N-41 Intro to Kinetics, Rate Expressions, and Average Rate

Target: I can describe factors that change the speed of a reaction, and can do calculations to find the average rate of a reaction.

Link to YouTube Presentation: https://youtu.be/sihC6aDsy3s

Thermo vs. Kinetics

Thermo

Energy (heat)

Q: is there enough energy for a reaction to happen? Is it GOING to happen?

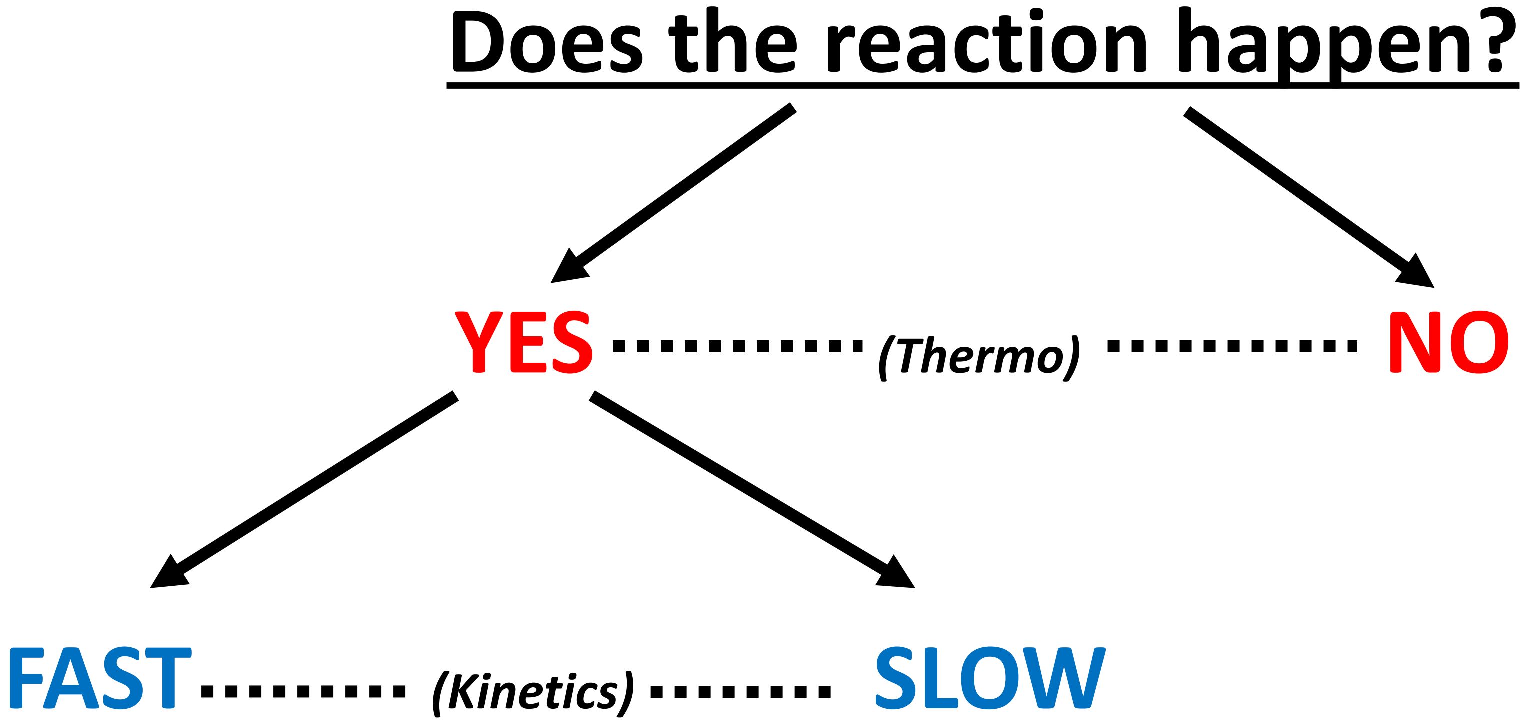
↙ YES ↘ NO

Kinetics

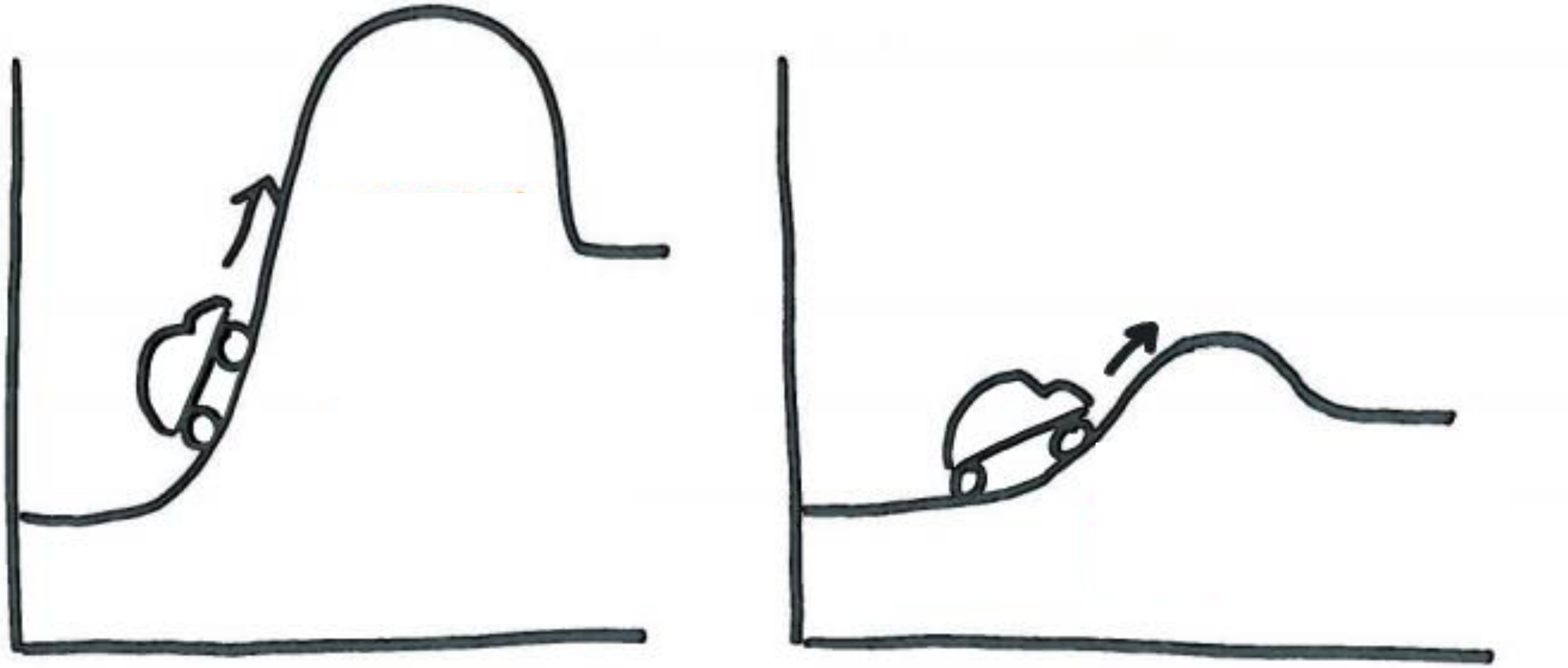
Speed

Q: Assuming the reaction does happen - How FAST is the reaction going to happen?

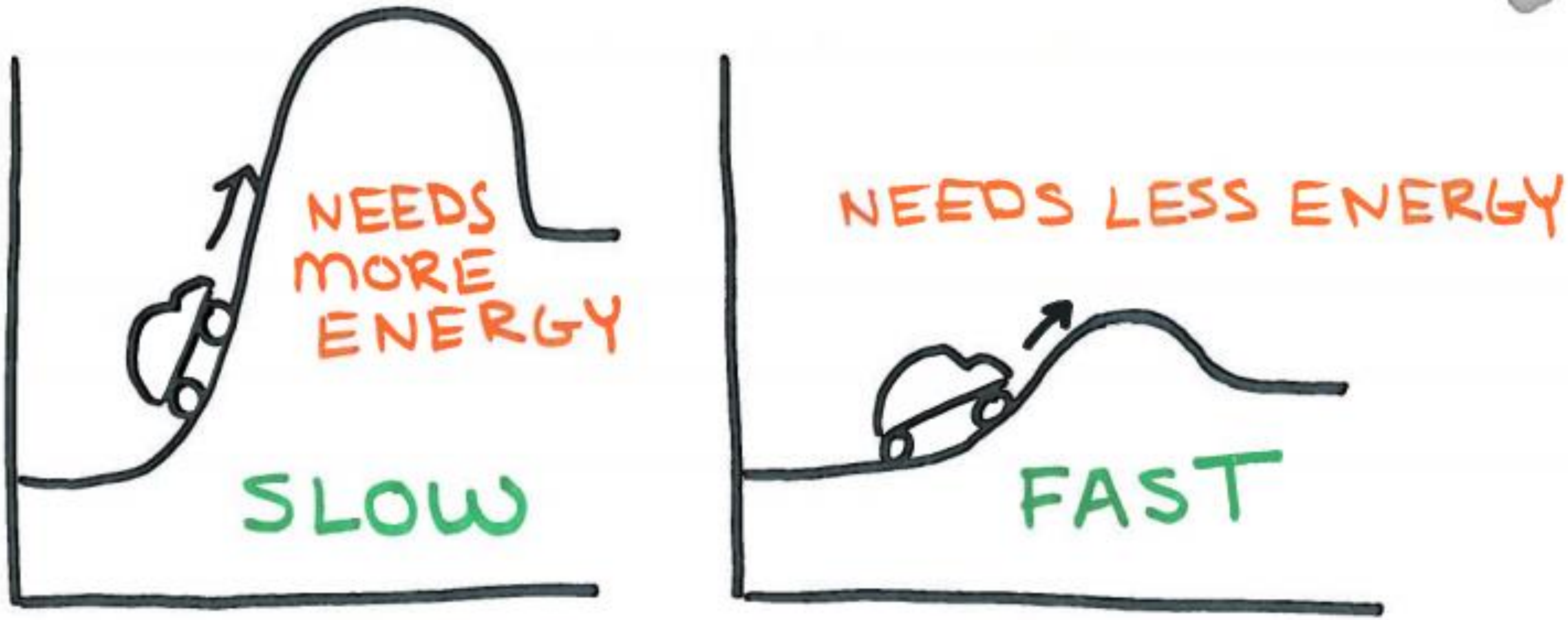
↙ FAST ↘ SLOW


Does the reaction happen?
YES
(Thermo)
NO
FAST
(Kinetics)
SLOW

SLOW ≠ DOESN'T HAPPEN



This is where THERMO turns into KINETICS



This is where THERMO turns into KINETICS

Collision theory

Reactants must collide in order to react

Activation energy

Minimum amount of energy colliding particles need in order to react.

EFFECTIVE Collisions have to be...

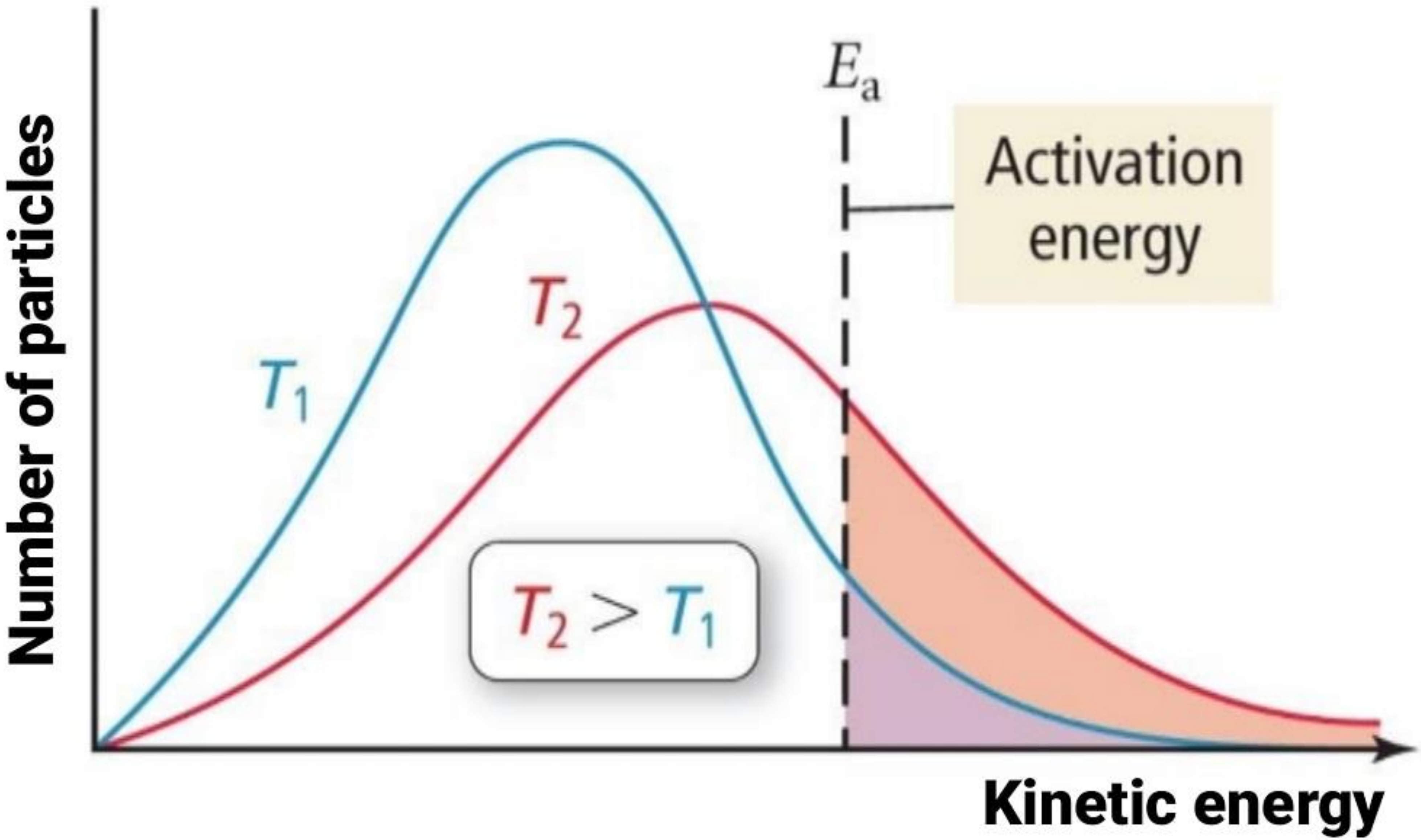
Fast Enough AND Correct Orientation

Factors of Reaction Rate

1. Temperature
2. Concentration/Pressure
3. Surface area
4. Catalysts

(Typically)
Increase any of these, you get more effective collisions…
so it goes faster!

Maxwell-Boltzmann Distribution for ∆Temp



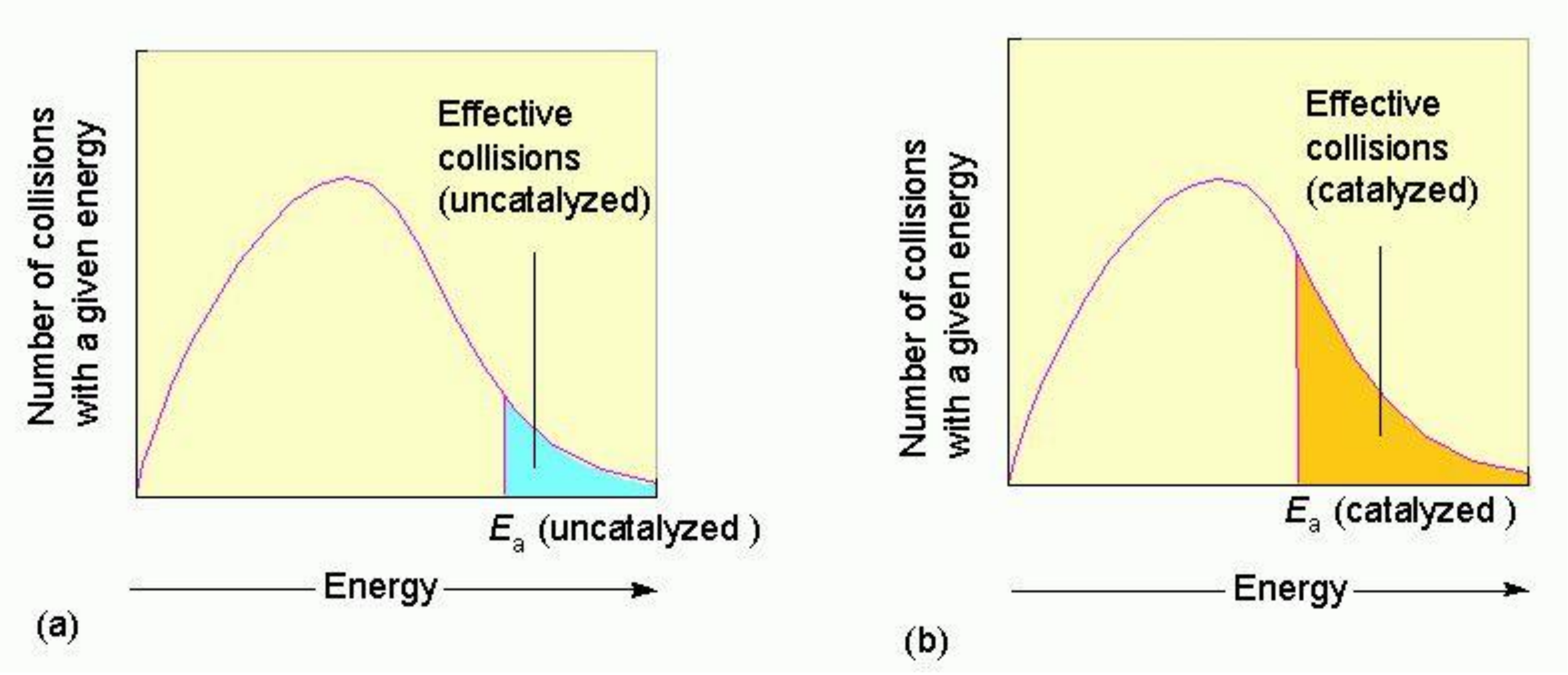
Catalysts

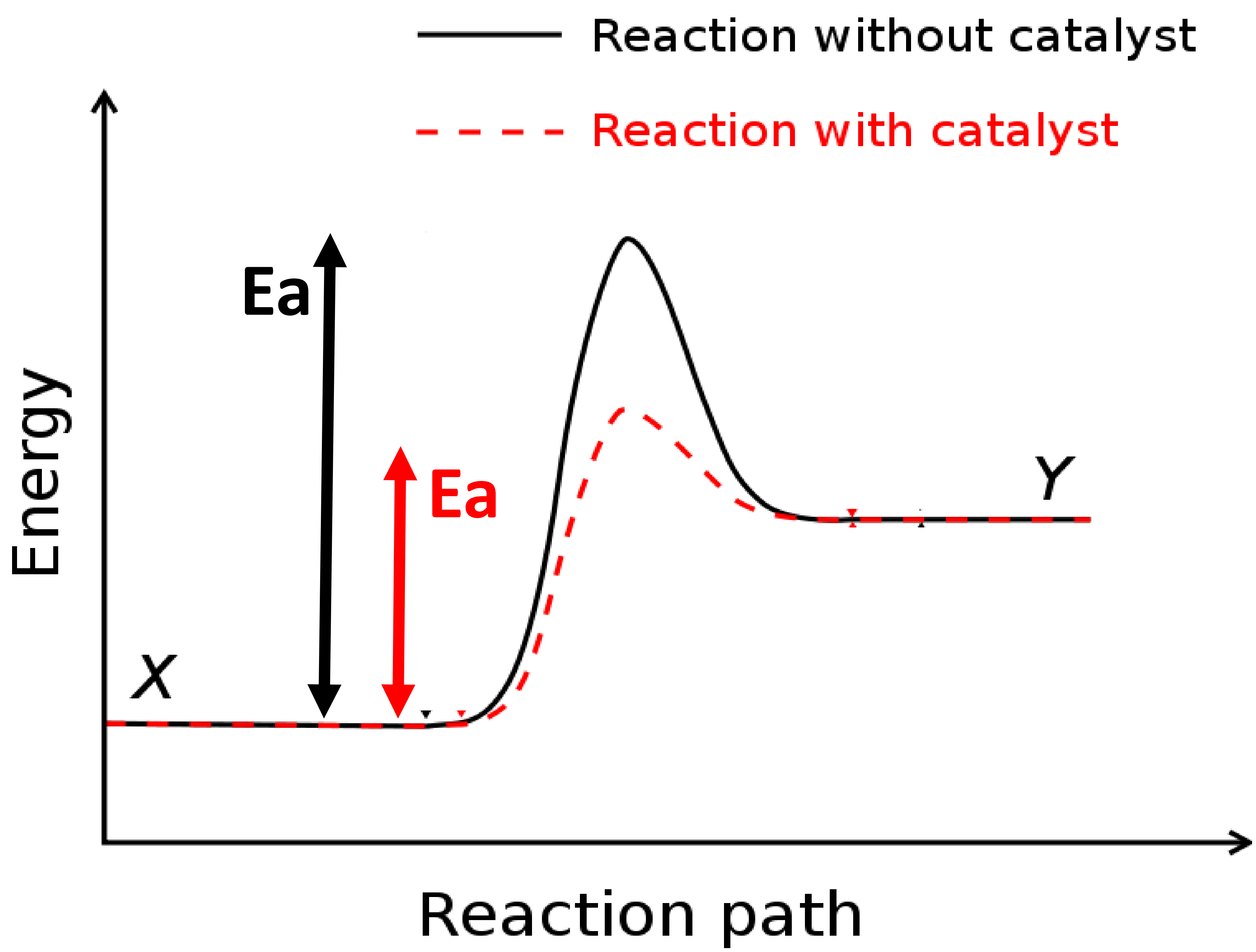
What is it?

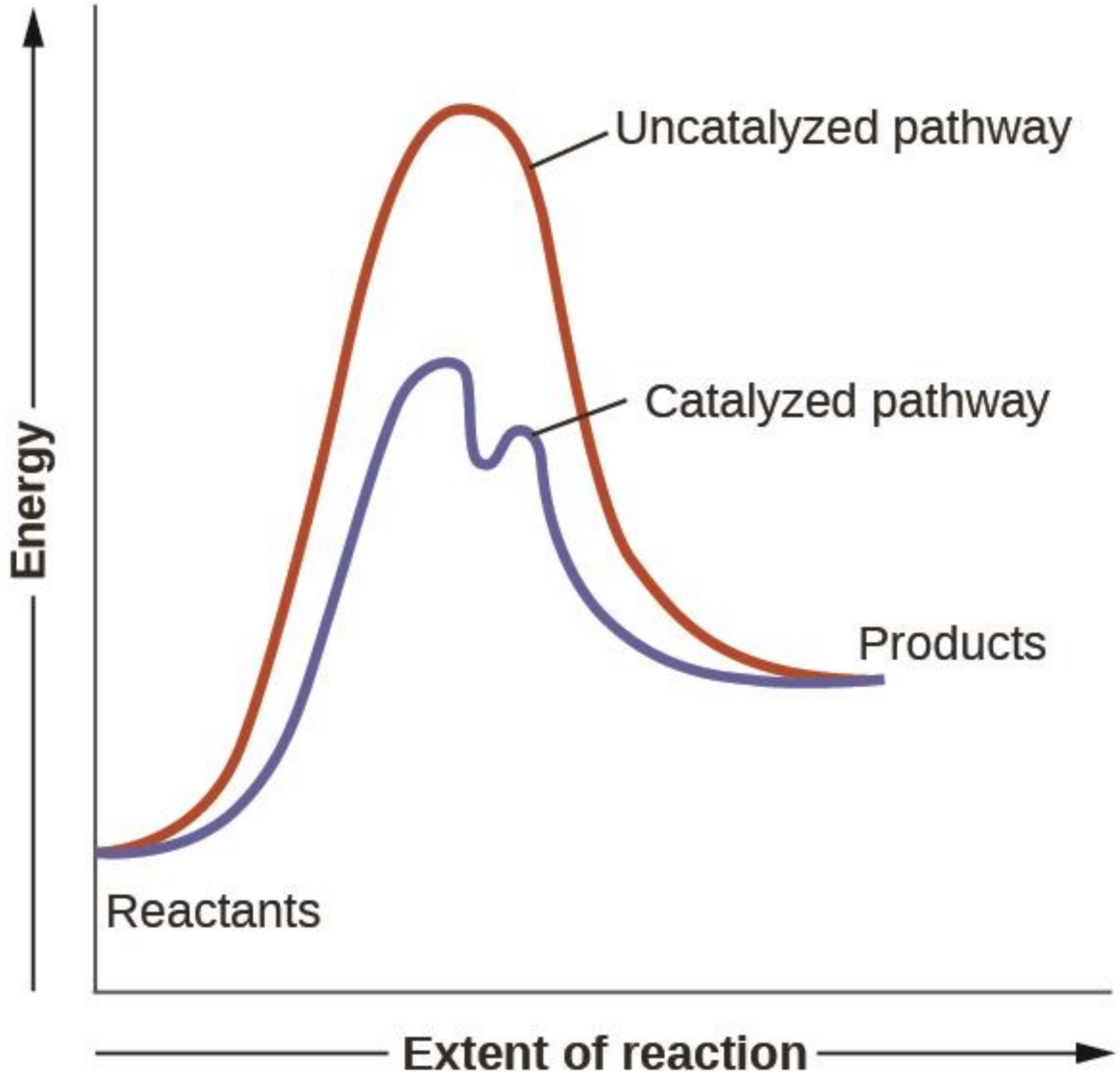
- A chemical that you add to rxn
- Does NOT get used up during reaction
- Helps orient molecules to reach transition state easier OR provides an alternate pathway/mechanism/set of steps for it to occur
  - So you do not need as much energy
    - **Lowers Activation Energy**
      = faster reaction BECAUSE more molecules will have the needed energy to get over Ea

**You don't get "more" collisions –
you just get more collisions that will be EFFECTIVE!**

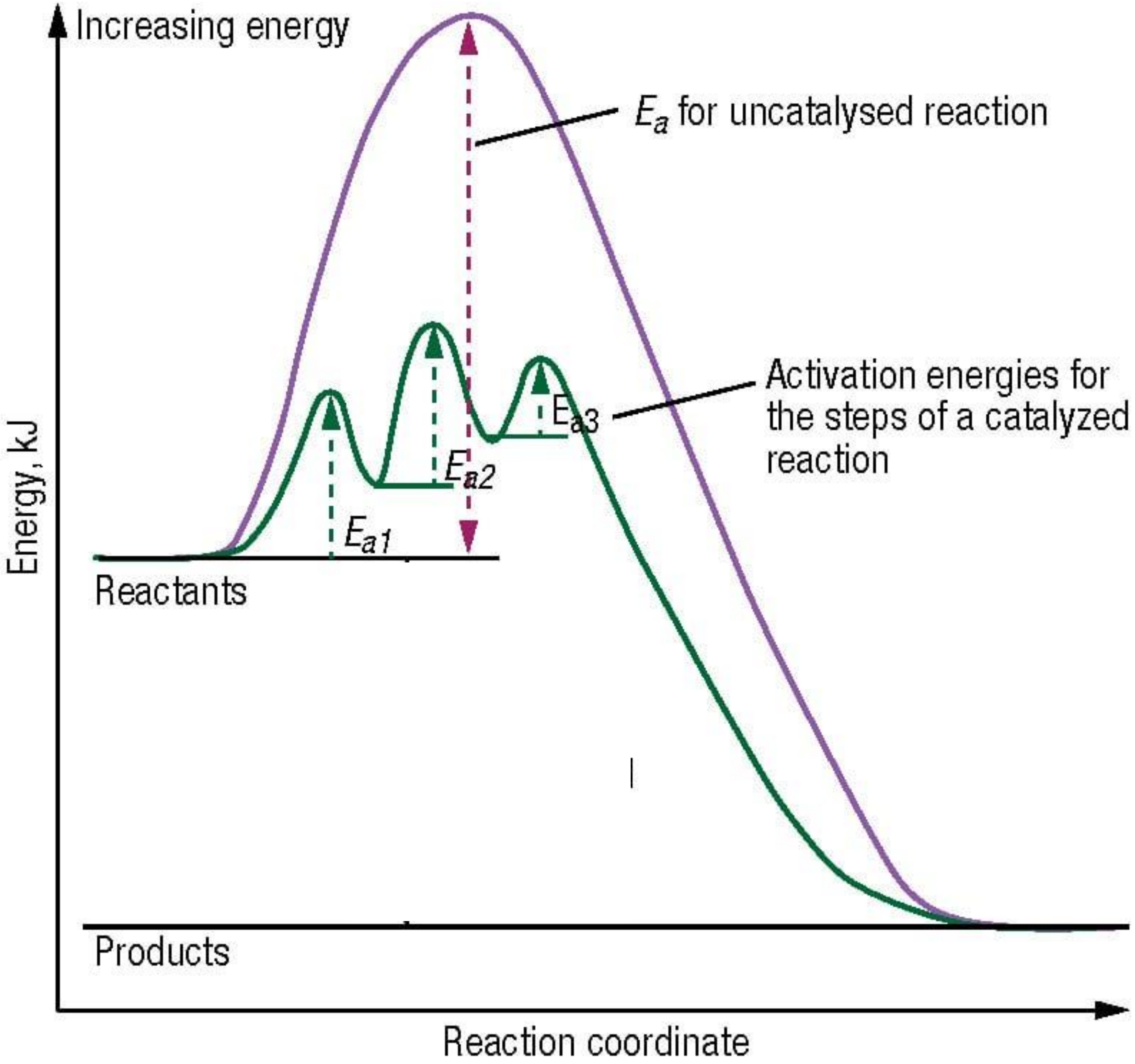
Maxwell-Boltzman Distribution for Catalyst



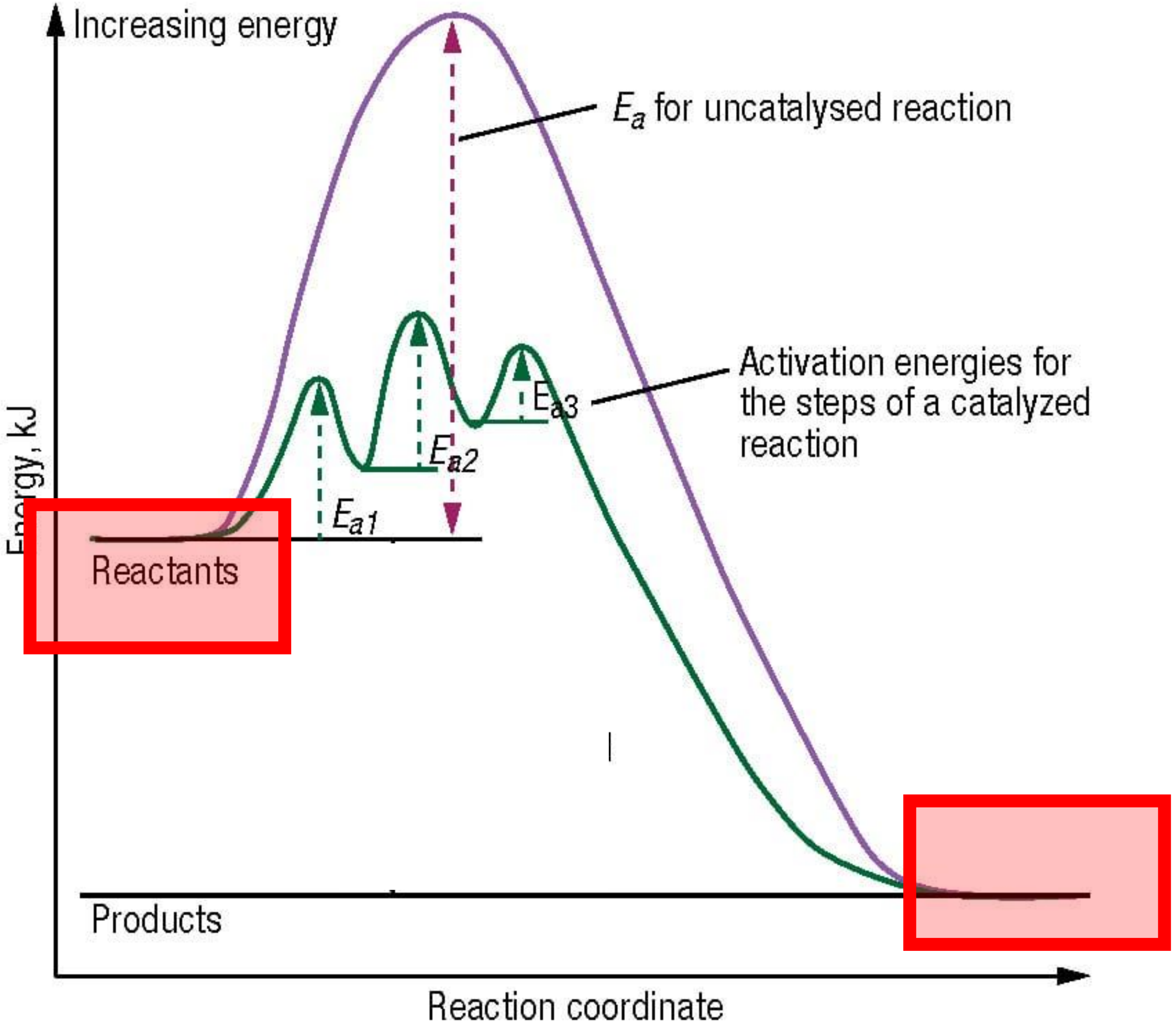

Reaction without catalyst
Reaction with catalyst
Energy
Ea
Ea
X
Y
Reaction path



Uncatalyzed pathway
Catalyzed pathway
Products
Reactants
Energy
Extent of reaction



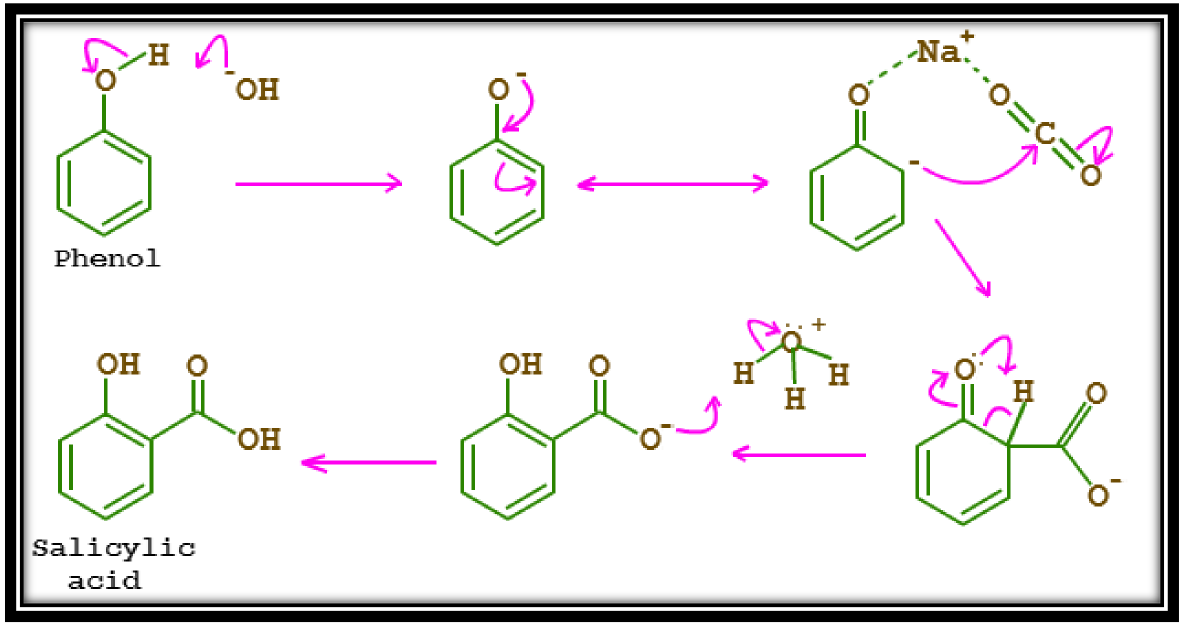
Increasing energy
E_a for uncatalysed reaction
Activation energies for the steps of a catalyzed reaction
Energy, kJ
E_{a1}
E_{a2}
E_{a3}
Reactants
Products
Reaction coordinate



Increasing energy
Energy, kJ
E_a for uncatalysed reaction
Activation energies for the steps of a catalyzed reaction
E_{a1}
E_{a2}
E_{a3}
Reactants
Products
Reaction coordinate

Reaction Mechanism

- A normal balanced chemical equation does not tell us **HOW** reactants become products; just a summary of the overall process.

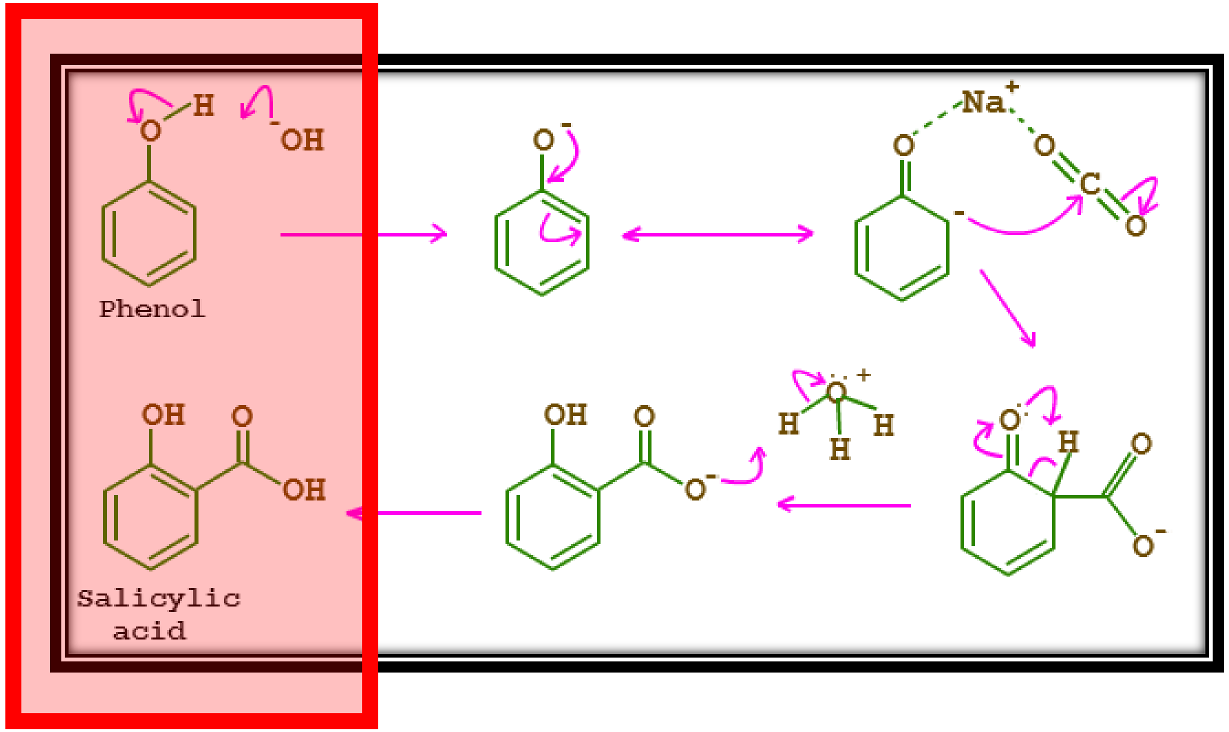


- The reaction mechanism is the series of steps by which a chemical reaction occurs.

- Some reactions take place in one step, two steps, three steps etc.

Reaction Mechanism

- A normal balanced chemical equation does not tell us **HOW** reactants become products; just a summary of the overall process.



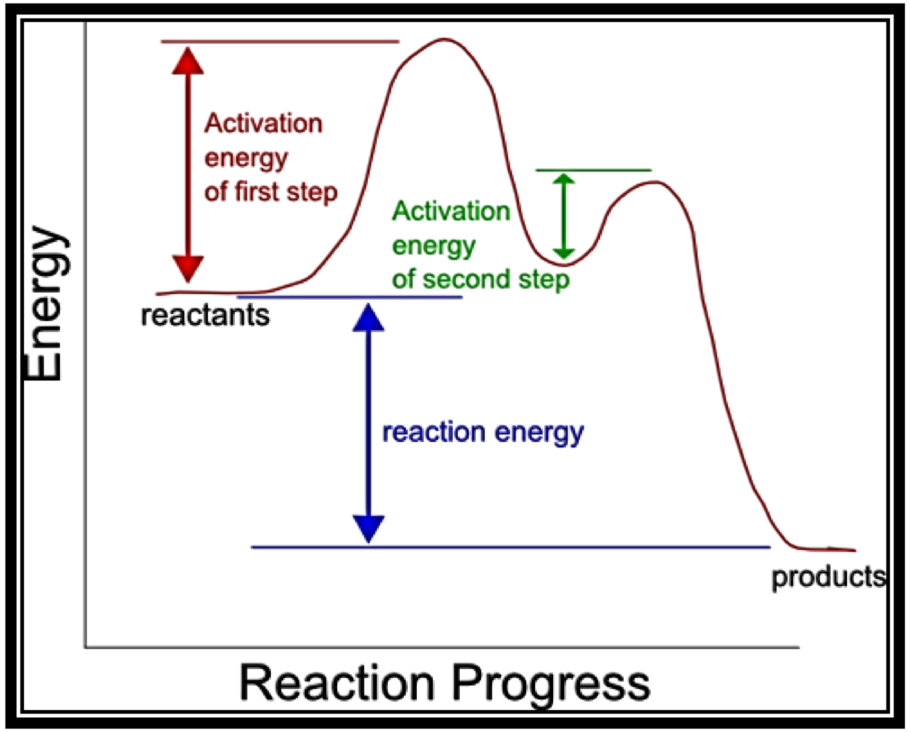
- The reaction mechanism is the series of steps by which a chemical reaction occurs.

- Some reactions take place in one step, two steps, three steps etc.

Rate Determining Step

In a multi-step reaction, the *slowest* step is the rate-determining step. It determines the rate of reaction.

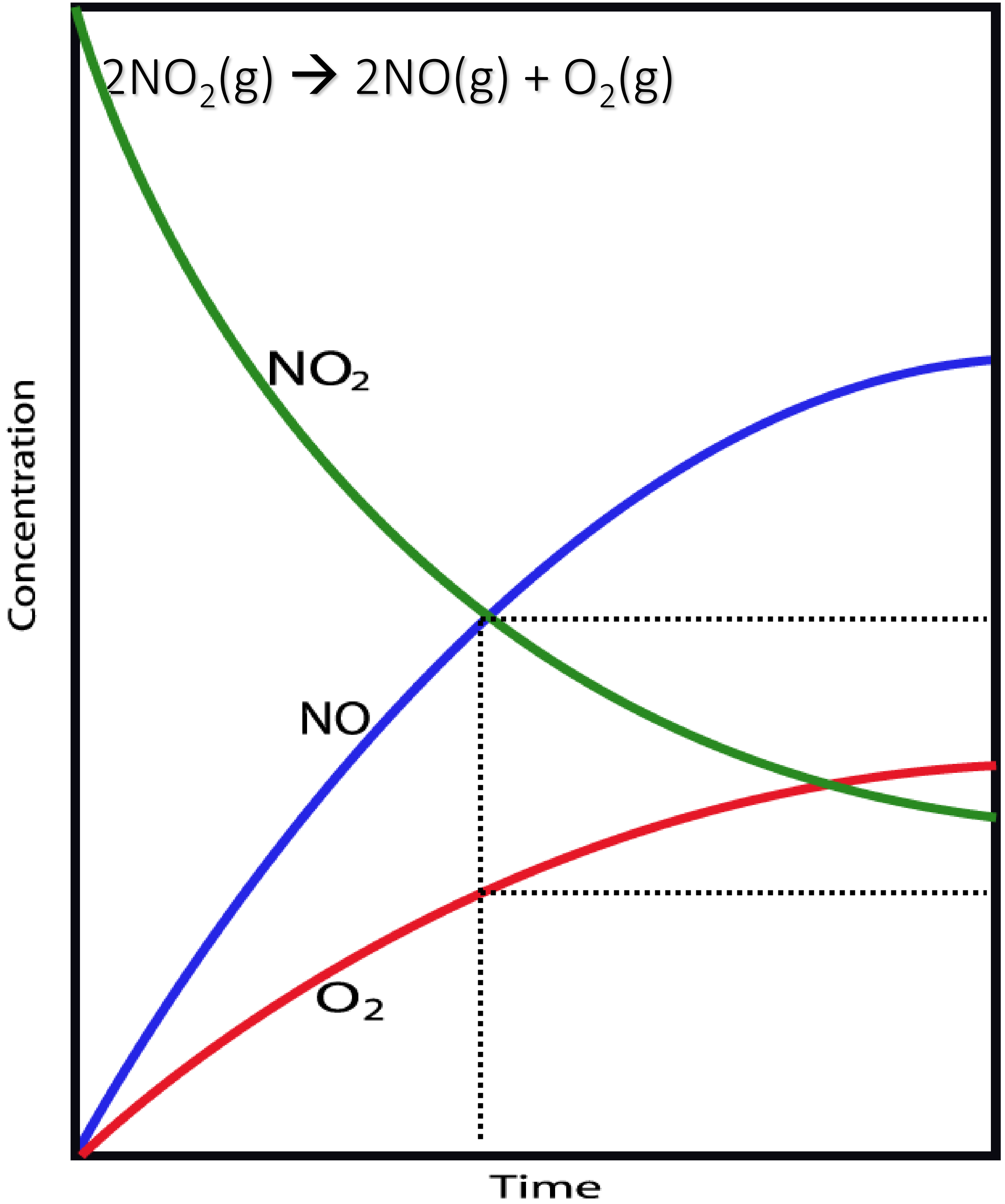
Can only go as fast as your slowest step!



Reaction Rates

Where	Units	Equation	Issue
Car	Miles / Hour	Δ Distance / Δ Time	SPEED
Kinetics	Molarity / second M / sec	Δ Concentration / Δ Time	SPEED

Using up reactants = decrease in # molecules = NEGATIVE rate
Making more products = increase in # molecules = POSTIVE rate



Reaction Rates

1) Can measure disappearance of reactants (NO_2)

2) Can measure appearance of products (NO and O_2)

3) Are proportional stoichiometrically

Have to take coefficients into account! We make twice as much NO as O_2 ever second

Average Rate

- Rate is not always constant!
- Can start fast and slow down, or start slow and speed up
- Sometimes it is sufficient to just calculate the *average rate* over a given time period

$$\boldsymbol{Average\ Rate = \frac{\Delta[X]}{\Delta t} = \frac{[X]_{final} - [X]_{initial}}{t_{final} - t_{initial}}}$$

Average Rate

In an experiment, the concentration of substance D was measured at different times. **Determine the average rate between 0.0 and 7.0 sec.**

Time , (s)	[D] , (M)
0	0.500
3.0	0.370
7.0	0.290

- Rate = $\frac{(0.290-0.500)}{(7.0 - 0.0)}$
- Rate = -0.0300 M/s
- Is "D" a reactant or a product?
- Reactant! Rate is negative!

Weird thing… Sometimes we will say "What is the rate of disappearance" and then we don't have to write the negative sign! We like that sometimes because of math reasons. Example: The rate of disappearance is 0.0300 M/s

Average Rate

In an experiment, the concentration of substance D was measured at different times. **Determine the average rate between 3.0 and 7.0 sec.**

Time , (s)	[D] , (M)
0	0.500
3.0	0.370
7.0	0.290

- Rate = $\dfrac{(0.290 - 0.370)}{(7.0 - 3.0)}$
- Rate = -0.0200 M/s
- Is "D" a reactant or a product?
- Reactant! Rate is negative!

See! Rate is not constant over the course of the reaction!
That is why "average rate" is not always very helpful.

Pause here!

WS #3 – Q's #1-16 can be done at this point

Reaction Rates and Stoichiometry

$$C_4H_9Cl + H_2O \rightarrow C_4H_9OH + HCl$$

- Ratio of C_4H_9Cl to C_4H_9OH is **1:1**. For every mole of C_4H_9Cl lost, there was a mole of C_4H_9OH created.
- Thus, the rate of ***disappearance* of C_4H_9Cl** is the ***same*** as the rate of ***appearance* of C_4H_9OH**. They are directly related.

$$\text{Rate} = \frac{-\Delta[C_4H_9Cl]}{\Delta t} = \frac{\Delta[C_4H_9OH]}{\Delta t}$$

But…what if NOT a 1:1 ratio?!

$H_2 + I_2 \rightarrow 2\ HI$

- For every 1 mole of H_2 that reacts, ***2 moles*** of HI are made!
- The rate of ***disappearance* of H_2** is ***HALF*** the rate of ***appearance* of HI**.
- Want to set them equal to each other? ***Divide the HI expression by 2***
- ***Always divide by your coefficients, don't multiply!***

$$\text{Rate} = \frac{-\Delta[H_2]}{\Delta t} = \frac{1}{2}\frac{\Delta[HI]}{\Delta t}$$

- **Remember! Reactants are negative!**

Reaction Rates and Stoichiometry

$$N_2 + 3\ H_2 \rightarrow 2\ NH_3$$

"Rate of Reaction" $= \dfrac{-\Delta[N_2]}{\Delta t} = \dfrac{-1\ \Delta[H_2]}{3\ \ \Delta t} = \dfrac{1\ \Delta[NH_3]}{2\ \ \Delta t}$

Entire thing is the RATE EXPRESSION

REMEMBER!

Reactants are negative, Products are positive. Your double negatives will work themselves out so the REACTION rate comes out positive. Its all semantics in kinetics!

Generic Rate Expression

$$aA + bB \longrightarrow cC + dD$$

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

Reactants decrease (Negative rates)

Products increase (Positive rates)

Practice Problem #1

Write the rate expression for the following Rxn:

$$2\ N_2O \rightarrow 2\ N_2 + O_2$$

$$\text{Rate} = -\frac{1}{2}\frac{\Delta[N_2O]}{\Delta t} = \frac{1}{2}\frac{\Delta[N_2]}{\Delta t} = \frac{\Delta[O_2]}{\Delta t}$$

The "Rate of Reaction" is

- ½ the rate of disappearance of N_2O
- OR ½ the rate of appearance of N_2
- OR the same as the rate of appearance of O_2

Practice Problem #1

GENERIC "REACTION RATE"

$$\text{Rate} = \frac{-1}{2}\frac{\Delta[N_2O]}{\Delta t} = \frac{1}{2}\frac{\Delta[N_2]}{\Delta t} = \frac{\Delta[O_2]}{\Delta t}$$

- The disappearance of N_2O occurs at a rate of $-3.25 \times 10^6\ Ms^{-1}$. What is the rate of N_2 appearance.

THIS IS $\frac{\Delta[N_2O]}{\Delta t}$

$$\frac{-1\,[-3.25 \times 10^6 Ms^{-1}]}{2} = \frac{1}{2}\frac{\Delta[N_2]}{\Delta t}$$

Rate N_2 = $3.25 \times 10^6\ Ms^{-1}$

SPECIFIC "RATE OF APPEARANCE OF N_2"

The "Reaction Rate" would be ½ the rate of appearance of N_2 = 1.63×10^6, or – ½ the rate of N_2O disappearance = 1.63×10^6 also! See how that works out?

Practice Problem #1

$$\text{Rate} = \frac{-1}{2}\frac{\Delta[N_2O]}{\Delta t} = \frac{1}{2}\frac{\Delta[N_2]}{\Delta t} = \frac{\Delta[O_2]}{\Delta t}$$

- The disappearance of N_2O occurs at a rate of $-3.25 \times 10^6\ Ms^{-1}$. What is the rate of O_2 appearance.

THIS IS $\frac{\Delta[N_2O]}{\Delta t}$

$$\frac{-1\ [-3.25 \times 10^6 Ms^{-1}]}{2} = \frac{\Delta[O_2]}{\Delta t}$$

Rate O_2 $= 1.63 \times 10^6\ Ms^{-1}$

The "Reaction Rate" would be the same as the rate of appearance of O_2 = 1.63 x 10^6, which was the same as the other two parts earlier! See how that works out?

Practice Problem #2

Write the rate expression for the following Rxn:

$4Fe + 3O_2 \rightarrow 2Fe_2O_3$

$$\text{Rate} = -\frac{1}{4}\frac{\Delta[Fe]}{\Delta t} = -\frac{1}{3}\frac{\Delta[O_2]}{\Delta t} = \frac{1}{2}\frac{\Delta[Fe_2O_3]}{\Delta t}$$

Practice Problem #2

$$\text{Rate} = -\frac{1}{4}\frac{\Delta[Fe]}{\Delta t} = -\frac{1}{3}\frac{\Delta[O_2]}{\Delta t} = \frac{1}{2}\frac{\Delta[Fe_2O_3]}{\Delta t}$$

- The appearance of Fe_2O_3 occurs at a rate of 7.05×10^{-2} Ms^{-1}. What is the rate of O_2 and Fe disappearance.

THIS IS $\frac{\Delta[Fe_2O_3]}{\Delta t}$

$$\frac{1}{2}[7.05\text{x } 10^{-2}Ms^{-1}] = \frac{-1}{3}\frac{\Delta[O_2]}{\Delta t}$$

Rate O_2 = - 0.106 Ms^{-1}

The "Reaction Rate" would be – $^1/_3$ the rate of disappearance of O_2 = 3.53 x 10^{-2}, or ½ the rate of Fe_2O_3 appearance = 3.53 x 10^{-2} also! See how that works out?

Practice Problem #2

$$\text{Rate} = -\frac{1}{4}\frac{\Delta[Fe]}{\Delta t} = -\frac{1}{3}\frac{\Delta[O_2]}{\Delta t} = \frac{1}{2}\frac{\Delta[Fe_2O_3]}{\Delta t}$$

- The appearance of Fe_2O_3 occurs at a rate of $7.05 \times 10^{-2}\ Ms^{-1}$. What is the rate of O_2 and Fe disappearance.

THIS IS $\frac{\Delta[Fe_2O_3]}{\Delta t}$

$$\frac{1\ [7.05x\ 10^{-2}Ms^{-1}]}{2} = -\frac{1}{4}\frac{\Delta[Fe]}{\Delta t}$$

Rate Fe = $-\ 0.141\ Ms^{-1}$

The "Reaction Rate" would be – $^1/_4$ the rate of disappearance of Fe = 3.53×10^{-2}, which was the same as the other two parts! See how that works out?

Practice Problem #3

Write the rate expression for the following Rxn:

$N_2 + 3\ H_2 \rightarrow 2NH_3$

$$\text{Rate} = -\frac{\Delta[N_2]}{\Delta t} = -\frac{1}{3}\frac{\Delta[H_2]}{\Delta t} = \frac{1}{2}\frac{\Delta[NH_3]}{\Delta t}$$

Practice Problem #3

$$\text{Rate} = -\frac{\Delta[N_2]}{\Delta t} = \frac{-1}{3}\frac{\Delta[H_2]}{\Delta t} = \frac{1}{2}\frac{\Delta[NH_3]}{\Delta t}$$

- The rate of reaction is $1.70 \times 10^4\ Ms^{-1}$. What is the rate of disappearance of H_2 and the disappearance of N_2 ?

$$1.70 \times 10^4 Ms^{-1} = -\frac{1}{3}\frac{\Delta[H_2]}{\Delta t}$$

Rate H_2 = $-5.1 \times 10^4\ Ms^{-1}$

"Rate of Reaction" can sometimes be given to you!
Sometimes you solve for it, sometimes you are solving for a appearance/disappearance rate, could be anything!

Practice Problem #3

$$\text{Rate} = -\frac{\Delta[N_2]}{\Delta t} = -\frac{1}{3}\frac{\Delta[H_2]}{\Delta t} = \frac{1}{2}\frac{\Delta[NH_3]}{\Delta t}$$

- The rate of reaction is $1.70 \times 10^4\ Ms^{-1}$. What is the rate of disappearance of H_2 and the disappearance of N_2 ?

$$1.70 \times 10^4 Ms^{-1} = \frac{-\Delta[N_2]}{\Delta t}$$

Rate N_2 = - $1.70 \times 10^4\ Ms^{-1}$

Link to YouTube Presentation

- https://youtu.be/sihC6aDsy3s