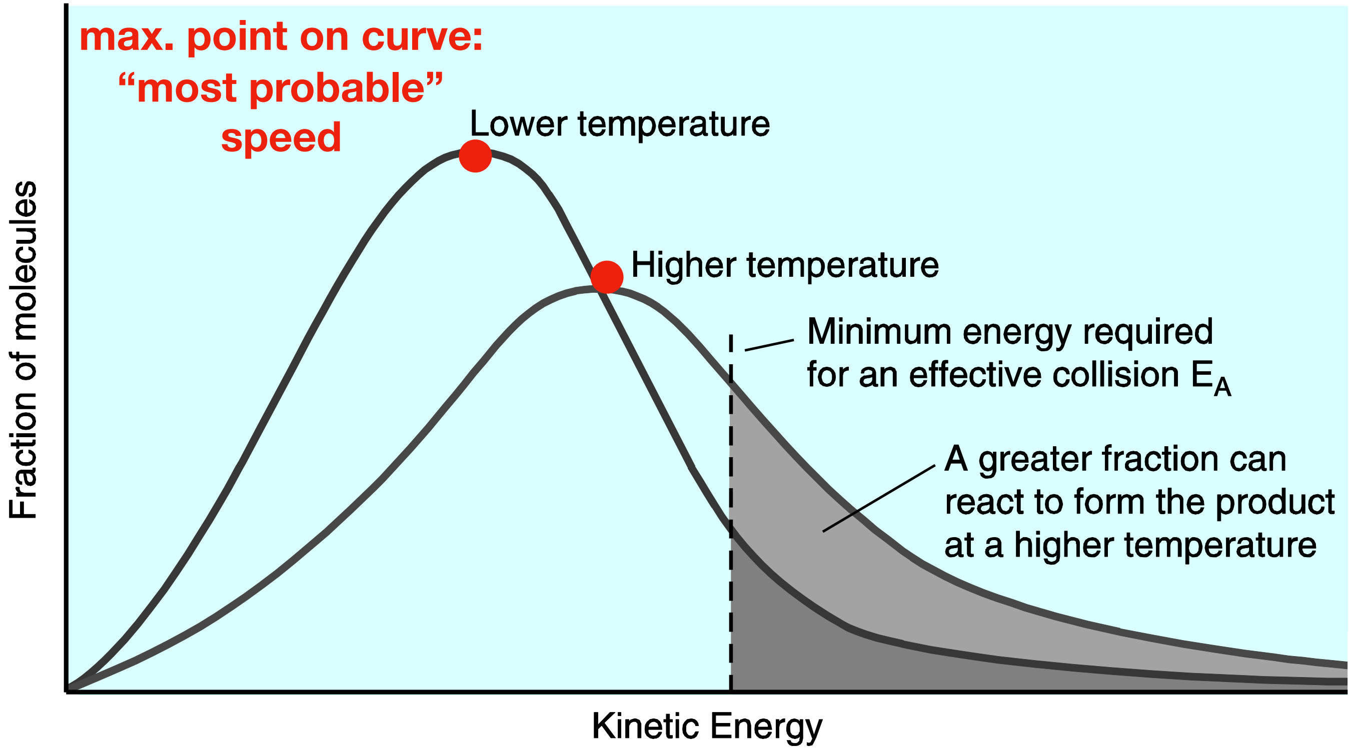
The one with the lower barrier.
Kinetically controlled product

Which makes the more stable product?

Product 1 is more stable, lower energy
Thermodynamically controlled product.

Effect of Temperature on Rates

Higher temperature
More molecules have K.E. larger than E_A



Remember, kinetic energy is related to speed: $E_K = 1/2\ mv^2$

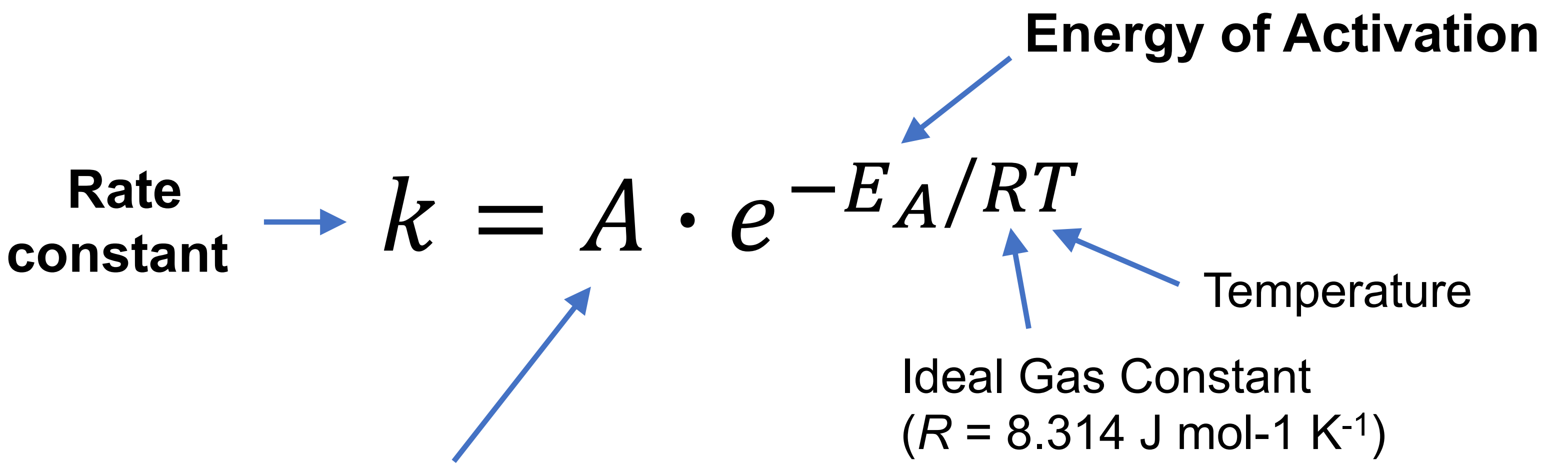
Note, this is graph of *kinetic energy* versus fraction. NOT speed.

Effect of Temperature on Rates

Temperature affects only the rate constant, not the order.

Arrhenius Equation

“What determines k (rate constant)?”



Energy of Activation

Rate constant

$$k = A \cdot e^{-E_A/RT}$$

Temperature

Ideal Gas Constant
(R = 8.314 J mol-1 K^{-1})

“Frequency factor”

- Orientation factor.
- If A is high, then the orientation requirement is not very high

Effect of Temperature on Rates

Arrhenius Equation (linear form)

Original Arrhenius Equation:

$$\boxed{k = A \cdot e^{-E_A/RT}}$$

Take natural log of both sides:

$$lnk = ln\left(Ae^{\frac{-E_A}{RT}}\right)$$

log of product = sum of logs:

$$lnk = lnA + ln\left(e^{\frac{-E_A}{RT}}\right)$$

simplify log of exponential:

$$= \ln A - \frac{E_A}{RT}$$

Effect of Temperature on Rates

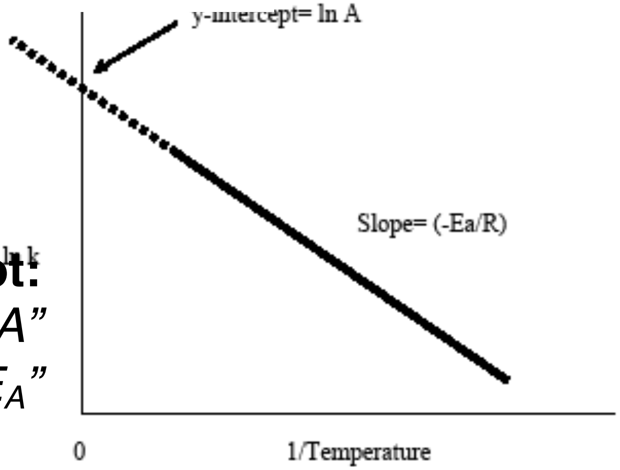
Linearized Arrhenius Equation

Original Arrhenius Equation: $$\boxed{k = A \cdot e^{-E_A/RT}}$$

Take natural log of both sides: $$\ln k = \ln\left(A \cdot e^{-E_A/RT}\right)$$

Log of product = sum of logs: $$\ln k = \ln A + \ln\left(e^{-E_A/RT}\right)$$

Simplify log of exponential: $$\ln k = \ln A - \frac{E_A}{RT}$$



From ln*k* vs 1/*T* plot:
Y-intercept: ln*A* → *"orientation factor A"*
Slope: -E_A/R → *"Activation energy* E_A*"*

Effect of Temperature on Rates

Arrhenius Equation (alternative linear form)

For two different temperatures, everything else the same:

$$\ln k_1 = \ln A - \frac{E_A}{RT_1}$$

$$\ln k_2 = \ln A - \frac{E_A}{RT_2}$$

Subtract eq. 2 from eq. 1:

$$\ln\left(\frac{k_1}{k_2}\right) = -\frac{E_A}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

Example: Effect of Temperature on Rates

Example: The rate of a reaction increases by a factor of 16 when the temperature is increased from 25 °C to 75 °C; what is the activation energy for the reaction?

$$\ln\left(\frac{k_1}{k_2}\right) = -\frac{E_A}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$E_A = \frac{-R \cdot \ln\left(\frac{k_1}{k_2}\right)}{\left(\frac{1}{T_1} - \frac{1}{T_2}\right)} = \frac{-8.314\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}} \cdot \ln(1/16)}{\left(\frac{1}{298.15\ \mathrm{K}} - \frac{1}{348.15\ \mathrm{K}}\right)}$$

$$= 48\ \mathrm{kJ \cdot mol^{-1}}$$

Reaction Mechanism

The sequence of events that occur at the molecular level to give rise to the overall chemical reaction

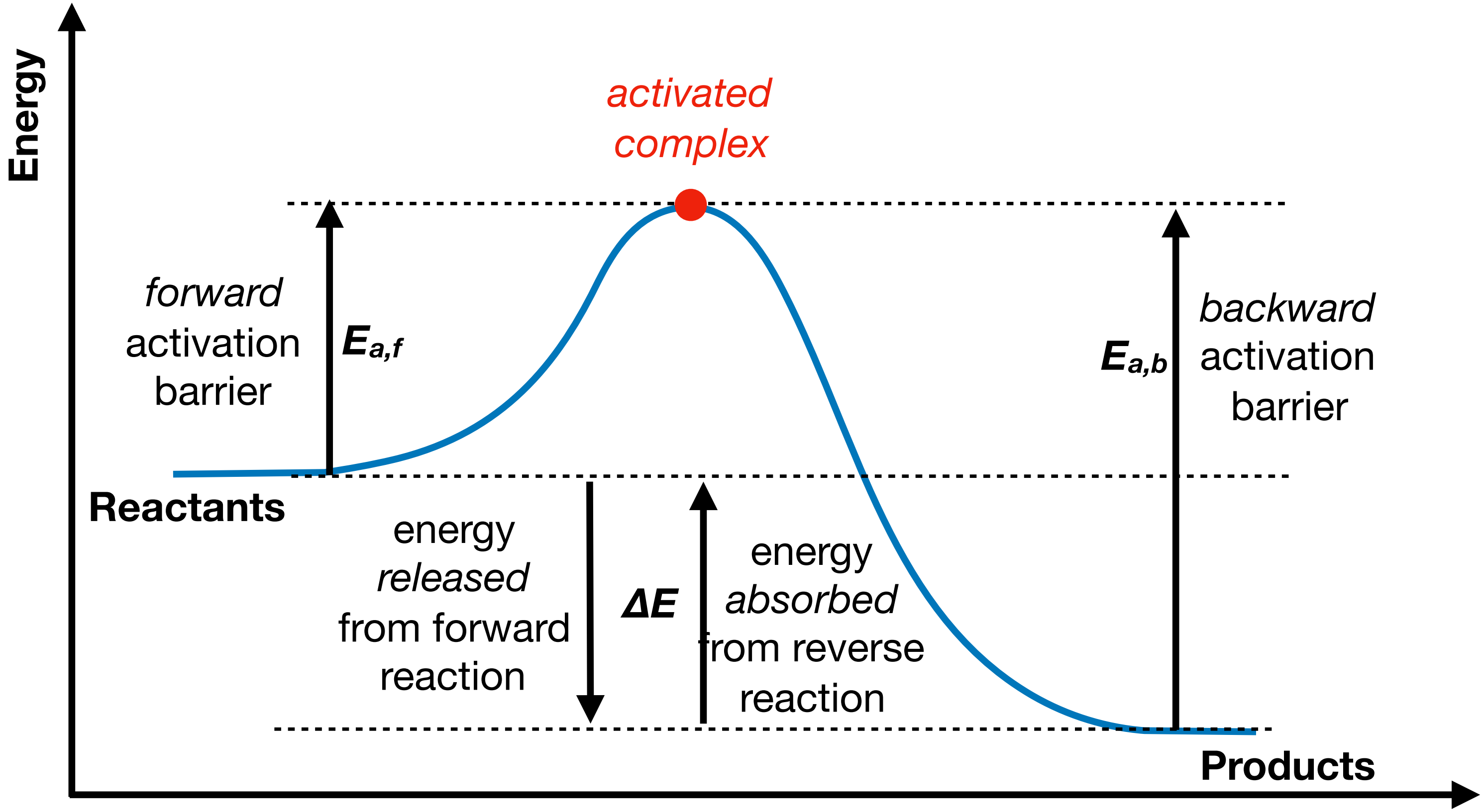
- Can be a single ***step***,
- Or a multitude of sequential **steps**
- Each single step is a chemical reaction on its own, called an **ELEMENTARY REACTION** (or *elementary step*)

What constitutes an Elementary Reaction?

Reaction mechanism
“Reversible reaction”

Reactant (R) $\rightleftharpoons$ Product (P)

- In general, a reaction can occur in both directions.
- How do the **rates** and **rate constants** determine the final concentration distribution of the reactant and product?



How do the **rates** and **rate constants** determine the final concentration distribution of the reactant and product?

$$\text{Reactant (R)} \quad \underset{\substack{\text{Reverse}\\\text{(backward)}}}{\overset{\text{Forward}}{\rightleftharpoons}} \quad \text{Product (P)}$$

Equilibrium (a given reaction is apparently "finished"):

- No net change in the reactant and product concentrations.
- The forward rate is equal to the backward rate (no **net** change overall)

At equilibrium: $\text{Rate}_f = \text{Rate}_r$

For a first order reaction. $k_f\,[\text{R}]_{eq} = k_r\,[\text{P}]_{eq}$

$[\text{R}]_{eq}$ and $[\text{P}]_{eq}$: concentrations of reactants and products at equilibrium

"Equilibrium constant" $$K_{eq} = \frac{k_f}{k_b} = \frac{[\text{P}]_{eq}}{[\text{R}]_{eq}}$$

Convention: Product concentration is at the top. Reactant concentration is at the bottom.

Two ways to describe equilibrium constants!

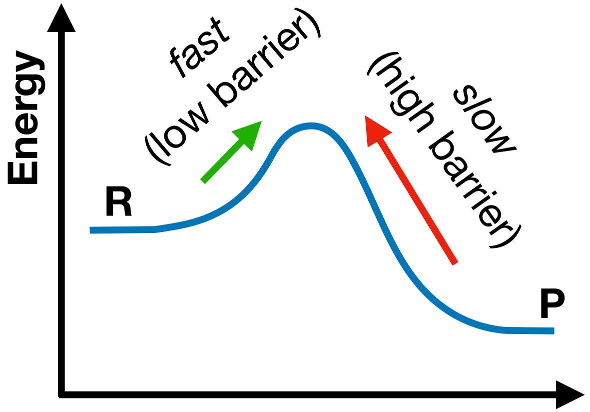
1) Ratio of rate constants (forward/backward);
2) Ratio of concentrations (products/reactants)

Two possibilities for $K_{eq} = \dfrac{k_f}{k_b} = \dfrac{[\mathrm{P}]_{eq}}{[\mathrm{R}]_{eq}}$

1) $K_{eq} > 1$

$[\mathrm{P}]_{eq} > [\mathrm{R}]_{eq}$
Products are favored.

$k_f > k_b$
Forward reaction is faster than backward reaction.

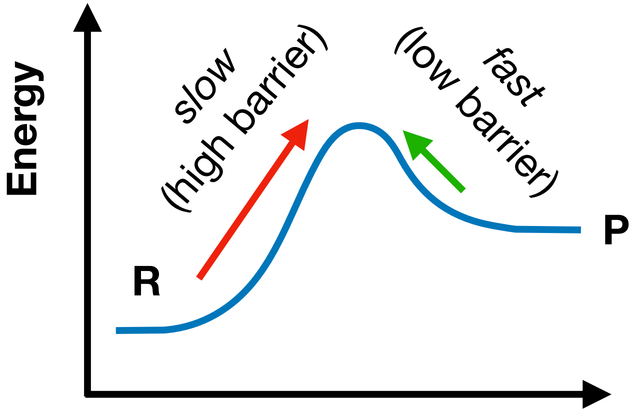


E(products) < E(reactants)

2) $K_{eq} < 1$

$[\mathrm{P}]_{eq} < [\mathrm{R}]_{eq}$
Reactants are favored.

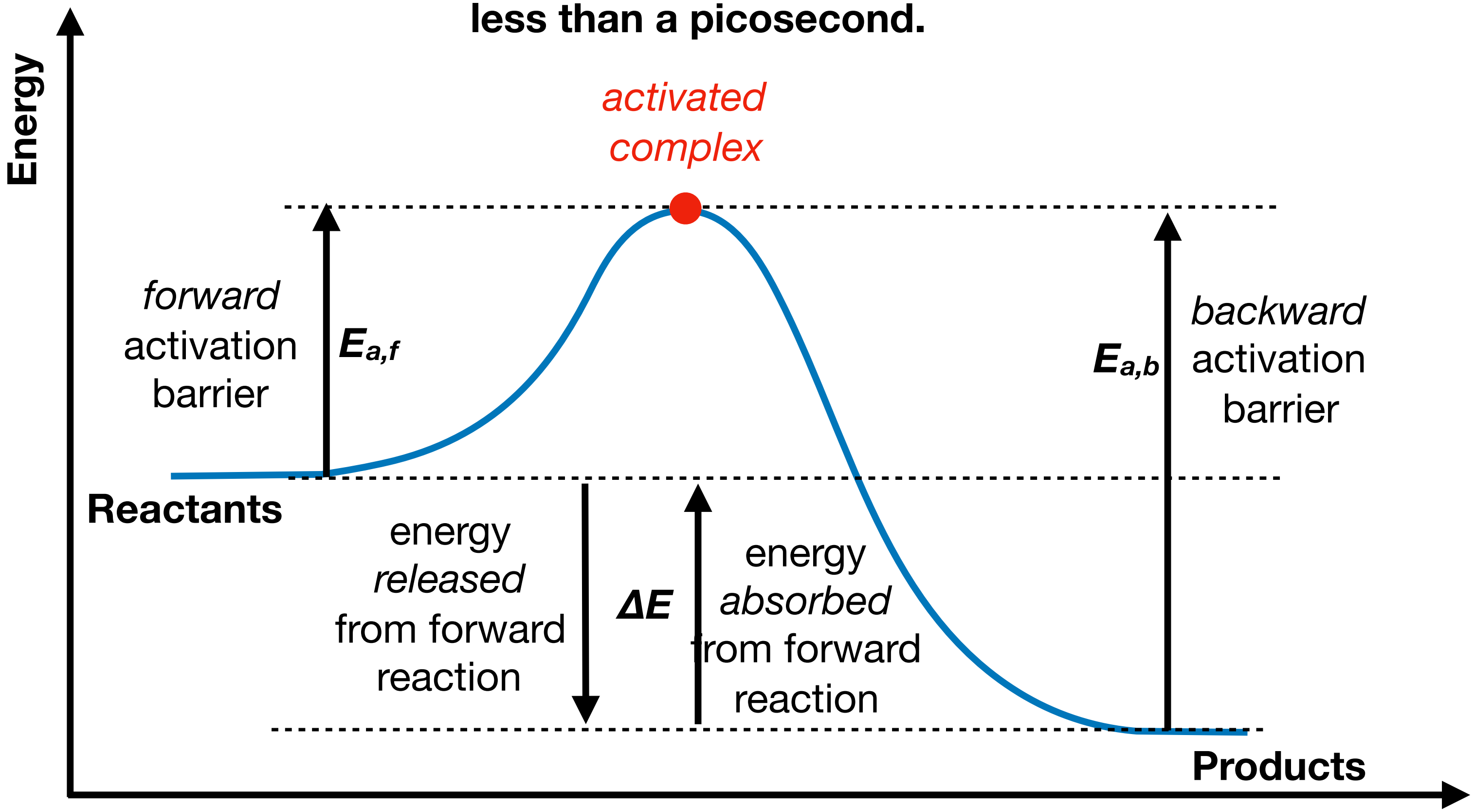
$k_f < k_b$
Forward reaction is slower than backward reaction.



E(products) > E(reactants)

Each Elementary Reaction has its own Energy Diagram.

Activated Complex, “Transition State”
has a lifetime of one vibration.
less than a picosecond.



Energy

activated complex

forward activation barrier

$E_{a,f}$

$E_{a,b}$

backward activation barrier

Reactants

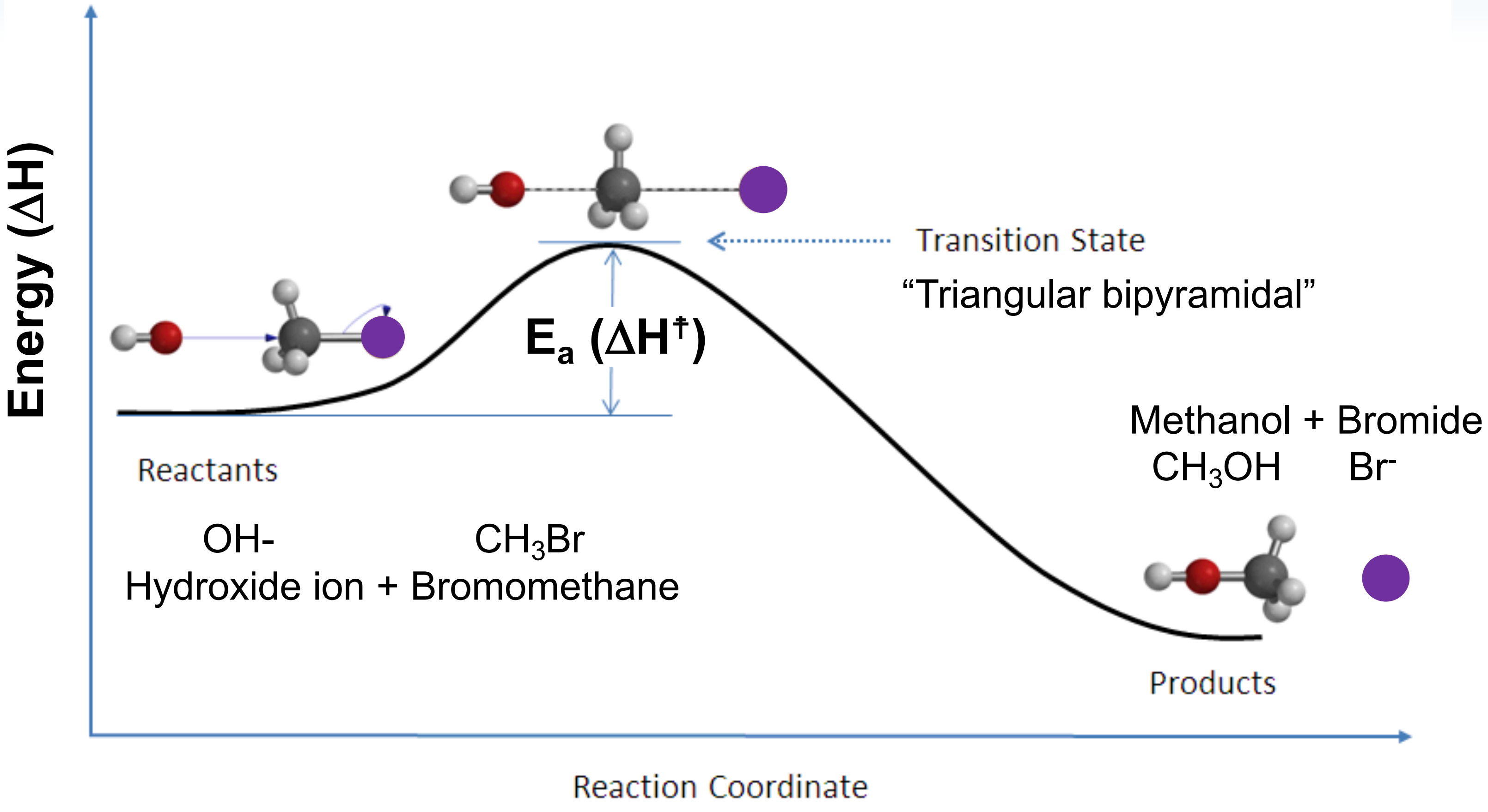
energy *released* from forward reaction

ΔE

energy *absorbed* from forward reaction

Products

Example: a bimolecular Elementary Reaction



Reaction: $HO^- + CH_3Br \rightarrow [HO\text{---}CH_3\text{---}Br]^\ddagger \rightarrow CH_3OH + Br^-$

By Chem540grp1f08 - Own work, CC BY-SA 3.0,
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Reaction Mechanisms: more definitions

MOLECULARITY:

- Defined for ***Elementary Reactions***.
- The number of individual molecules/atoms/species involved in that *Elementary Reaction*.
- Also The "***reaction order***" for the rate equation of an *elementary reaction*

Examples of MOLECULARITY:

- **Unimolecular** reaction: involves a single molecule (e.g., Rate = $k[A]$)
- **Bimolecular** reaction: two molecules/atoms collide (e.g., Rate = $k[A]^2$)
- **Termolecular** reaction: simultaneous collision of 3 species (extremely rare) (e.g., Rate = $k[A]^3$)

Remind: Examples of Rate Laws

1) Rate laws do NOT depend on product concentrations.

2) There is NO link between the balanced reaction formula and the rate law.

3) But how can that be? How can there NOT be a connection between them?

1) $2\ N_2O_5 \longrightarrow 4\ NO_2 + O_2$

$\text{Rate} = k[N_2O_5]$

first order in N_2O_5, first order overall

2) $2\ NO + Cl_2 \longrightarrow 2\ NOCl$

$\text{Rate} = k[NO]^2[Cl_2]$

second order in NO, first order in Cl_2,
third order overall

3) $2\ NO + 2H_2 \longrightarrow N_2 + 2\ H_2O$

$\text{Rate} = k[NO]^2[H_2]$

second order in NO, first order in H_2,
third order overall

4) $NO_2 + CO \longrightarrow NO + CO_2$

$\text{Rate} = k[NO_2]^3$

third order in NO_2, zeroth order in CO,
third order overall

Reaction Mechanisms

Previously, I mentioned that

There is NO link between the reaction stoichiometry and the reaction order.

Unless: The reaction is an ***elementary reaction***
Then: The rate law can be directly written based on the stoichiometry!

Example:

$A + B \longrightarrow C$ An Elementary reaction (or step) Rate = $k[A][B]$

$A + A \longrightarrow C$ An Elementary reaction (or step) Rate = $k[A]^2$

THIS IS ONLY TRUE FOR ELEMENTARY REACTIONS:

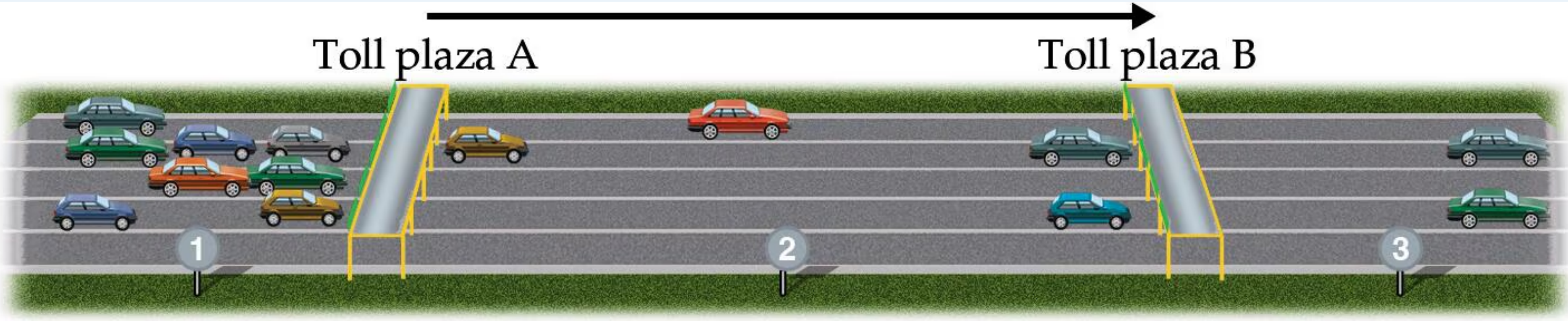
In general, a reaction rate cannot be written directly from the chemical equation!

Why? Because in an elementary reaction, ***the stoichiometry describes the mechanism!***

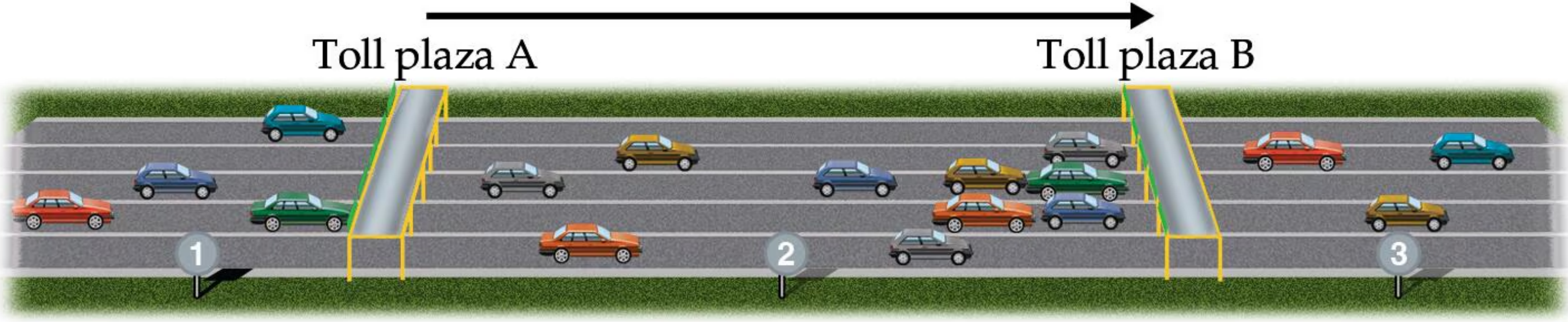
Definition of Rate-Determining step

- Most reactions are multi-step reactions.
  - They are composed of *several* elementary reaction steps.
- The overall rate of a multi-step reaction is most affected by the **slowest** step: ***Often defines the overall rate.***
- **A + B → C (fast)**
- **C + C → D. (slow)**

- **In this case, the second step will define the rate.**
  - **It doesn’t matter how fast the first step is.**
  - **You gotta wait around for the second step.**



(a) Cars slowed at toll plaza A, but not at B; rate-determining step is passage through A

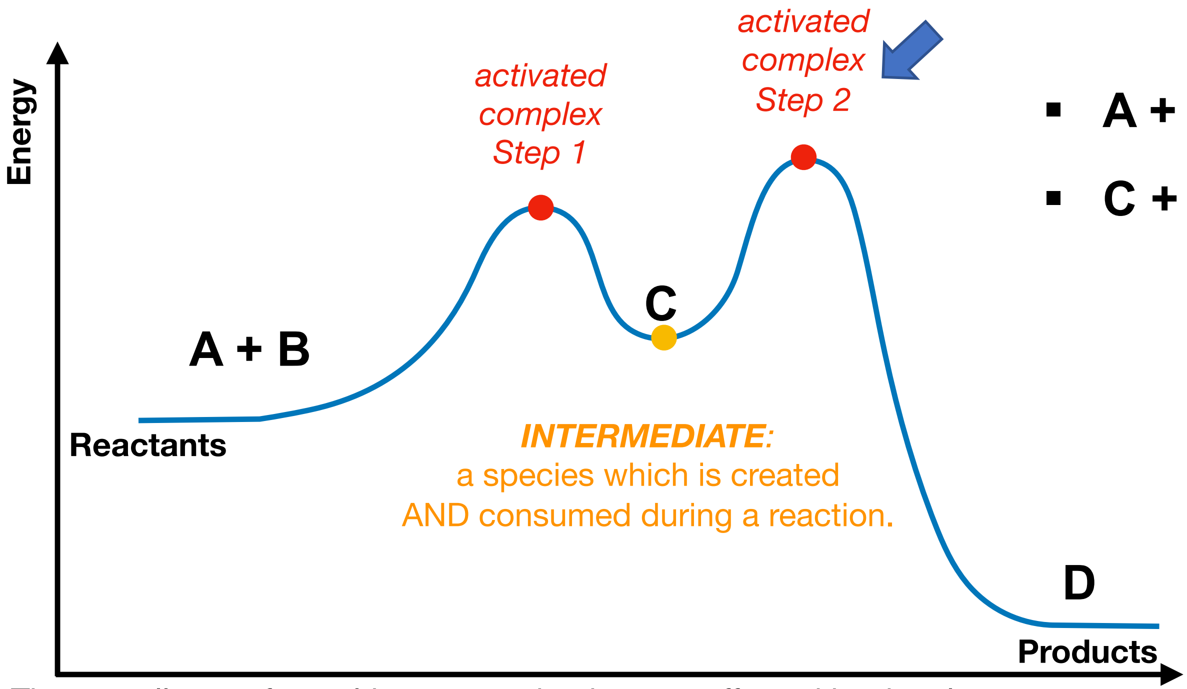


(b) Cars slowed at toll plaza B, but not at A; rate-determining step is passage through B

Definition of Rate-Determining step

- Most reactions are multi-step reactions.
  - They are composed of a number of elementary reactions.
- The overall rate of a multi-step reaction is most affected by the **slowest** step: ***Often defines the overall rate.***
- The slowest step is called **“RATE-DETERMINING STEP”.**
- **It is the step with the HIGHEST ACTIVATION ENERGY.**

Example: Two step reaction



INTERMEDIATE:
a species which is created AND consumed during a reaction.

- A + B → C (fast)
- C + C → D. (slow)

Reaction Mechanisms

Example: Oxidation of nitric oxide in the gas phase

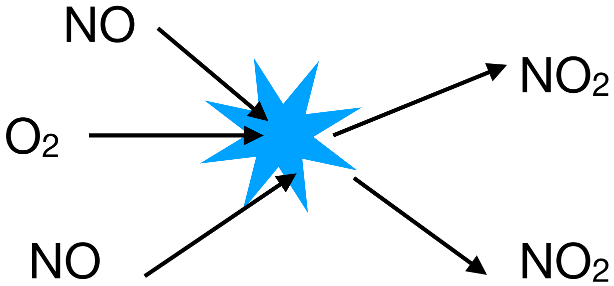
What's the mechanism?

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

Nitric oxide Oxygen Nitrogen dioxide

With this rate law: **Rate = $\boldsymbol{k[NO]^2[O_2]}$**

Option 1: a single termolecular collision leads to the product.



This would of course give::

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

But… Requires 3 gas molecules to simultaneously collide.

The odds are low….

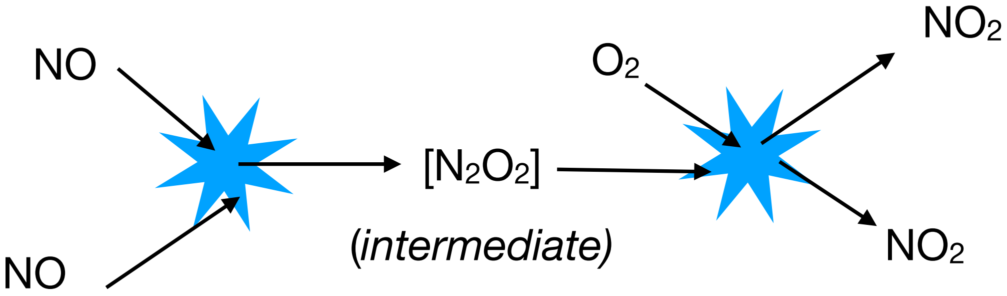
Reaction Mechanisms

Example: Oxidation of nitric oxide in the gas phase

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

Is there another way to explain this?

Option 2: two bimolecular collisions occur in sequence.



Elementary Reactions

$$\text{Step 1:} \quad NO + NO \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} N_2O_2 \qquad (fast)$$

$$\text{Step 2:} \quad N_2O_2 + O_2 \xrightarrow{k_2} 2NO_2 \qquad (slow)$$

How can we distinguish?
We can write the rate law for each option.
Then compare it to the experiment.

Reaction Mechanisms

Example: $2\mathrm{NO}_{(g)} + \mathrm{O}_{2(g)} \longrightarrow 2\mathrm{NO}_{2(g)}$

Option 2: two bimolecular collisions occur in sequence.

Elementary Reactions

$$\text{Step 1:} \quad \mathrm{NO} + \mathrm{NO} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{N_2O_2} \qquad (\mathit{fast})$$

$$\text{Step 2:} \quad \mathrm{N_2O_2} + \mathrm{O_2} \xrightarrow{k_2} 2\mathrm{NO_2} \qquad (\mathit{slow})$$

How do we know the second step is slow?

If the first step was slow, *rate determining*: Rate = $k[\mathrm{NO}]^2$

But, it ain't.

These steps are elementary reactions, so we can write individual rate laws:

$$\text{Rate}(\text{step 1}) = k_1[\mathrm{NO}]^2$$

$$\text{Rate}(\text{inverse step 1}) = k_{-1}[\mathrm{N_2O_2}]$$

$$\text{Rate}(\text{step 2}) = k_2[\mathrm{N_2O_2}][\mathrm{O_2}]$$

Example: $2\mathrm{NO}_{(g)} + \mathrm{O}_{2(g)} \longrightarrow 2\mathrm{NO}_{2(g)}$

Option 2: two bimolecular collisions occur in sequence.

Elementary Reactions

Step 1: $\mathrm{NO} + \mathrm{NO} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{N_2O_2}$ (fast)

Step 2: $\mathrm{N_2O_2} + \mathrm{O_2} \xrightarrow{k_2} 2\mathrm{NO_2}$ (slow)

Rate laws of elementary reactions:

$$\mathrm{Rate}(\text{step } 1) = k_1[\mathrm{NO}]^2$$

$$\mathrm{Rate}(\text{inverse step } 1) = k_{-1}[\mathrm{N_2O_2}]$$

$$\mathrm{Rate}(\text{step } 2) = k_2[\mathrm{N_2O_2}][\mathrm{O_2}]$$

Since Step 2 is the slowest, the **rate limiting step** is Step 2. That is, the rate of the overall reaction can be approximated to the rate of Step 2.

$$\text{overall Rate} = \mathrm{Rate}(\text{step } 2) = k_2[\mathrm{N_2O_2}][\mathrm{O_2}]$$

But how do we deal with an *intermediate* in the rate law?
NOT the reactants we start with and whose concentrations we can monitor?

Example: $$2NO_{(g)} + O_{2(g)} \longrightarrow 2NO_{2(g)}$$

Option 2: two bimolecular collisions occur in sequence.

$$\text{Step 1:} \quad NO + NO \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} N_2O_2 \qquad (\textit{fast})$$

$$\text{Step 2:} \quad N_2O_2 + O_2 \xrightarrow{k_2} 2NO_2 \qquad (\textit{slow})$$

Rate laws of elementary reactions:

$$\text{Rate}(\text{step 1}) = k_1[NO]^2$$

$$\text{Rate}(\text{inverse step 1}) = k_{-1}[N_2O_2]$$

$$\text{Rate}(\text{step 2}) = k_2[N_2O_2][O_2]$$

Rate determining step: $$\text{overall Rate} = \text{Rate}(\text{step 2}) = k_2[N_2O_2][O_2]$$

One way: assume Step 1 is an equilibrium. Why is it possible?

Because the forward (k_1) and backward (k_{-1}) reactions in Step 1 are *faster* than k_2 in Step 2. Thus, Step 1 reaction is finished faster than Step 2. That means the equilibrium will be established before the last step happens.

This is called The "Pre-Equilibrium" condition.

Example: $2\mathrm{NO}_{(g)} + \mathrm{O}_{2(g)} \longrightarrow 2\mathrm{NO}_{2(g)}$

Option 2: two bimolecular collisions occur in sequence.

$$\text{Step 1:} \quad \mathrm{NO} + \mathrm{NO} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{N_2O_2} \qquad (\mathit{fast})$$

$$\text{Step 2:} \quad \mathrm{N_2O_2} + \mathrm{O_2} \xrightarrow{k_2} 2\mathrm{NO_2} \qquad (\mathit{slow})$$

Rate laws of elementary reactions:

$$\mathrm{Rate}(\text{step 1}) = k_1[\mathrm{NO}]^2$$

$$\mathrm{Rate}(\text{inverse step 1}) = k_{-1}[\mathrm{N_2O_2}]$$

$$\mathrm{Rate}(\text{step 2}) = k_2[\mathrm{N_2O_2}][\mathrm{O_2}]$$

Rate determining step: $\text{overall Rate} = \mathrm{Rate}(\text{step 2}) = k_2[\mathrm{N_2O_2}][\mathrm{O_2}]$

Since Step 1 is at an equilibrium.

$$Rate_f = Rate_b$$

$$k_1[\mathrm{NO}]^2 = k_{-1}[\mathrm{N_2O_2}] \quad \Rightarrow [N_2O_2] = \frac{k_1}{k_{-1}}[\mathrm{NO}]^2 = K_{eq1}[\mathrm{NO}]^2$$

Now we have an expression for $[\mathrm{N_2O_2}]$, in terms of the reactant conc, $[\mathrm{NO}]$ and K_{eq}

Example: $2NO_{(g)} + O_{2(g)} \longrightarrow 2NO_{2(g)}$

Option 2: two bimolecular collisions occur in sequence.

Step 1: $NO + NO \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} N_2O_2$ $(fast)$

Step 2: $N_2O_2 + O_2 \xrightarrow{k_2} 2NO_2$ $(slow)$

Rate laws of elementary reactions:

$$\text{Rate}(\text{step 1}) = k_1[\text{NO}]^2$$

$$\text{Rate}(\text{inverse step 1}) = k_{-1}[\text{N}_2\text{O}_2]$$

$$\text{Rate}(\text{step 2}) = k_2[\text{N}_2\text{O}_2][\text{O}_2]$$

Rate determining step: $\text{overall Rate} = \text{Rate}(\text{step 2}) = k_2[\text{N}_2\text{O}_2][\text{O}_2]$

$$[N_2O_2] = \frac{k_1}{k_{-1}}[\text{NO}]^2 = K_{eq1}[\text{NO}]^2$$

Now that we know [N_2O_2], we know the overall rate:

$$\text{overall Rate} = k_2[\text{O}_2] \times K_{eq1}[\text{NO}]^2 = k_{eff}[\text{NO}]^2[\text{O}_2]$$

k_2 x K_{eq1} = k_{eff} (“effective rate constant”)

A reasonable mechanism that agrees with the rate law

Reaction Mechanisms

Example 2: Decomposition of Ozone

$$2O_{3(g)} \longrightarrow 3O_{2(g)}$$

Proposed reaction mechanism:

Elementary steps:

$$\text{Step 1:} \quad O_3 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} O_2 + \underbrace{O}_{\text{intermediate}} \qquad (\textit{fast})$$

$$\text{Step 2:} \quad O_3 + \underbrace{O}_{\text{intermediate}} \xrightarrow{k_2} 2O_2 \qquad (\textit{slow})$$

The experimentally observed rate law for this process is unusual:

$$\text{Overall Rate} = k[O_3]^2[O_2]^{-1}$$

→ **"-1" order in O_2 (a product!)**

Is the proposed mechanism consistent with this rate law?

Reaction Mechanisms

Example 2: $2O_{3(g)} \longrightarrow 3O_{2(g)}$

Elementary steps:

$$\text{Step 1:} \quad O_3 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} O_2 + \underbrace{\color{red}{O}}_{\color{red}{\text{intermediate}}} \qquad (fast)$$

$$\text{Step 2:} \quad O_3 + \underbrace{\color{red}{O}}_{\color{red}{\text{intermediate}}} \xrightarrow{k_2} 2O_2 \qquad (slow)$$

$$\text{Overall Rate} = k[O_3]^2[O_2]^{-1}$$

Step 2 is the *rate-limiting* step.
Thus, the overall rate can be approximated as Step 2:

$$\text{overall Rate} = k_2[O_3][O]$$

Again, we want to express the overall rate using only reactant concentrations.

Again, assume the pre-equilibrium condition to find [O]:

$$K_{eq,1} = \frac{[O_2][O]}{[O_3]} \quad \Rightarrow \quad [O] = \frac{K_{eq,1}[O_3]}{[O_2]}$$

Insert this Eq to

Reaction Mechanisms

Example 2: $$2O_{3(g)} \longrightarrow 3O_{2(g)}$$

Elementary steps:

$$\text{Step 1:} \quad O_3 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} O_2 + \underbrace{\color{red}{O}}_{\color{red}{\text{intermediate}}} \qquad (\textit{fast})$$

$$\text{Step 2:} \quad O_3 + \underbrace{\color{red}{O}}_{\color{red}{\text{intermediate}}} \xrightarrow{k_2} 2O_2 \qquad (\textit{slow})$$

How can we obtain this overall rate?

$$\text{Overall Rate} = k[O_3]^2[O_2]^{-1}$$

We proved this!

The rate of Step 2 can be approximated to the overall rate:

$$\text{overall Rate} = k_2[O_3][O]$$

We want to express the overall rate using only reactant concentrations.

$$K_{eq,1} = \frac{[O_2][O]}{[O_3]} \quad \Rightarrow \quad [O] = \frac{K_{eq,1}[O_3]}{[O_2]}$$

$$\text{overall Rate} = k_2[O_3] \times \frac{K_{eq,1}[O_3]}{[O_2]} = \underbrace{k_2 K_{eq,1}}_{\text{combine into one constant}} [O_3]^2[O_2]^{-1} = \underbrace{k[O_3]^2[O_2]^{-1}}_{\text{this is the observed rate law...}}$$

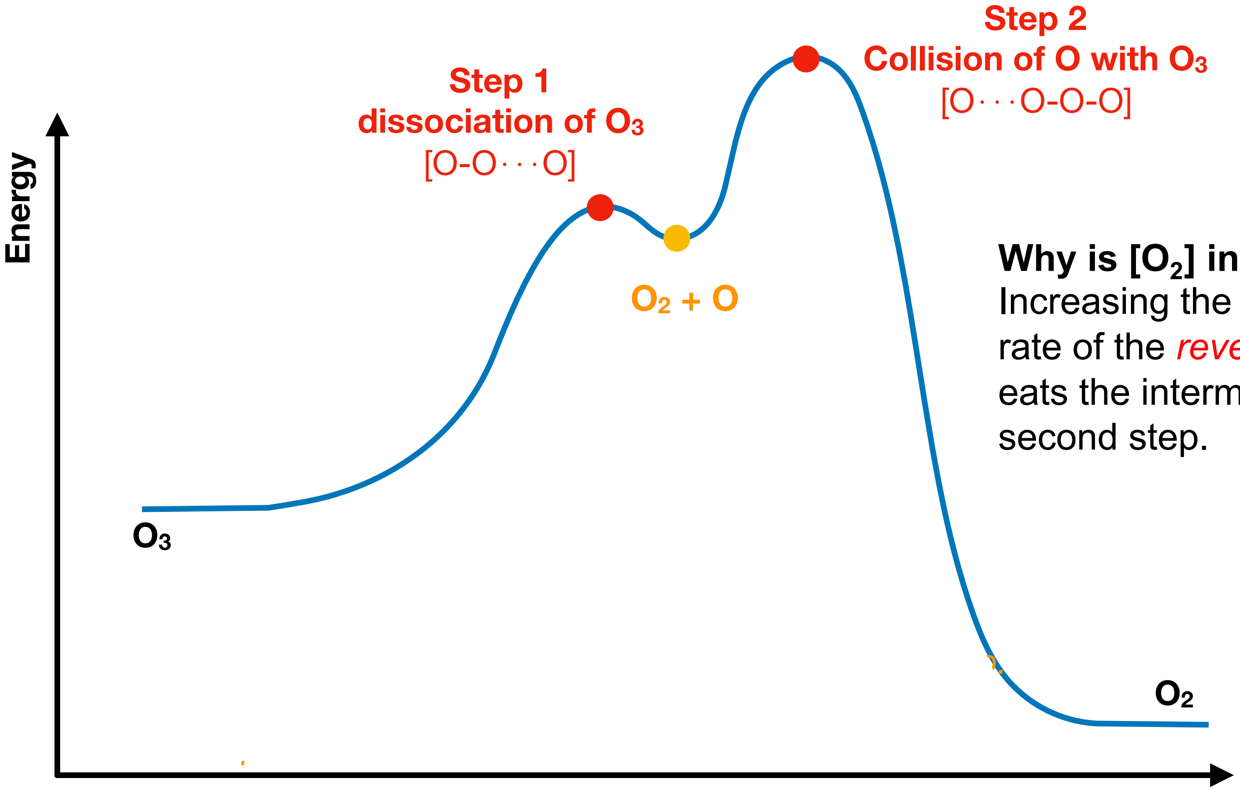
Reaction Mechanisms

Example 2:

$$\text{Step 1:}\quad O_3 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} O_2 + \underbrace{O}_{\text{intermediate}} \qquad (\textit{fast})$$

$$\text{Step 2:}\quad O_3 + \underbrace{O}_{\text{intermediate}} \xrightarrow{k_2} 2O_2 \qquad (\textit{slow})$$

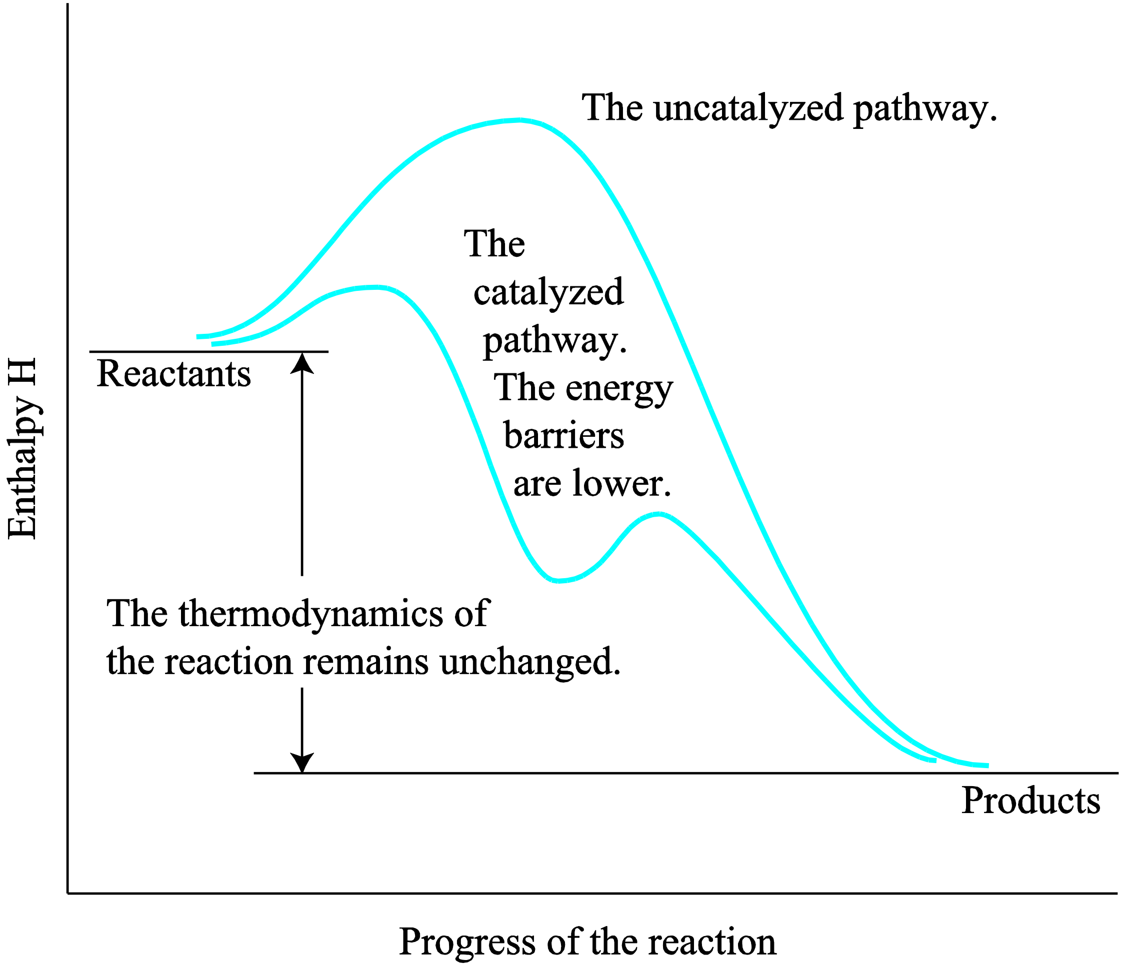
$$\text{Overall Rate} = k[O_3]^2[O_2]^{-1}$$



Why is $[O_2]$ in the rate law?
Increasing the concentration of O_2 increases the rate of the *reverse* reaction of the first step. That eats the intermediate species (O) necessary for the second step.

Catalysts

- Increase the rate of a reaction by decreasing the activation energy of the reaction.
- **Change the mechanism** by which the process occurs.
  - **Catalysts are never consumed in the reaction.**
  - **They cannot change the equilibrium of the reaction.**



The uncatalyzed pathway.

The catalyzed pathway. The energy barriers are lower.

The thermodynamics of the reaction remains unchanged.

From Arrhenius Equation:

if this goes down…

$$k = A \cdot e^{-E_A/RT}$$

then this goes up

Homogeneous vs. Heterogeneous Catalysts

There are two kinds of catalysts:

1) HOMOGENEOUS catalysts: (homo = same)

The catalyst is in the same phase as the reactants.

- Reactants (in gas) – Catalyst (in gas)
- Reactants (in solution) – Catalyst (in solution)

2) HETEROGENEOUS catalysts: (hetero = different)

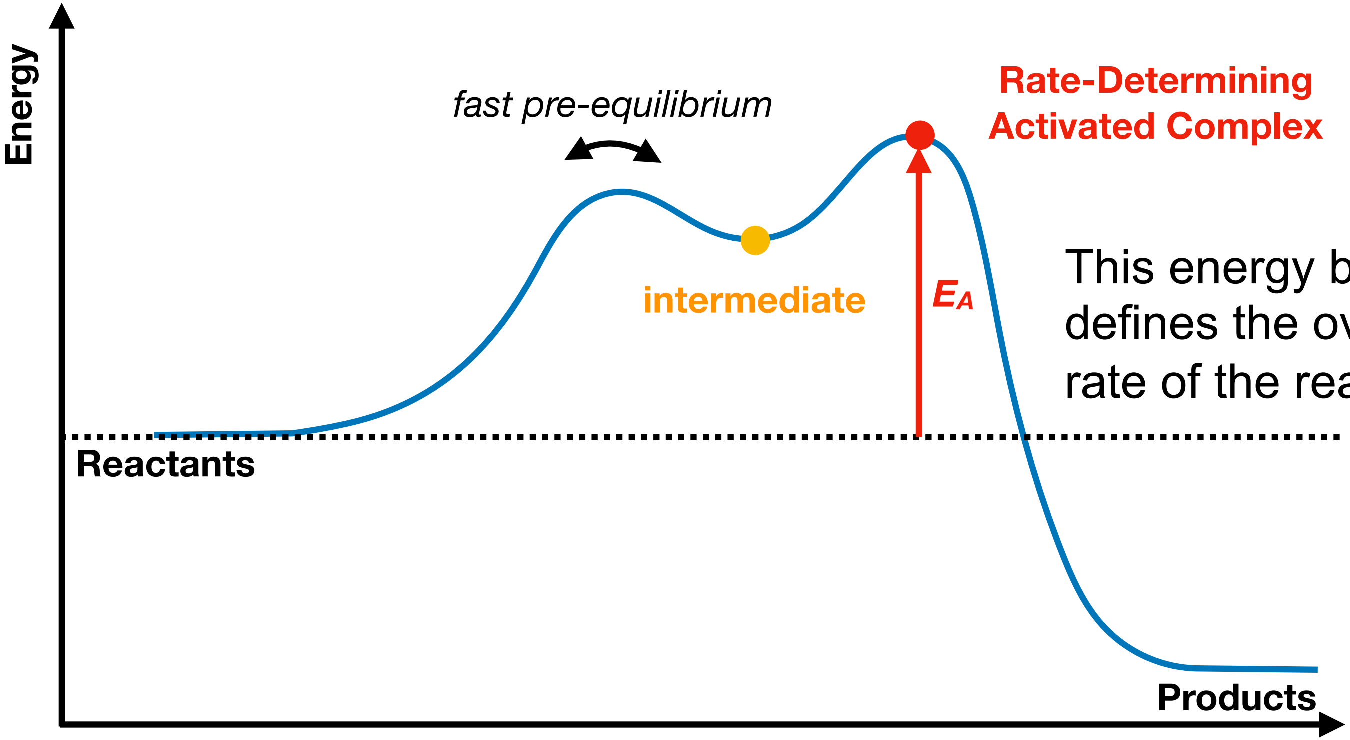
The catalyst is in a different phase from the reactants.

- In most cases, this refers to the catalyst being the surface of a solid.
- The reactants (gaseous or solution) can adsorb to the surface, which facilitates the reaction. Once formed, the products (gaseous or solution) desorb from the surface.

Rate-Determining Step

- The overall reaction cannot occur faster than the slowest reaction in the mechanism. We call that the **rate-determining step**.
- The overall rate can be approximated to the rate in the rate-determining step.

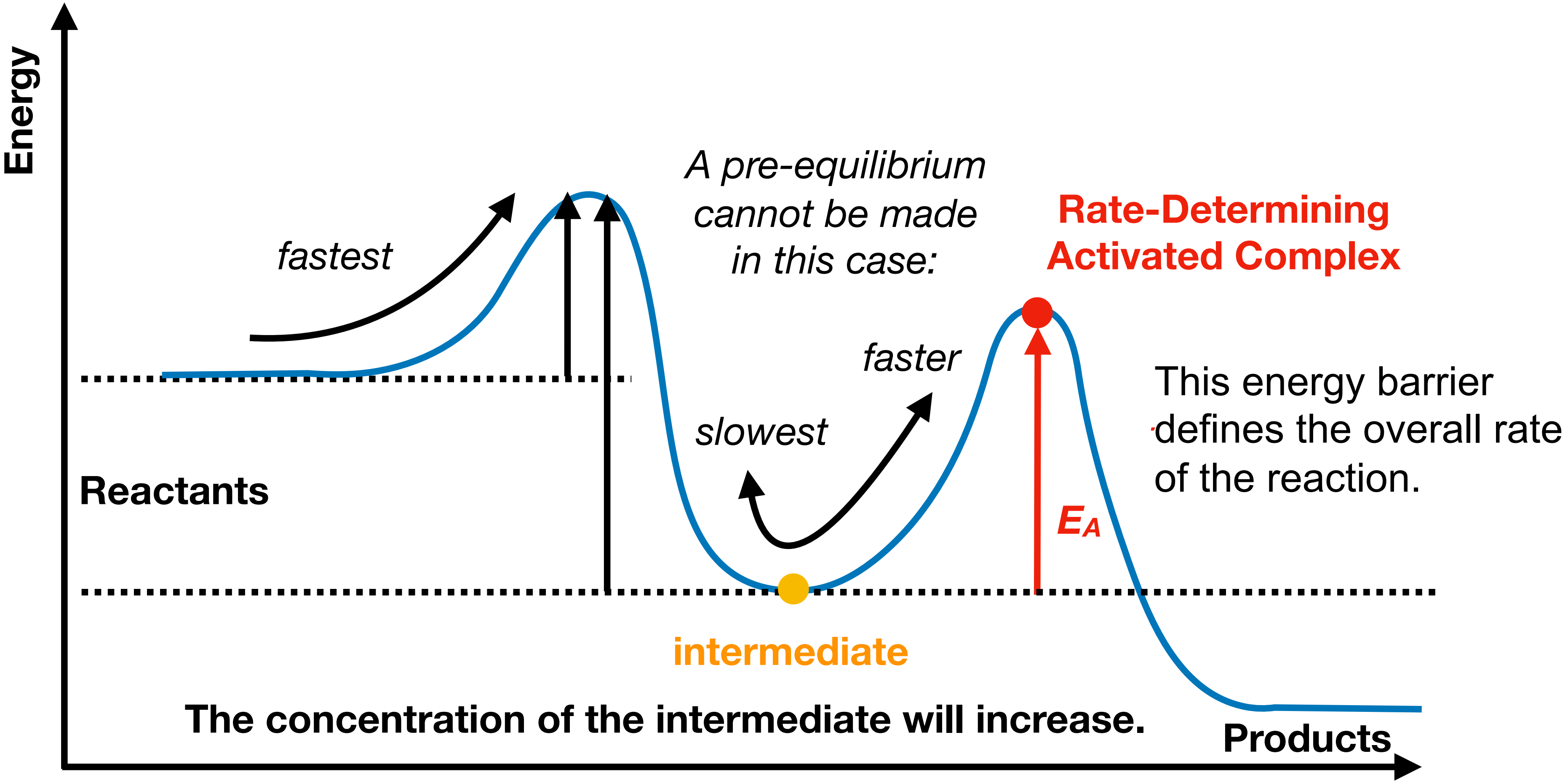
Scenario 1 The Intermediate is HIGHER in energy than the reactant. In this case, the energy of activation is the energy to reach the highest-energy activated complex:



This energy barrier defines the overall rate of the reaction.

Rate-Determining Step

Scenario 2 The Intermediate is LOWER in energy than the reactant. In this case, the rate is limited by the step with the highest barrier.



Energy

fastest

A pre-equilibrium cannot be made in this case:

Rate-Determining Activated Complex

faster

slowest

This energy barrier defines the overall rate of the reaction.

E_A

Reactants

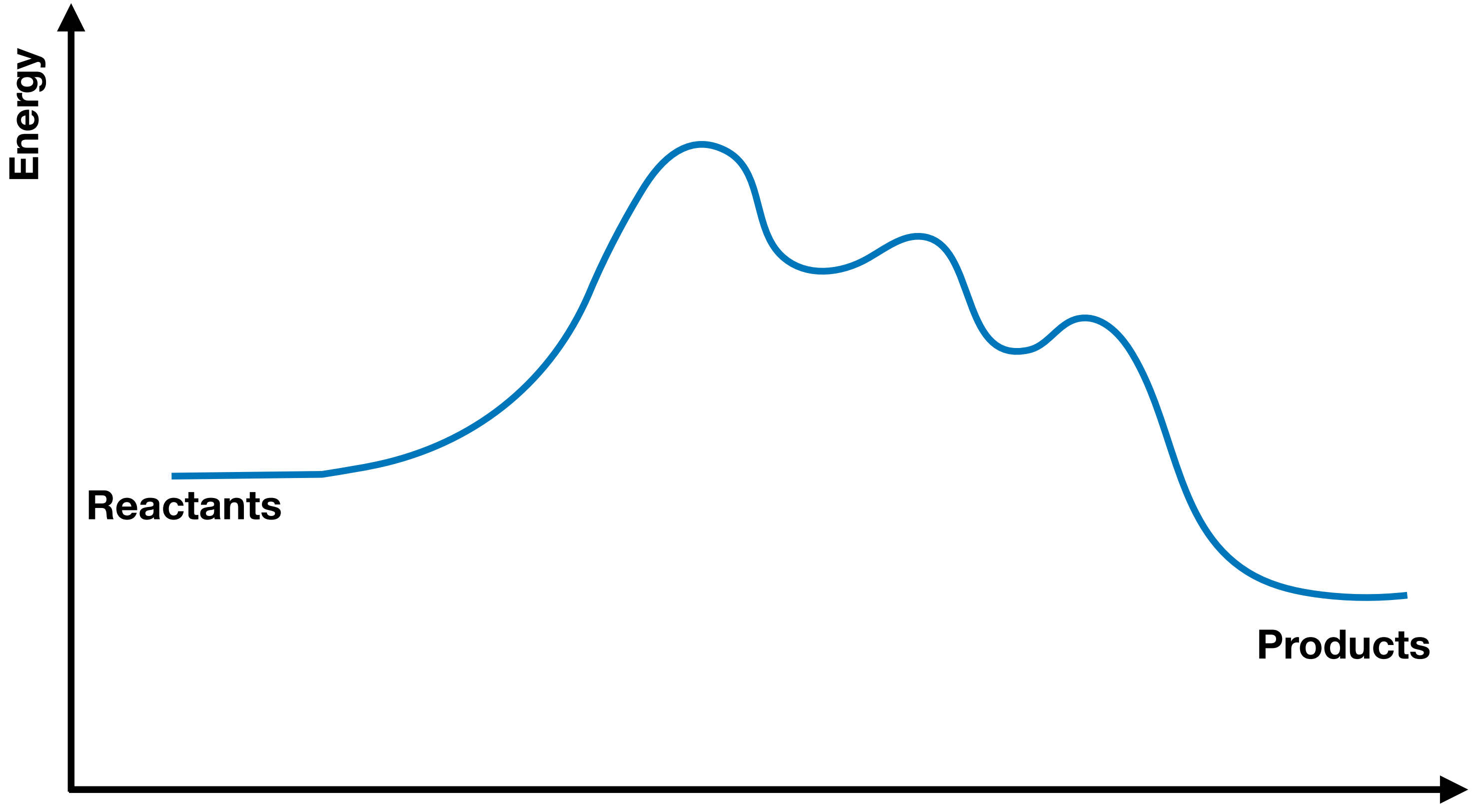
intermediate

The concentration of the intermediate will increase.

Products

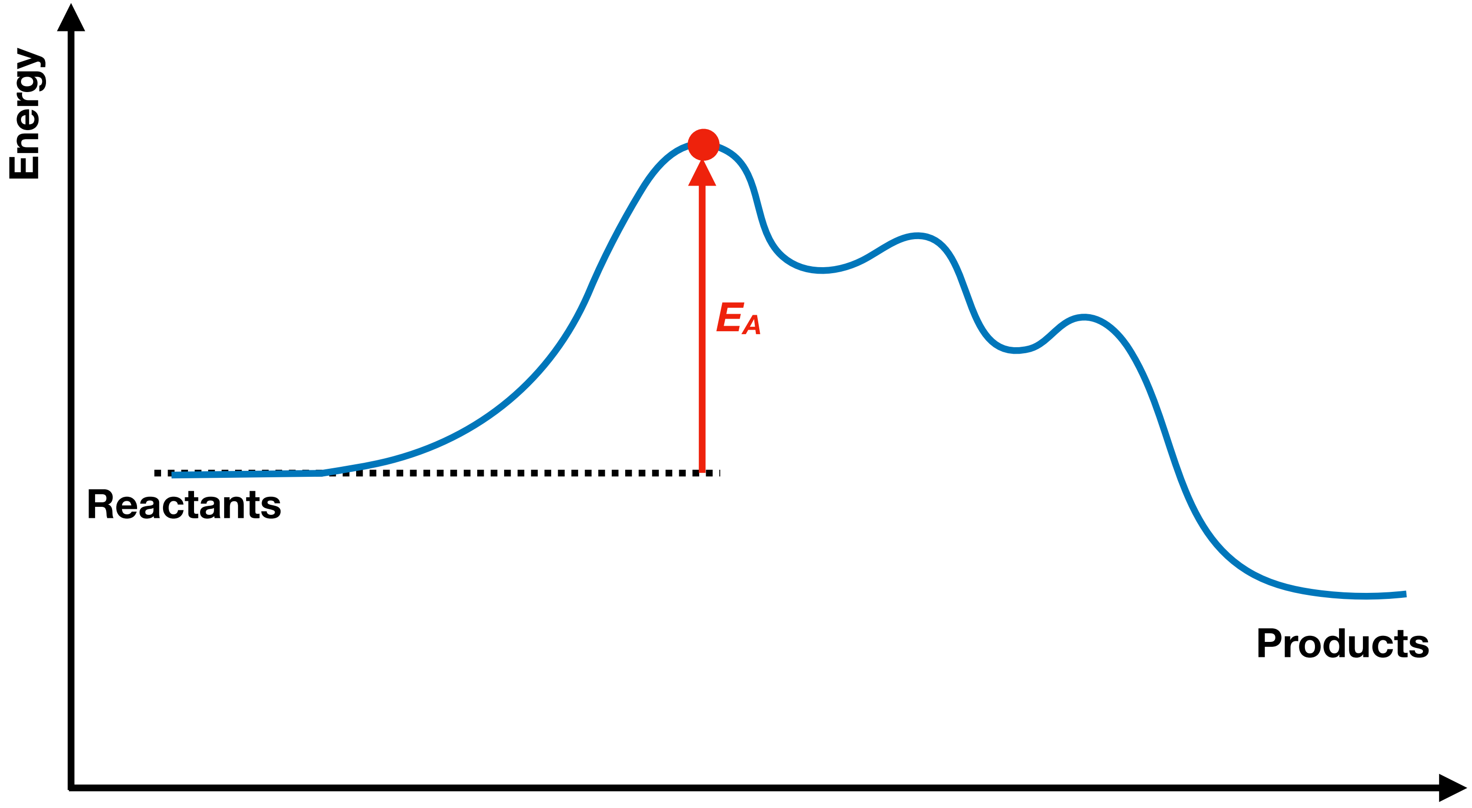
Rate-Determining Step

Which step is the rate-determining step here?



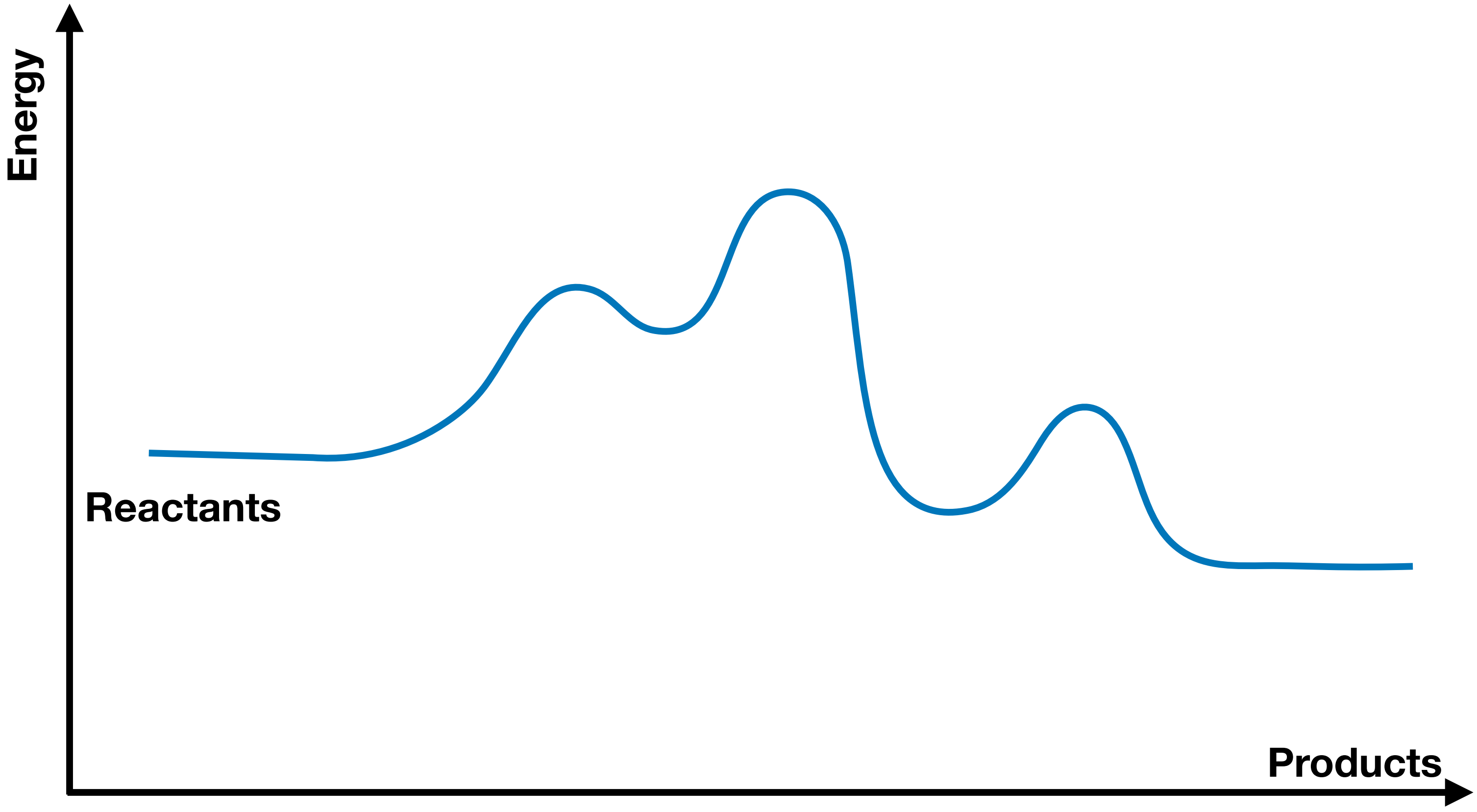
Rate-Determining Step

Answer: Because all intermediates are HIGHER in energy than the reactants, it is the energy of the highest point on the curve. Here, this corresponds to the first step.



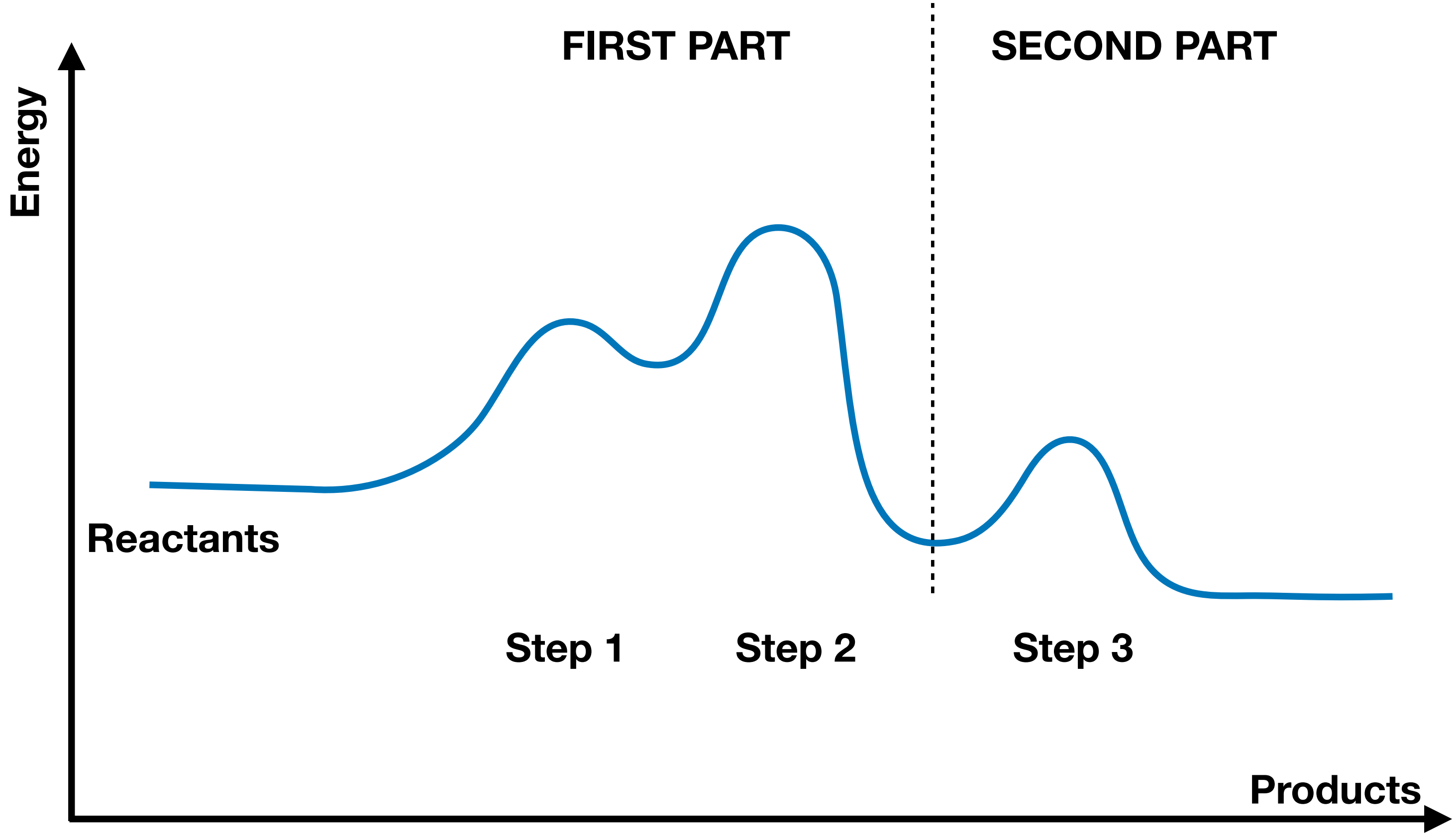
Rate-Determining Step

A harder one! Which one is the rate-determining step here?



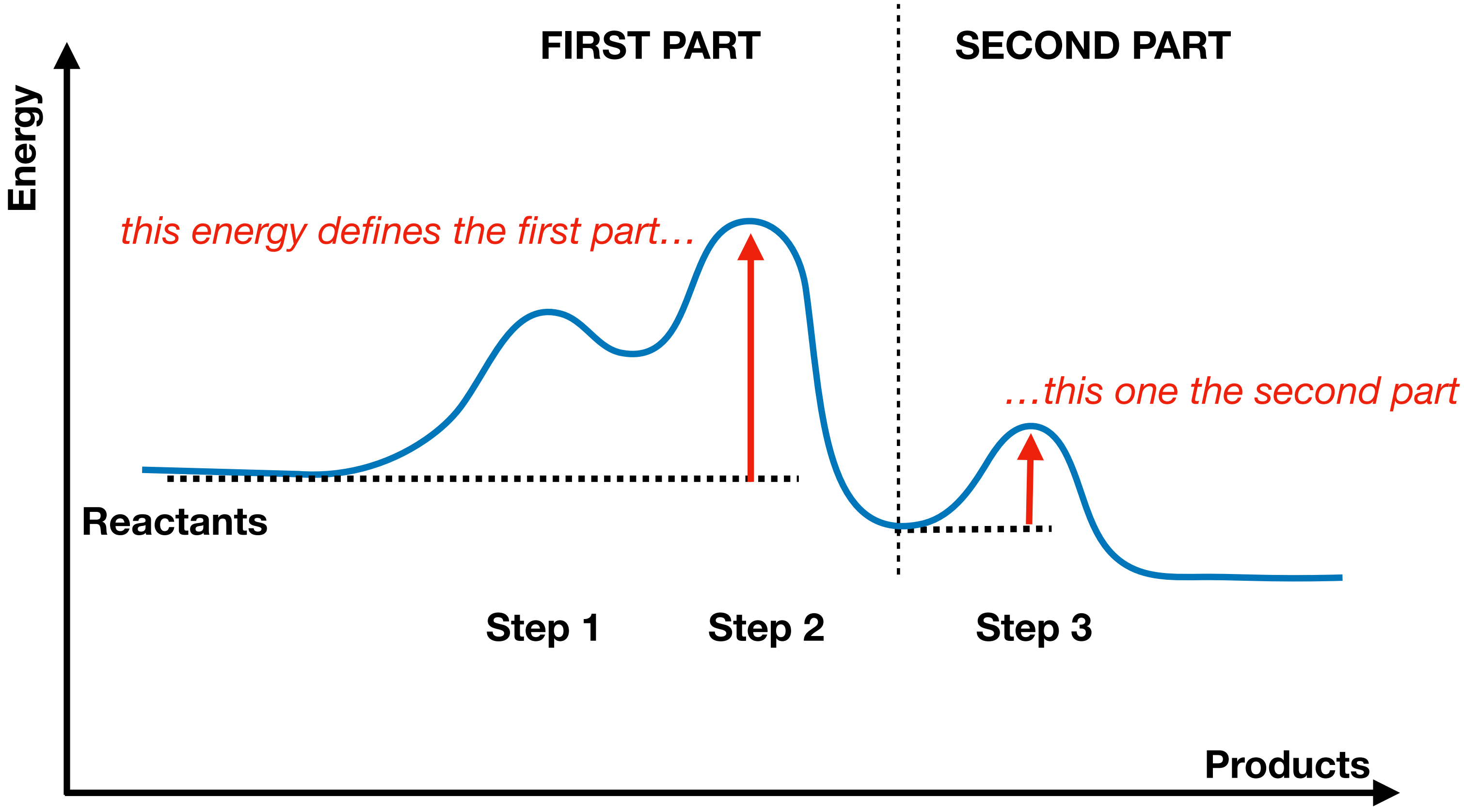
Rate-Determining Step

You can think of this reaction as being two distinct parts:
before and after the stable intermediate is formed:



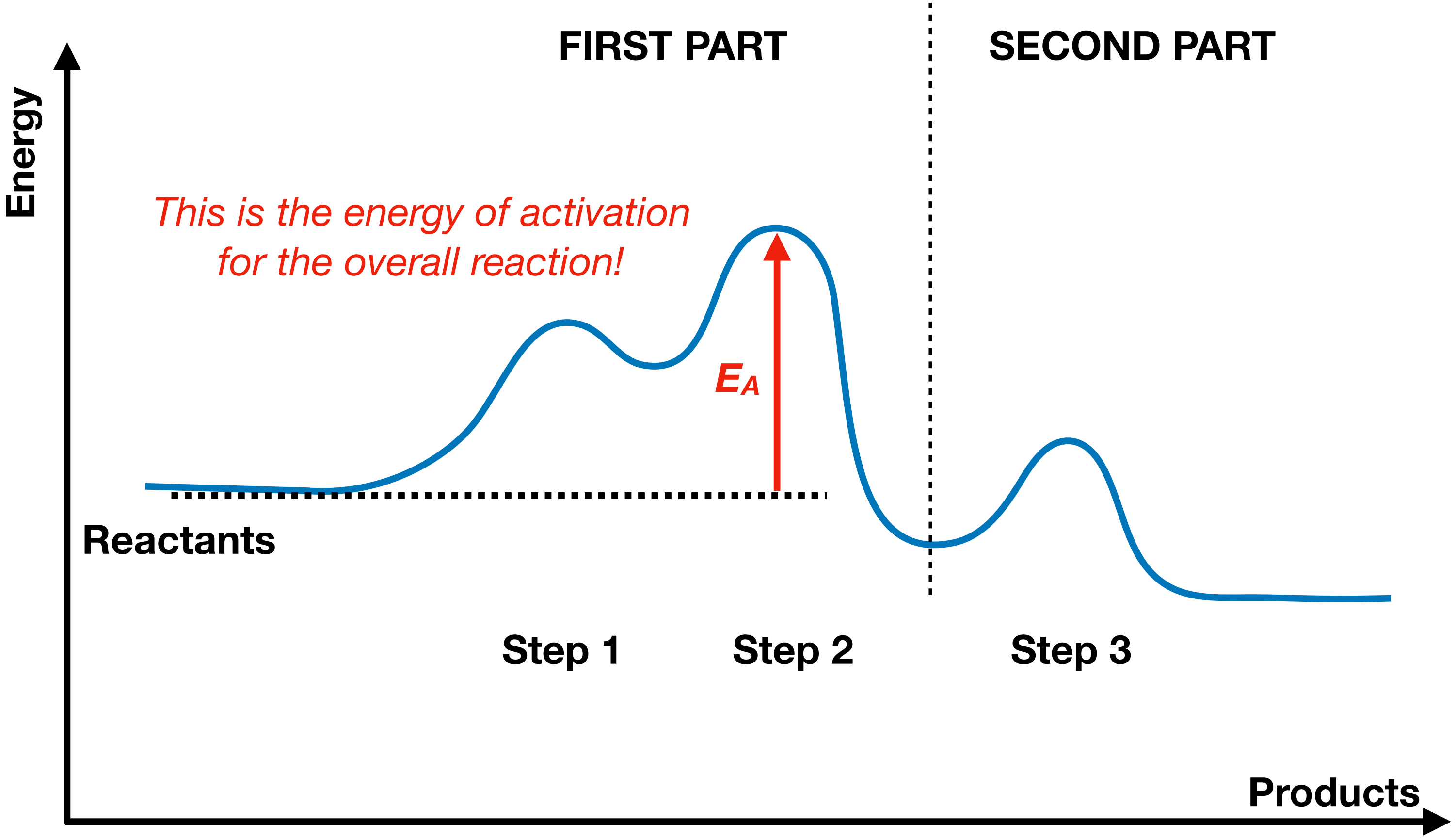
Rate-Determining Step

In the first part, the second step defines the rate;
In the second part, there is only one step that defines the rate.

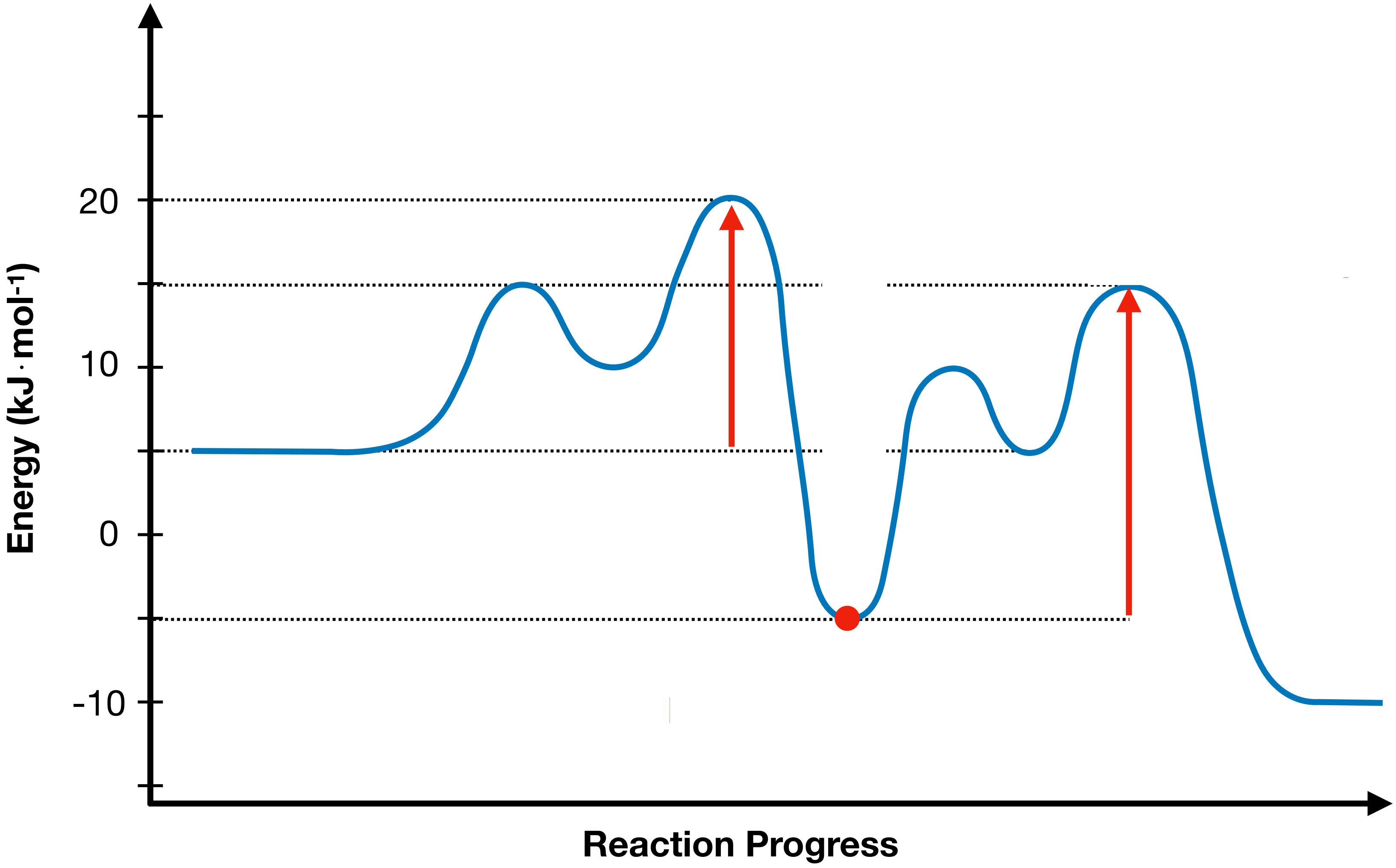


Rate-Determining Step

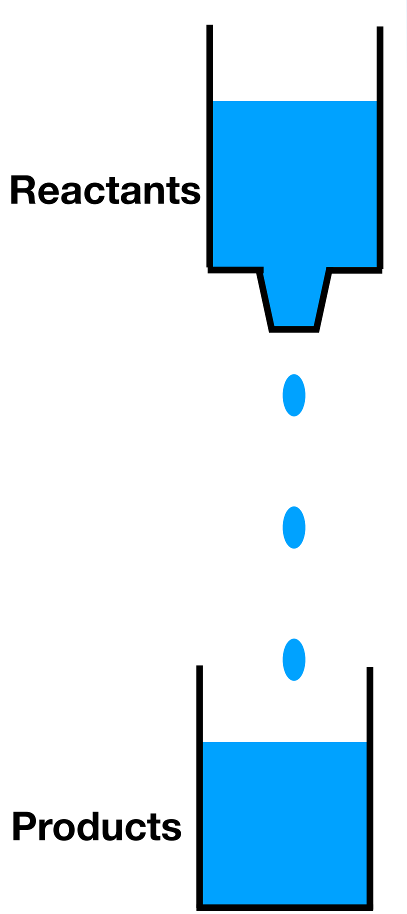
The larger of the two energies defines the overall reaction rate!



Rate-Determining Step



Flow Analogy

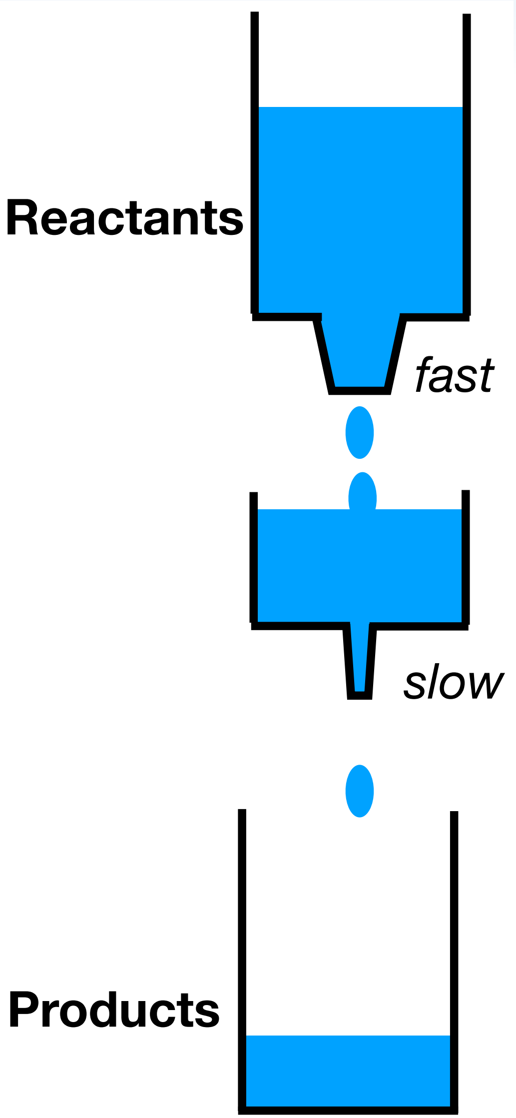


How fast volume drops:
Rate of consumption of the reactants

How fast volume rises:
Rate of formation of the products

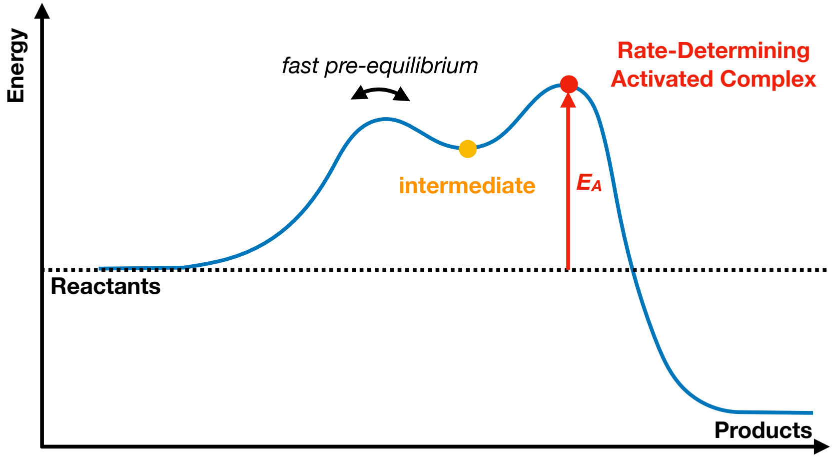
For an elementary reaction,
Rate of reactant consumption = Rate of product formation

Flow Analogy

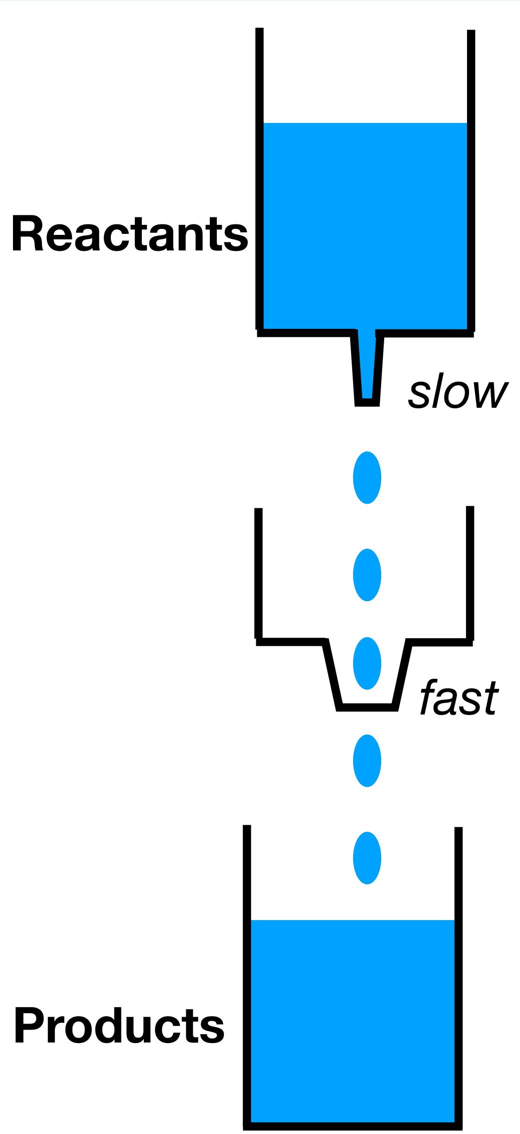


Here, the rate is clearly limited by the 2nd step.

- The consumption rate of the reactants is high.
- The appearance rate of products is small.
- The two rates are NOT equal.

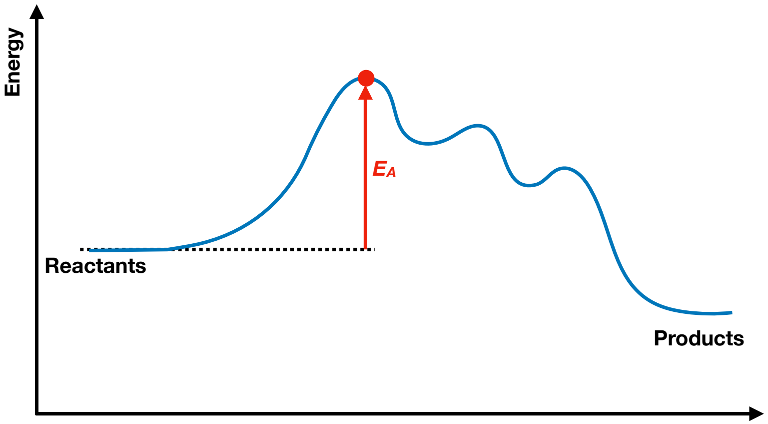


Flow Analogy



The 2nd step does NOT limit the overall rate.

- The rate of consumption of the reactants is EQUAL to the rate of formation of the products!
- By definition, the overall rate of a reaction CANNOT be faster than the rate of formation of the products.
- The best, most definitive way to monitor the speed of a reaction is to follow the concentration of the product vs. time.



Steady-State Approximation

“Steady state” is a situation in which:
the concentration of an intermediate remains constant vs. time throughout a reaction, as it forms and disappears equally fast”

Under the steady state condition, the RATE of change of the concentration of the intermediate can be approximated to ZERO:

$$\mathrm{R} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{I} \xrightarrow{k_2} \mathrm{P}$$

$$\boxed{\frac{d[\mathrm{I}]}{dt} \approx 0 \quad \text{(steady-state approximation)}}$$

When do we have a ”steady state” condition?
Either “depopulation” rate of the intermediate (here Rate_{-1} or Rate_2) is dominant.

$\text{Rate}_{-1} > \text{Rate}_2$ (e.g., $k_{-1} > k_2$):
The reverse reaction from I to R is faster than the forward reaction from I to P.

$\text{Rate}_{-1} < \text{Rate}_2$ (e.g., $k_{-1} < k_2$):
The forward reaction from I to P is faster than the reverse reaction from I to R.

Comparison between the pre-equilibrium vs steady state approximation

Example: $$2NO_{(g)} + H_{2(g)} \longrightarrow N_2O_{(g)} + H_2O_{(g)}$$

intermediate

Proposed elementary reactions:

Step 1: $NO + NO \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} N_2O_2$ $(fast)$

Step 2: $N_2O_2 + H_2 \xrightarrow{k_2} N_2O + H_2O$ $(slow)$

Pre-Equilibrium approximation (step 1 is at equilibrium)

$$K_{eq1} = \frac{[N_2O_2]}{[NO]^2}$$

Steady-State Approximation (the intermediate is at constant concentration)

$$\frac{d[N_2O_2]}{dt} = 0$$

How do you know which approximation to use?

Depending on the situation given (decision is not that difficult).

Predicting the Rate Law from the elementary reactions

Example: $$2\mathrm{NO}_{(g)} + \mathrm{H}_{2(g)} \longrightarrow \mathrm{N_2O}_{(g)} + \mathrm{H_2O}_{(g)}$$

intermediate

Proposed elementary reactions:

$$\text{Step 1:} \quad \mathrm{NO} + \mathrm{NO} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{N_2O_2} \qquad (\mathit{fast})$$

$$\text{Step 2:} \quad \mathrm{N_2O_2} + \mathrm{H_2} \xrightarrow{k_2} \mathrm{N_2O} + \mathrm{H_2O} \qquad (\mathit{slow})$$

First, the reaction rate must be equal to the rate of formation of the product:

$$\text{Rate} = \frac{d[\mathrm{N_2O}]}{dt} \quad \left(\text{or } = \frac{d[\mathrm{H_2O}]}{dt}, \text{ the two are the same}\right)$$

The overall rate can be approximated to the rate in Step 2 (the rate limiting step):

Overall rate: $$\frac{d[\mathrm{N_2O}]}{dt} = k_2[\mathrm{N_2O_2}][\mathrm{H_2}]$$

Goal: N_2O_2 is an intermediate. We need to find a way to express the overall rate using only reactant concentrations.

The Rate Law from the pre-equilibrium approximation

Example: $$2NO_{(g)} + H_{2(g)} \longrightarrow N_2O_{(g)} + H_2O_{(g)}$$

Proposed elementary reactions:

$$\text{Step 1:} \quad NO + NO \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} N_2O_2 \qquad (fast)$$

$$\text{Step 2:} \quad N_2O_2 + H_2 \xrightarrow{k_2} N_2O + H_2O \qquad (slow)$$

Overall rate: $$\frac{d[N_2O]}{dt} = k_2[N_2O_2][H_2]$$

If we use the pre-equilibrium approximation (like before):

$$K_{eq1} = \frac{[N_2O_2]}{[NO]^2} \quad \Rightarrow \quad [N_2O_2] = K_{eq1}[NO]^2$$

Insert N_2O_2 into the overall rate.

$$\begin{aligned} \text{Rate} &= k_2[N_2O_2][H_2] \\ &= k_2 \times \left(K_{eq1}[NO]^2\right) \times [H_2] \\ &= k_2 K_{eq1}[NO]^2[H_2] \end{aligned}$$

From the pre-equilibrium approximation, the overall reaction is 2nd order in NO and 1st order in H_2.

The Rate Law from the steady state approximation

Example: $$2NO_{(g)} + H_{2(g)} \longrightarrow N_2O_{(g)} + H_2O_{(g)}$$

Proposed elementary reactions:

$$\text{Step 1:} \quad NO + NO \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} N_2O_2 \qquad (fast)$$

$$\text{Step 2:} \quad N_2O_2 + H_2 \xrightarrow{k_2} N_2O + H_2O \qquad (slow)$$

Overall rate: $$\frac{d[N_2O]}{dt} = k_2[N_2O_2][H_2]$$

Steady state approximation: $$\frac{d[N_2O_2]}{dt} = 0$$

The change in N_2O_2 is due to three processes:

1) Creation in Step 1: $\text{Rate} = +k_1[NO]^2$

2) Consumption in reverse Step 1: $\text{Rate} = -k_{-1}[N_2O_2]$

3) Consumption in Step 2: $\text{Rate} = -k_2[N_2O_2][H_2]$

Therefore, the change in N_2O_2 can be described as follows:

$$\frac{d[N_2O_2]}{dt} = \underbrace{+k_1[NO]^2}_{\substack{\text{rate of formation}\\ \text{in Step 1}}} - \underbrace{k_{-1}[N_2O_2]}_{\substack{\text{rate of disappearance}\\ \text{in reverse Step 1}}} - \underbrace{k_2[N_2O_2][H_2]}_{\substack{\text{rate of disappearance}\\ \text{in Step 2}}} = 0$$

The Rate Law from the steady state approximation

Example: $2NO_{(g)} + H_{2(g)} \longrightarrow N_2O_{(g)} + H_2O_{(g)}$

Proposed elementary reactions:

$$\text{Step 1:} \quad NO + NO \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} N_2O_2 \qquad (\textit{fast})$$

$$\text{Step 2:} \quad N_2O_2 + H_2 \xrightarrow{k_2} N_2O + H_2O \qquad (\textit{slow})$$

Overall rate: $$\frac{d[N_2O]}{dt} = k_2[N_2O_2][H_2]$$

Steady state approximation:

From the steady approximation, we can obtain [N_2O_2]:

$$k_1[NO]^2 - k_{-1}[N_2O_2] - k_2[N_2O_2][H_2] = 0$$

$$k_1[NO]^2 = k_{-1}[N_2O_2] + k_{-2}[N_2O_2]$$

$$\Rightarrow [N_2O_2] = \frac{k_1[NO]^2}{k_{-1} + k_2[H_2]}$$

Plug this back into the overall rate equation:

$$\text{Rate} = k_2[N_2O_2][H_2] = k_2\left(\frac{k_1[NO]^2}{k_{-1} + k_2[H_2]}\right)[H_2]$$

Comparing the two methods

Pre-Equilibrium Approximation

$$\text{Rate} = k_2 K_{eq1} [\text{NO}]^2 [\text{H}_2]$$

Steady-State Approximation

$$\text{Rate} = k_2 \left(\frac{k_1 [\text{NO}]^2}{k_{-1} + k_2 [\text{H}_2]} \right) [\text{H}_2]$$

They look different… but let's look at it more carefully.

In the steady-state expression, the denominator is a sum of two terms.
If one of the two is much bigger than the other, then we can neglect the smaller one:
(a large number + a small number ~ the large number)

Proposed elementary reactions:

$$\text{Step 1:} \quad \text{NO} + \text{NO} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{N}_2\text{O}_2 \qquad (\textit{fast})$$

$$\text{Step 2:} \quad \text{N}_2\text{O}_2 + \text{H}_2 \xrightarrow{k_2} \text{N}_2\text{O} + \text{H}_2\text{O} \qquad (\textit{slow})$$

Because Step 1 is FAST, then we know that $k_{-1} >> k_2[H_2]$ (the intermediate converts more often to the reactant than to the product).
Therefore,

$$\text{Rate} = \frac{k_1 k_2}{k_{-1}} [\text{NO}]^2 [\text{H}_2]$$

The same rate law predicted for the pre-equilibrium!

Comparing the two methods

Pre-Equilibrium Approximation

$$\text{Rate} = k_2 K_{eq1}[\text{NO}]^2[\text{H}_2]$$

Steady-State Approximation

$$\text{Rate} = k_2\left(\frac{k_1[\text{NO}]^2}{k_{-1} + k_2[\text{H}_2]}\right)[\text{H}_2]$$

Then, are the two always predicting the same thing?

NO: the steady-state approximation can predict a situation when the pre-equilibrium assumption is not valid. For instance, imagine that $[\text{H}_2]$ can be increased enough that $k_{-1} \ll k_2[\text{H}_2]$; then the steady-state approximation predicts:

Proposed elementary reactions:

$$\text{Step 1:} \quad \text{NO} + \text{NO} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{N}_2\text{O}_2 \qquad (\textit{fast})$$

$$\text{Step 2:} \quad \text{N}_2\text{O}_2 + \text{H}_2 \xrightarrow{k_2} \text{N}_2\text{O} + \text{H}_2\text{O} \qquad (\textit{slow})$$

Therefore,

$$\text{Rate} \approx k_2\left(\frac{k_1[\text{NO}]^2}{k_2[\text{H}_2]}\right)[\text{H}_2] = k_1[\text{NO}]^2$$

Under this condition (large $[\text{H}_2]$, the second step becomes fast enough that the rate is now limited by Step 1: the reaction becomes zeroth-order in H_2…

Enzyme Kinetics.

What are Enzymes?

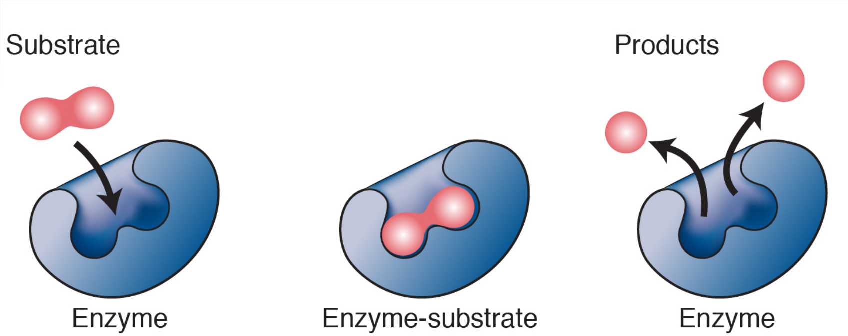
They are the proteins that do pretty much everything in your body. They break down your food and turn it into energy. They make all the stuff that your cells are made of. They breakdown all that stuff when it needs to.

All of these enzyme functions are basically chemical reactions, turning stuff into other stuff.

How do they do that? They are catalysts that accelerate a reaction. In most cases, they are homogeneous catalysts.

Enzyme Kinetics.

The classic mechanism:



slow

$$E + S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ES \xrightarrow{k_2} E + P$$

Overall rate: Rate = $k_2[ES]$

Steady state approximation:

$$\frac{d[ES]}{dt} = k_1[E][S] - k_{-1}[ES] - k_2[ES] = 0$$

$$k_1[E][S] = (k_{-1} + k_2)[ES]$$

$$[ES] = \frac{k_1[E][S]}{(k_{-1} + k_2)}$$

Overall rate:

$$\text{Rate} = \frac{k_2 k_1[E][S]}{(k_{-1}+k_2)}$$

Enzyme Kinetics Super bonus!.

$$E + S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ES \overset{\text{slow}}{\xrightarrow{k_2}} E + P$$

Overall rate: Rate = k_2[ES]

Steady state approximation: $$\frac{d[ES]}{dt} = k_1[E][S] - k_{-1}[ES] - k_2[ES] = 0$$

Overall rate:

$$E_{tot} = [E] + [ES]\text{: } [E] = E_{tot} - [ES]$$

$$k_1[E][S] = (k_{-1} + k_2)[ES]$$

$$k_1(E_{tot} - [ES])[S] = (k_{-1} + k_2)[ES]$$

$$(k_1 E_{tot} - k_1 [ES])[S] = (k_{-1} + k_2)[ES]$$

$$k_1 E_{tot}[S] = (k_{-1} + k_2 + k_1[S])[ES]$$

$$[ES] = \frac{k_1 E_{tot}[S]}{k_{-1} + k_2 + k_1[S]}$$

$$[ES] = \frac{E_{tot}[S]}{(k_{-1}+k_2)/k_1) + [S]}$$

$$\text{Rate} = k_2[ES] = \frac{k_2 E_{tot}[S]}{(k_{-1}+k_2)/k_1)+[S]}$$

$$\text{Rate} = k_2[ES] = \frac{k_2 E_{tot}[S]}{K_M+[S]}$$