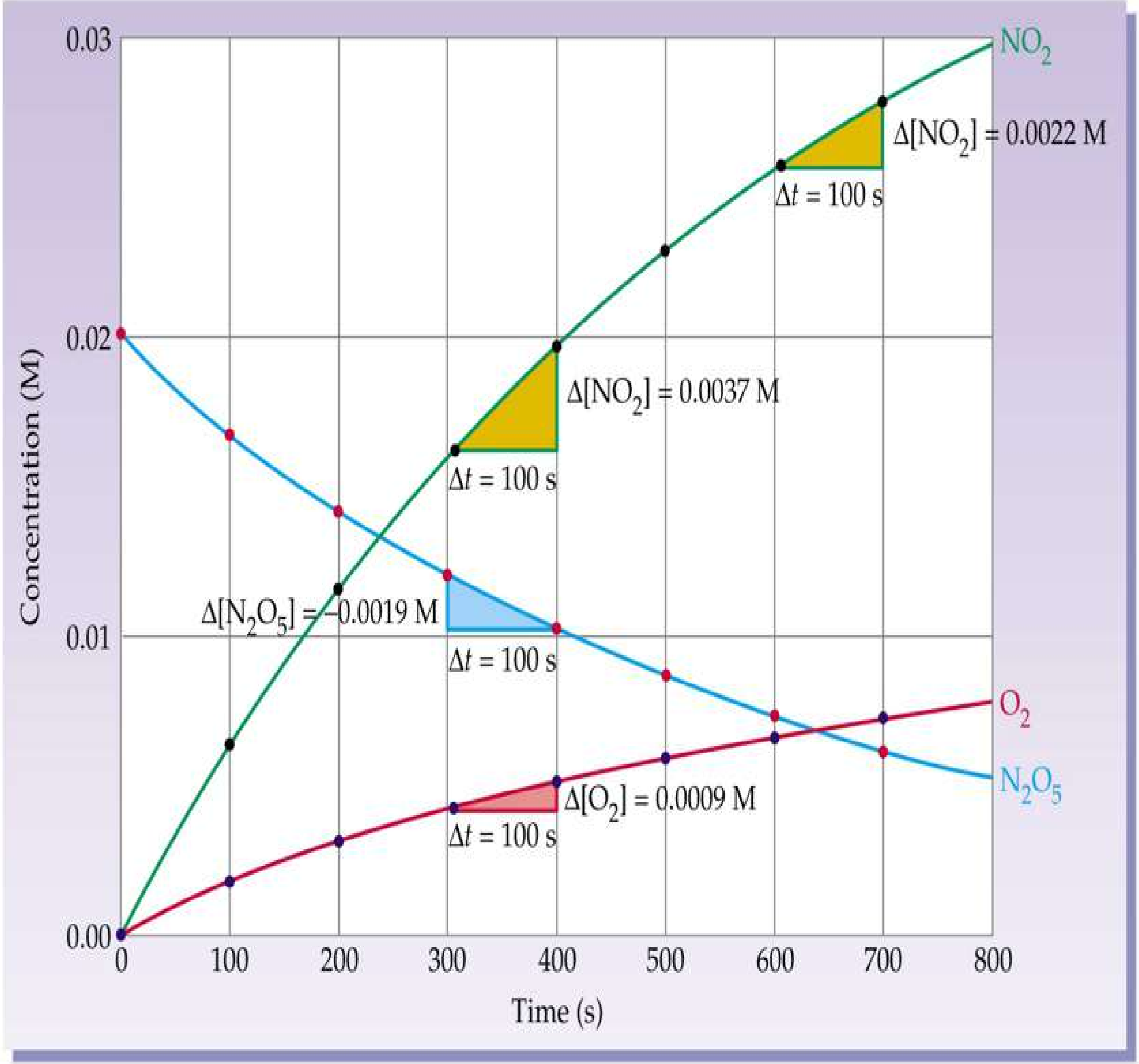
Kinetics

Chapter 12

- Here we deal with how fast a reaction happens - its rate
- Can only be determined experimentally!!!
- See how fast reactants disappear or how fast products appear
- So... reaction rate units look like concentration or amount per time



0.03
0.02
0.01
0.00
Concentration (M)
0
100
200
300
400
500
600
700
800
Time (s)
NO_2
$\Delta[NO_2] = 0.0022$ M
$\Delta t = 100$ s
$\Delta[NO_2] = 0.0037$ M
$\Delta t = 100$ s
$\Delta[N_2O_5] = -0.0019$ M
$\Delta t = 100$ s
O_2
N_2O_5
$\Delta[O_2] = 0.0009$ M
$\Delta t = 100$ s

The Rate Law Using Initial Concentrations

- The rate law here depends on the initial concentrations of reactants, and...
- The Arrhenius constant, k
- k (we call “rate constant”) takes into account
  - 1) activation energy
  - 2) temperature
- Not too tough...

- For $A + 2B + C \rightleftarrows D$
- The basic rate law is:
- $\text{Rate} = k[A]^x[B]^y[C]^z$
- What is x, y, and z???
- It's easy! but you HAVE to experiment!!!
- Let's see how changing each reactant changes the making of product...

Example

- How is it changing with A?

exp	[A]	[B]	[C]	formation of D
1	0.10	0.10	0.10	0.01
2	0.10	0.10	0.20	0.01
3	0.10	0.20	0.10	0.02
4	0.20	0.20	0.10	0.08

- Exp 3 and 4 show that when A is doubled and the others held constant, the rate goes from 0.02 M/sec to 0.08 M/sec
- We doubled A and the rate quadrupled
- So the power “x” is.... 2
- This is called “second order with respect to A”
- Rate = $k[A]^2[B]^y[C]^z$

Example

- How is it changing with B?

exp	[A]	[B]	[C]	formation of D
1	0.10	0.10	0.10	0.01
2	0.10	0.10	0.20	0.01
3	0.10	0.20	0.10	0.02
4	0.20	0.20	0.10	0.08

- From experiment 1 to 3

- B was doubled, so was rate!
  it’s a direct relationship!

- So the exponent y = 1, and it is “first order with respect to B,” and...

- Rate = $k[A]^2[B][C]^z$

Example

- How is it changing with C?

exp	[A]	[B]	[C]	formation of D
1	0.10	0.10	0.10	0.01
2	0.10	0.10	0.20	0.01
3	0.10	0.20	0.10	0.02
4	0.20	0.20	0.10	0.08

- From experiment 1 to 2, C was doubled and nothing happened to the rate!!!
- So Z = 0, and the rate is zero order with respect to C, so...
- Rate = $k[A]^2[B]$
- And now we can find the rate constant!!!

- Rate = $k[A]^2[B]$
- $k = \text{Rate}/[A]^2[B]$
- $k = (0.02\ \text{M/sec})/(0.10\ \text{M})^2(0.20\ \text{M})$
- $k = 10\ \text{M}^{-2}\text{sec}^{-1}$

$2A + B + 3C \rightarrow D + 2E$

Exp	[A] mol L^{-1}	[B] mol L^{-1}	[C] mol L^{-1}	Initial Rate [E] mol L^{-1} s^{-1}
1	0.10	0.20	0.10	5.0×10^{-4}
2	0.20	0.20	0.30	1.5×10^{-3}
3	0.30	0.20	0.10	5.0×10^{-4}
4	0.40	0.60	0.30	4.5×10^{-3}

1. What is the order of the reaction for each reactant?
2. What is the overall order of the reaction?
3. Determine the rate law?
4. Calculate the rate constant.
5. In experiment 1, what is the rate of disappearance of A, B, and C?

Homework

25, 26, 29

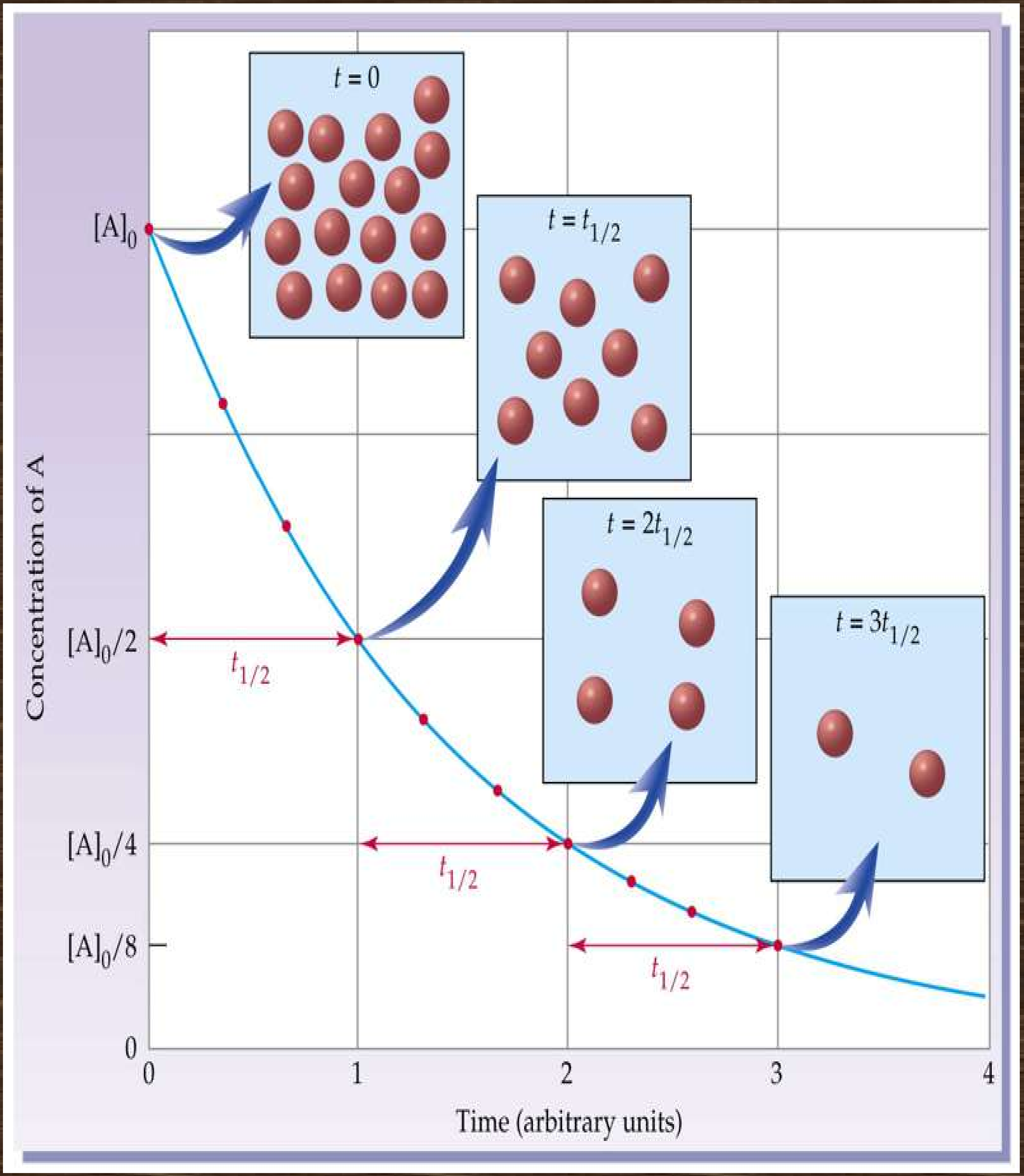
The Rate Law Using Concentration and Time

- rate laws can be expressed as graphs
- they show rate constant, [reactant], and time

first-order rate laws

1

- if it’s a first order reaction, then obviously the rate will slow as the reactant starts disappearing (make sense?)
- the graph of this looks like a decay curve
- in fact plotting [P] vs time can show us rate by looking at the slope at a given time.

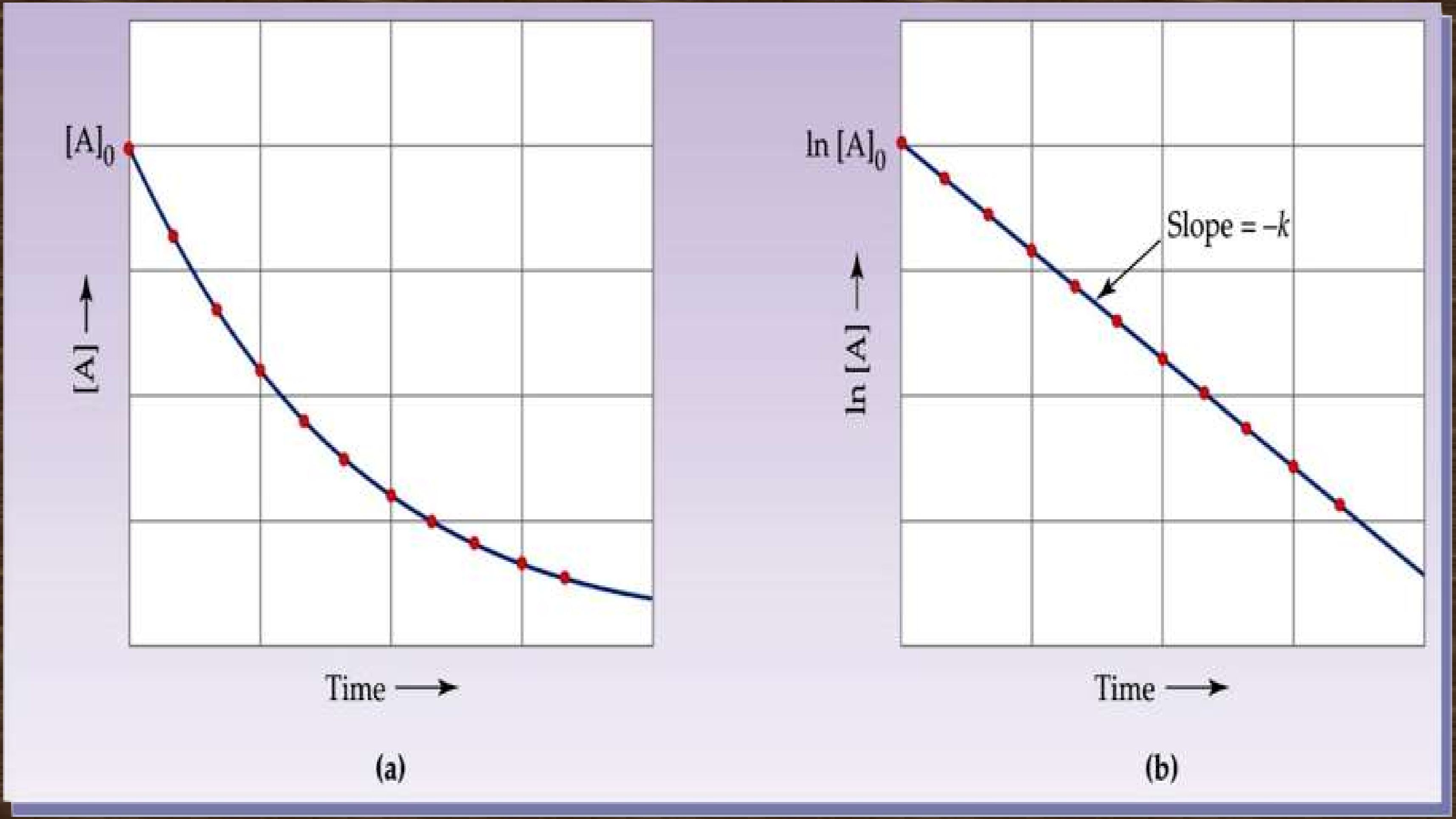

$t = 0$
$t = t_{1/2}$
$t = 2t_{1/2}$
$t = 3t_{1/2}$
$[A]_0$
$[A]_0/2$
$[A]_0/4$
$[A]_0/8$
0
$t_{1/2}$
$t_{1/2}$
$t_{1/2}$
Concentration of A
0
1
2
3
4
Time (arbitrary units)

first-order rate laws

- $\ln[A]_t - \ln[A]_o = -kt$
  - $[A]_t$ = concentration of A at time t
  - $[A]_0$ = original concentration of A
  - k = rate constant
  - t = time elapsed

- using ln we can get a linear graph, where...
- slope = -k
- y-intercept = $\ln[A]_0$

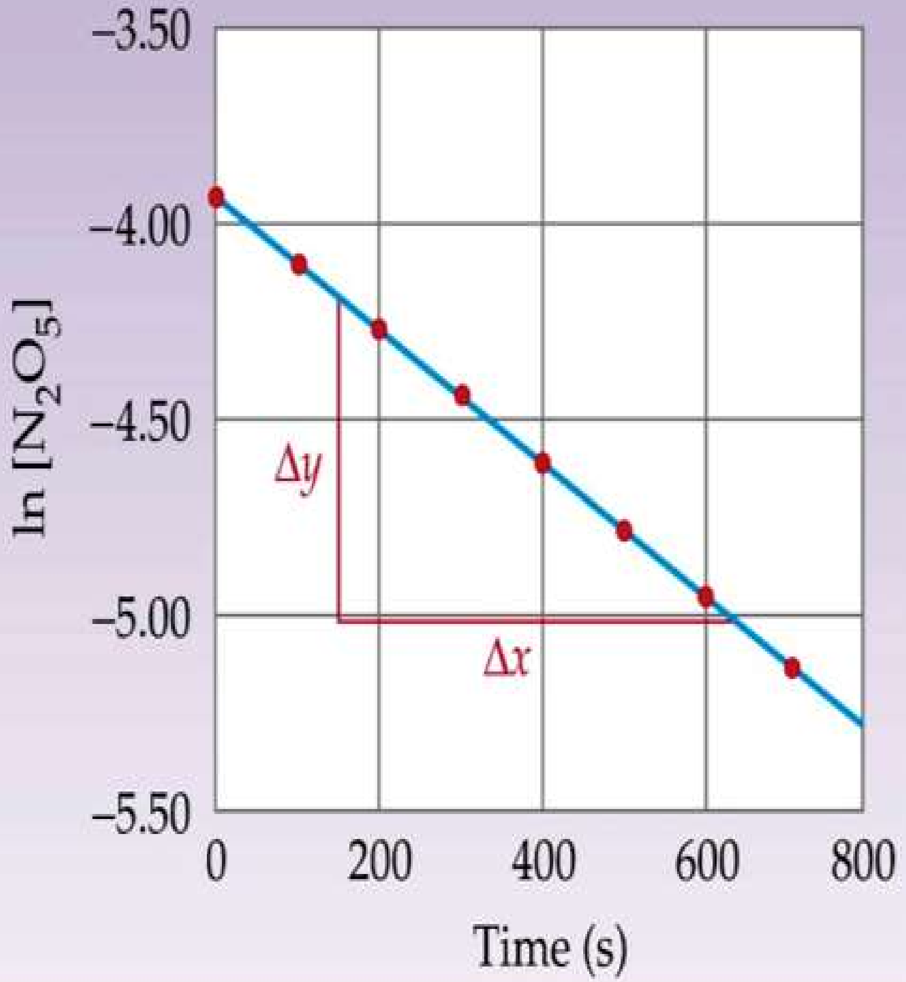
$$\underset{\underset{y}{\uparrow}}{\ln\,[\mathrm{A}]_t} = \underset{\underset{m}{\uparrow}}{(-k)}\underset{\underset{x}{\uparrow}}{t} + \underset{\underset{b}{\uparrow}}{\ln\,[\mathrm{A}]_0}$$



(a) (b)

- see how it straightens out when you natural log it?

Time (s)	$[N_2O_5]$	$\ln [N_2O_5]$
0	0.0200	−3.912
100	0.0169	−4.080
200	0.0142	−4.255
300	0.0120	−4.423
400	0.0101	−4.595
500	0.0086	−4.756
600	0.0072	−4.934
700	0.0061	−5.099



half-life

- one can find half life based on this, too...
- $t_{1/2}$ = ln2/k = 0.693/k
- if we can find k for this reaction we can find half-life
- $\ln[A]_t - \ln[A]_o = -kt$
- $\ln(1.6) - \ln(2.0) = -k(5\text{min})$
- $-0.22 = -k(5\text{min})$
- $k = 0.045\ \text{min}^{-1}$...

[A] (M)	time (min)
2.0	0
1.6	5
1.2	10

- $t_{1/2} = \ln 2/k = 0.693/k$
- $t_{1/2} = 0.693/0.045\ \text{min}^{-1}$
- = 15.4 minutes
- that is, every 15.4 minutes our concentration cuts in half
- and we can figure out concentration at any given time...

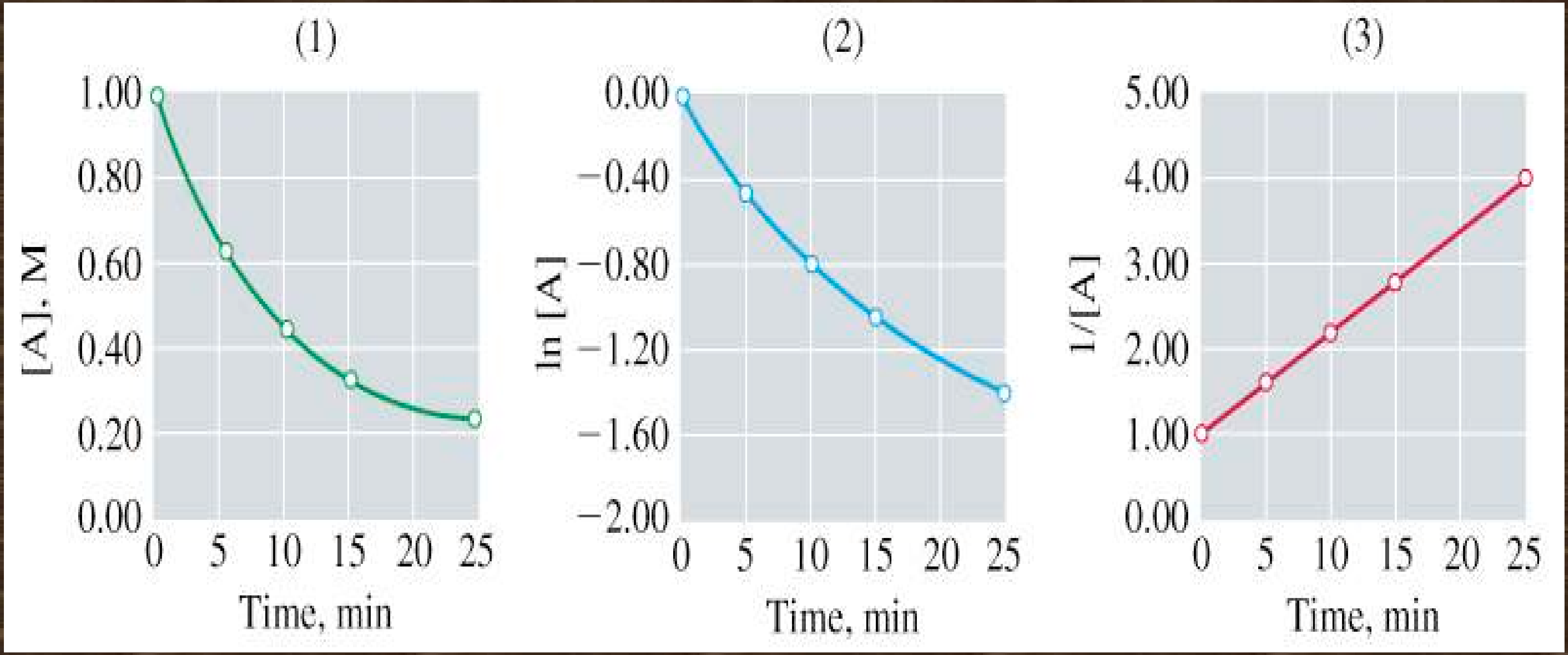
- what is [A] after 20 minutes have gone by?
- $\ln[A]_t - \ln[A]_o = -kt$
- $\ln[A]_t - \ln(2.0) = -(0.045 \text{ min}^{-1})(20 \text{ min})$
- $\ln[A]_t = -0.21$
- $[A]_t = e^{-0.21} = .81M$

Second-Order Rate Laws

2

- Rate = $k[A]^2$
- “integrated” rate law here goes like this:
- $1/[A]_t - 1/[A]_0 = kt$
- here slope = k, y-incpt = $1/[A]_o$

$$\underset{\substack{\uparrow \\ y}}{\frac{1}{[\mathrm{A}]_t}} = \underset{\substack{\uparrow \\ m}}{k}\,\underset{\substack{\uparrow \\ x}}{t} + \underset{\substack{\uparrow \\ b}}{\frac{1}{[\mathrm{A}]_0}}$$



- see how plotting 1/[A] gives away that it is 2° order?
- warning! the "inverse" causes the curve to go up!

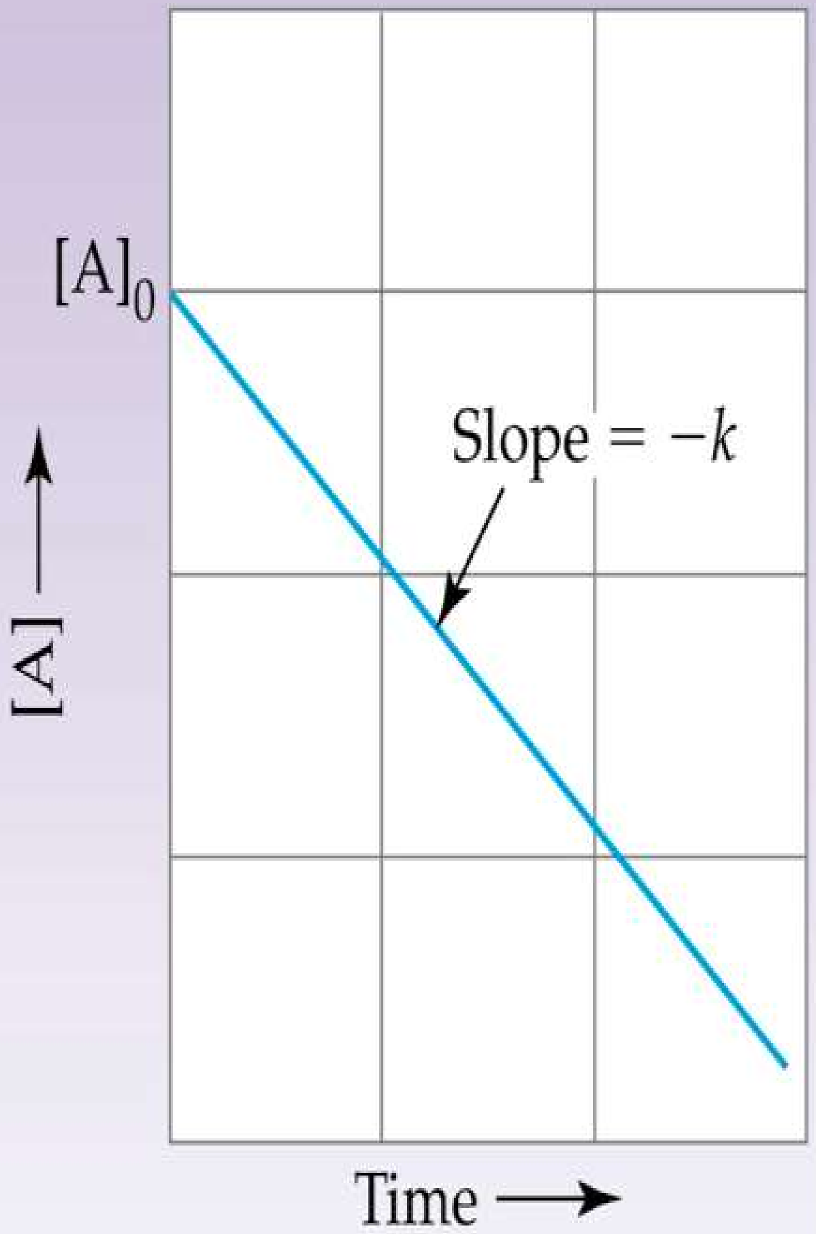
example

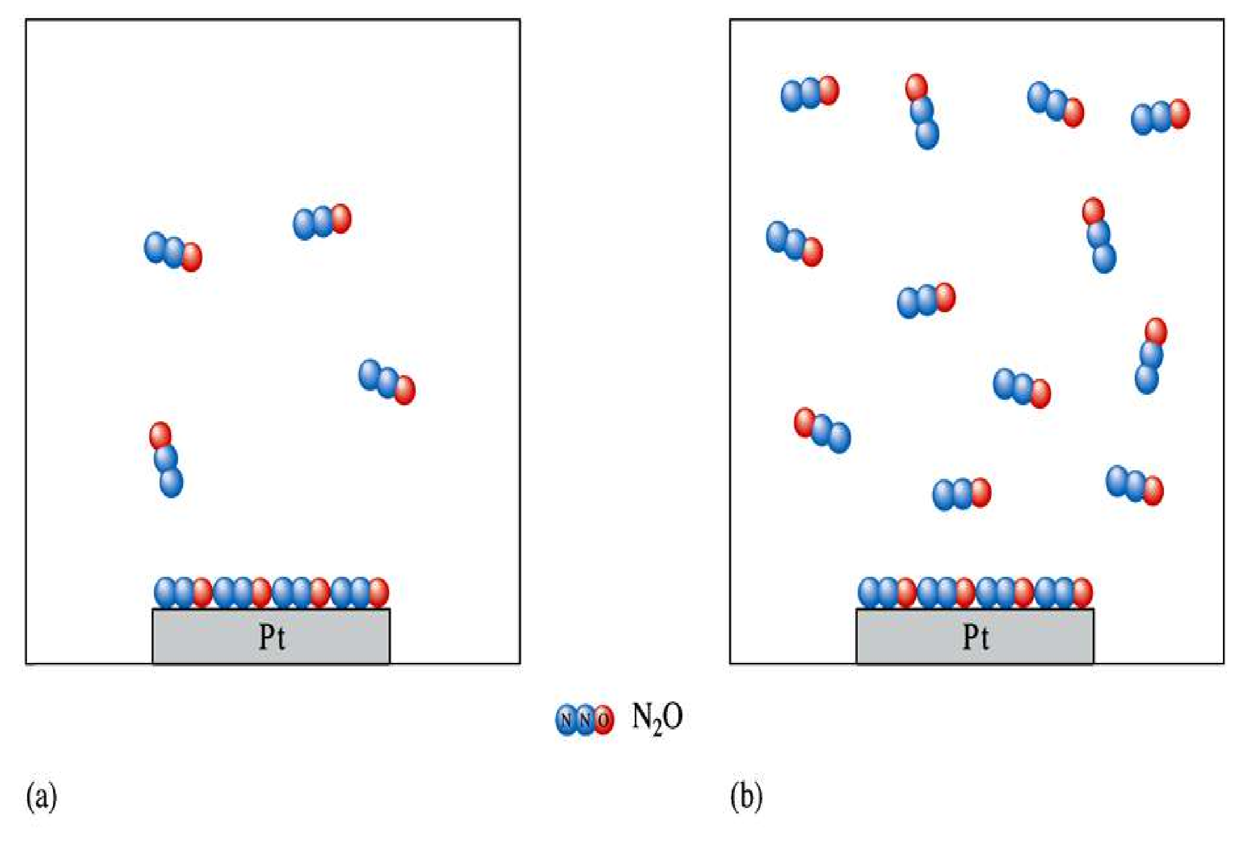
- 12.5 (578)

Zero-Order Rate Laws

0

- doesn’t depend on concentration of reactants.
- the rate is always the same (at given T)
- rate = k
- straight line with slope = -k


$[A]_0$
Slope = $-k$
$[A] \longrightarrow$
Time $\longrightarrow$



- usually happens with catalysts or enzymes
- add forever and the rate depends on how fast the enzyme can work

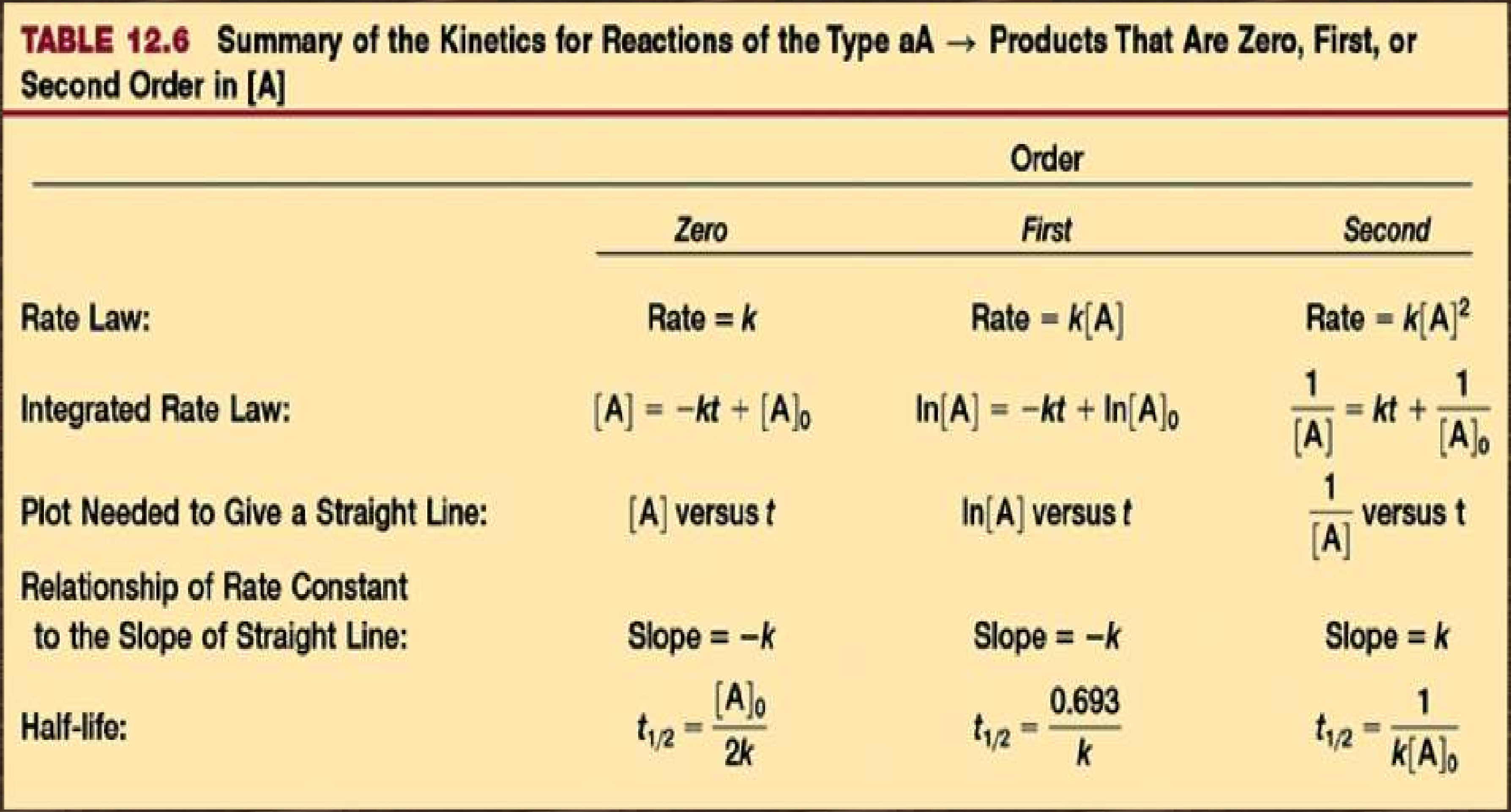


TABLE 12.6 Summary of the Kinetics for Reactions of the Type aA → Products That Are Zero, First, or Second Order in [A]

	Order		
	Zero	*First*	*Second*
Rate Law:	Rate = k	Rate = $k[\mathrm{A}]$	Rate = $k[\mathrm{A}]^2$
Integrated Rate Law:	$[\mathrm{A}] = -kt + [\mathrm{A}]_0$	$\ln[\mathrm{A}] = -kt + \ln[\mathrm{A}]_0$	$\frac{1}{[\mathrm{A}]} = kt + \frac{1}{[\mathrm{A}]_0}$
Plot Needed to Give a Straight Line:	$[\mathrm{A}]$ versus t	$\ln[\mathrm{A}]$ versus t	$\frac{1}{[\mathrm{A}]}$ versus t
Relationship of Rate Constant to the Slope of Straight Line:	Slope = $-k$	Slope = $-k$	Slope = k
Half-life:	$t_{1/2} = \frac{[\mathrm{A}]_0}{2k}$	$t_{1/2} = \frac{0.693}{k}$	$t_{1/2} = \frac{1}{k[\mathrm{A}]_0}$

eocs

- 12.31 graph it!
- make sure you express rate law (e.g. rate = k[A], the “integrated” rate law (e.g. $\ln[A]_t = -kt + [A]_0$ and k, and how much is left after 4000 seconds.
- you can do it!

Reaction Mechanism

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

- The sum of the elementary steps must give the overall balanced equation for the reaction
- The mechanism must agree with the experimentally determined rate law

Rate-Determining Step

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

The *experimental rate law* must agree with the *rate-determining step*

Identifying the Rate-Determining Step

For the reaction:

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

The experimental rate law is:

Rate = $k[NO]^2[H_2]$

Which step in the reaction mechanism is the rate-determining (slowest) step?

Step #1 $\boxed{H_2(g) + 2NO(g) \rightarrow N_2O(g) + H_2O(g)}$

Step #2 $N_2O(g) + H_2(g) \rightarrow N_2(g) + H_2O(g)$

Step #1 agrees with the experimental rate law

Identifying Intermediates

For the reaction:

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

Which species in the reaction mechanism are intermediates (do not show up in the final, balanced equation?)

Step #1 $H_2(g) + 2NO(g) \rightarrow \boxed{N_2O(g)} + H_2O(g)$

Step #2 $\boxed{N_2O(g)} + H_2(g) \rightarrow N_2(g) + H_2O(g)$

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

∴ $N_2O(g)$ is an intermediate

Example

Step 1: $HBr + O_2 \rightarrow HOOBr$ 1 year

Step 2: $HOOBr + HBr \rightarrow 2\ HOBr$ 0.1 s

Step 3: $HOBr + HBr \rightarrow H_2O + Br_2$ 0.1 min

Step 4: $HOBr + HBr \rightarrow H_2O + Br_2$ 0.1 min

1. Write the net equation.
2. What is the rate determining step?
3. Write the overall rate law.

Homework

\# 49-52

Collision Model

Molecules must collide to react. However, only a small fraction of collisions produces a reaction. Why?

Collision Model

- Collisions must have sufficient energy to produce the reaction (must equal or exceed the activation energy).
- Colliding particles must be correctly oriented to one another in order to produce a reaction.

Factors Affecting Rate

Increasing temperature always increases the rate of a reaction.

- Particles collide more frequently
- Particles collide more energetically

Increasing surface area increases the rate of a reaction

Increasing Concentration USUALLY increases the rate of a reaction

Presence of Catalysts which lower the activation energy by providing alternate pathways

Catalysis

- **Catalyst**: A substance that speeds up a reaction without being consumed

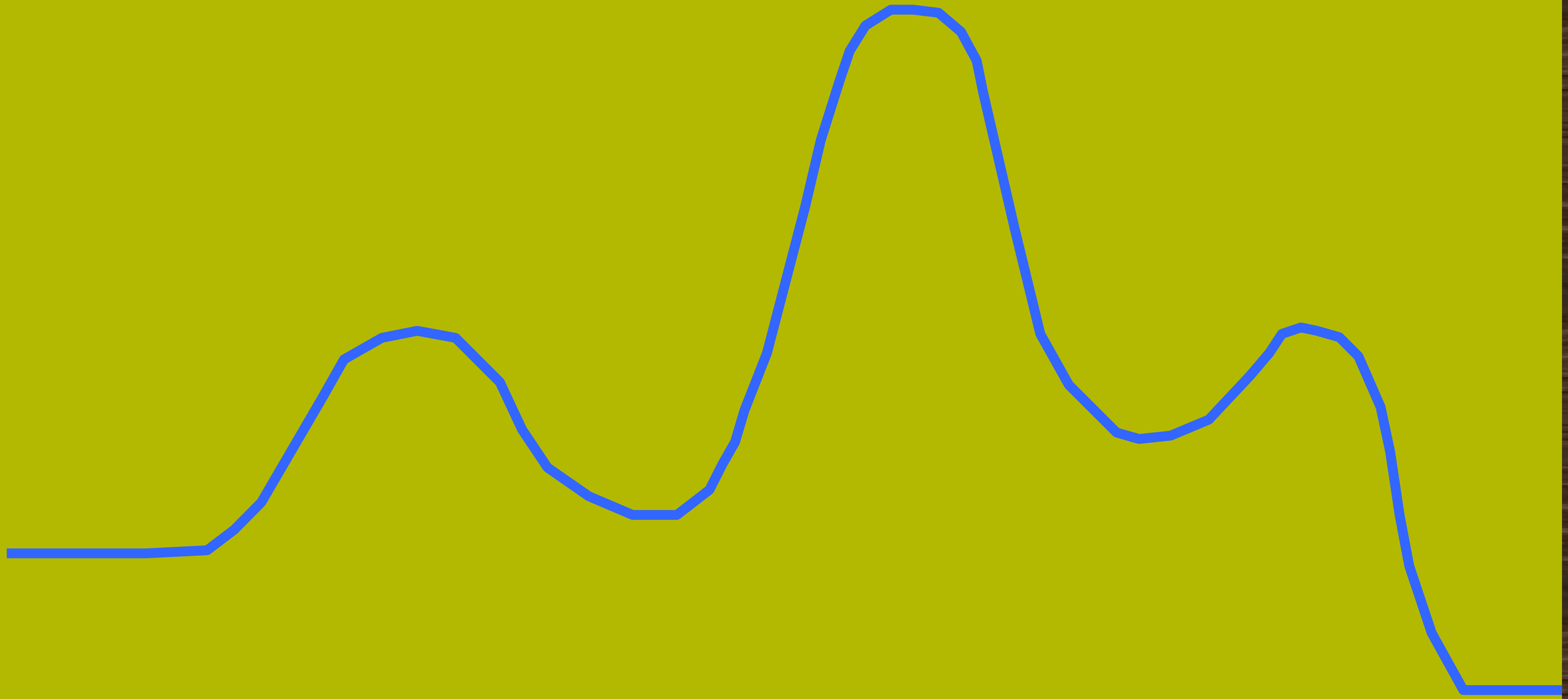
- **Enzyme**: A large molecule (usually a protein) that catalyzes biological reactions.

- **Homogeneous catalyst**: Present in the same phase as the reacting molecules.

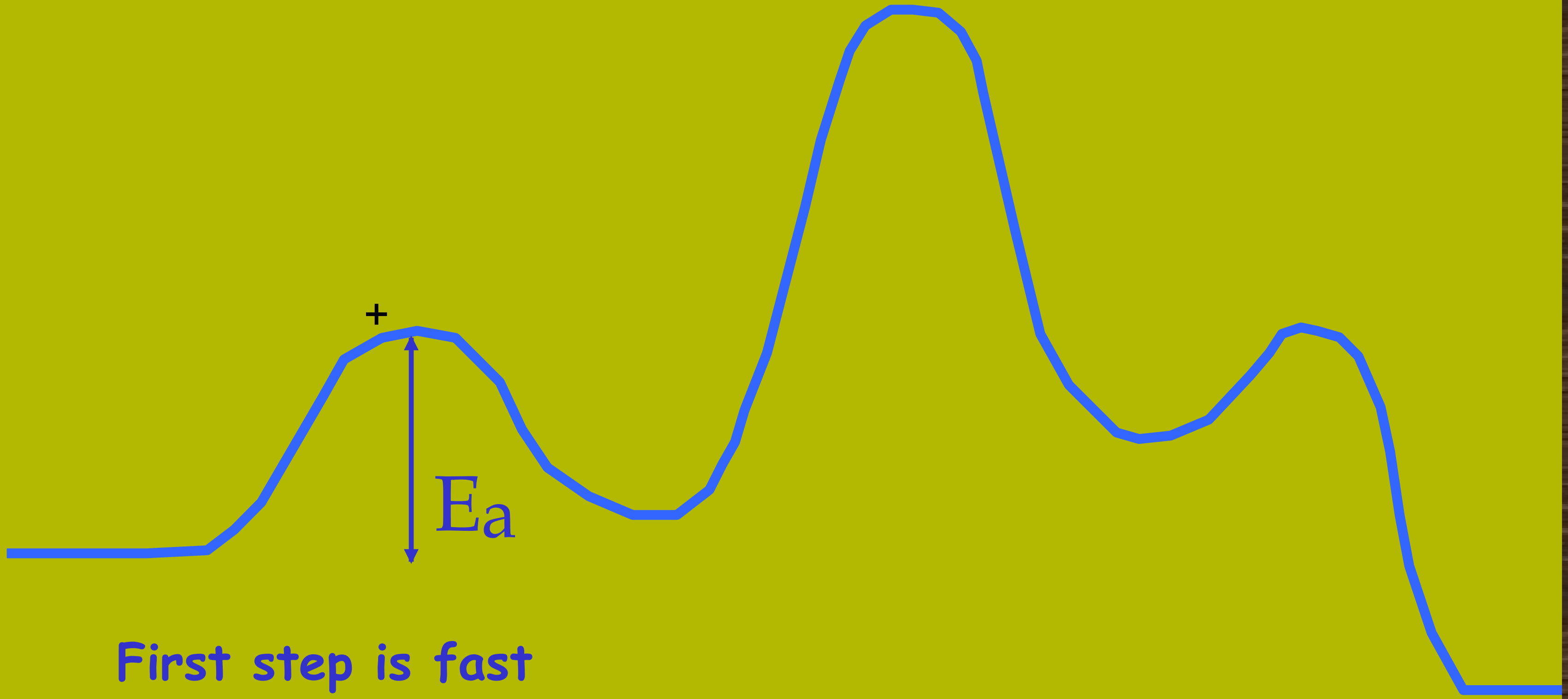
- **Heterogeneous catalyst**: Present in a different phase than the reacting molecules.

Arrhenius Equation

- $\ln(k) = -(E_a/R)(1/T) + \ln A$
- **Another line !!!!**
- **Ea = Activation Energy**
- **R = Universal Gas Constant**
- **T = Temperature in Kelvin**
- **A = Frequency Factor**

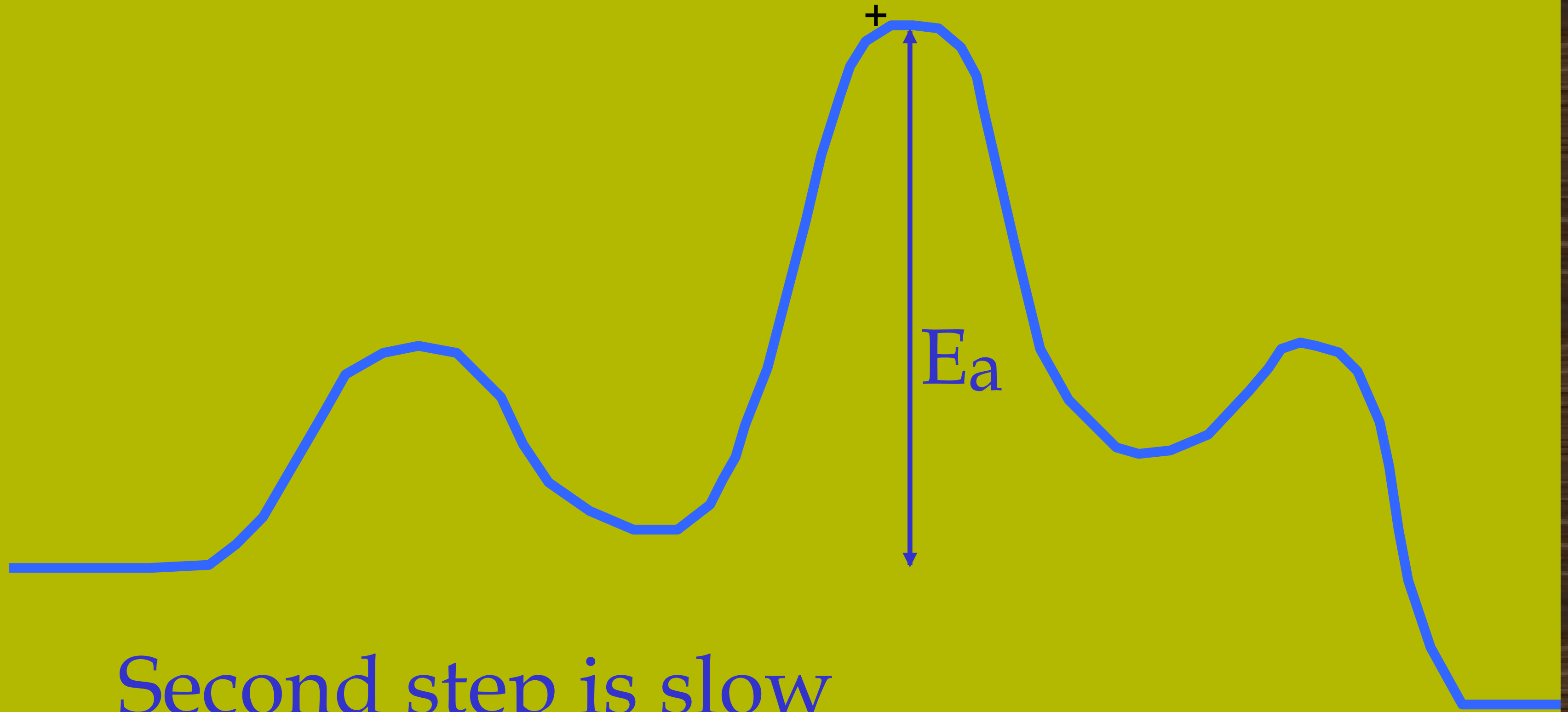


- This reaction takes place in three steps



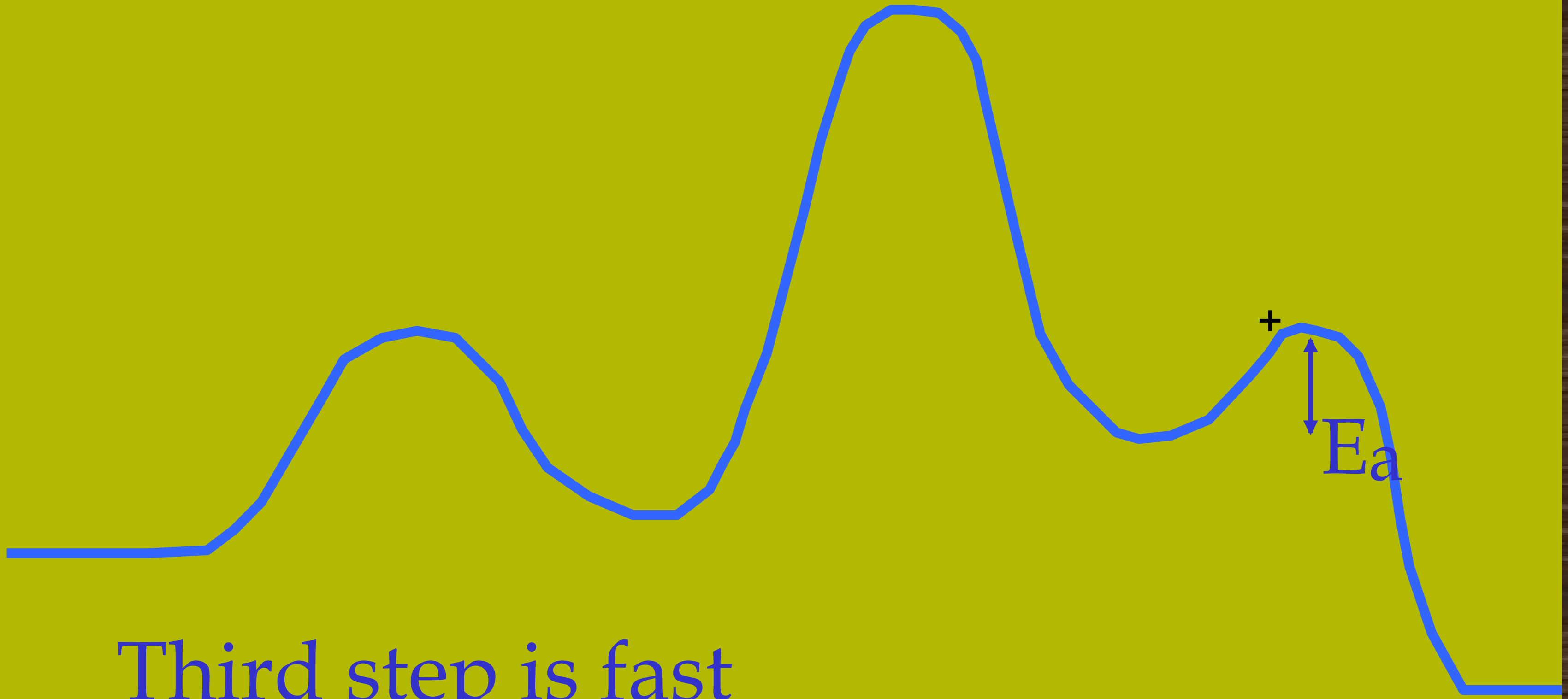
First step is fast

Low activation energy



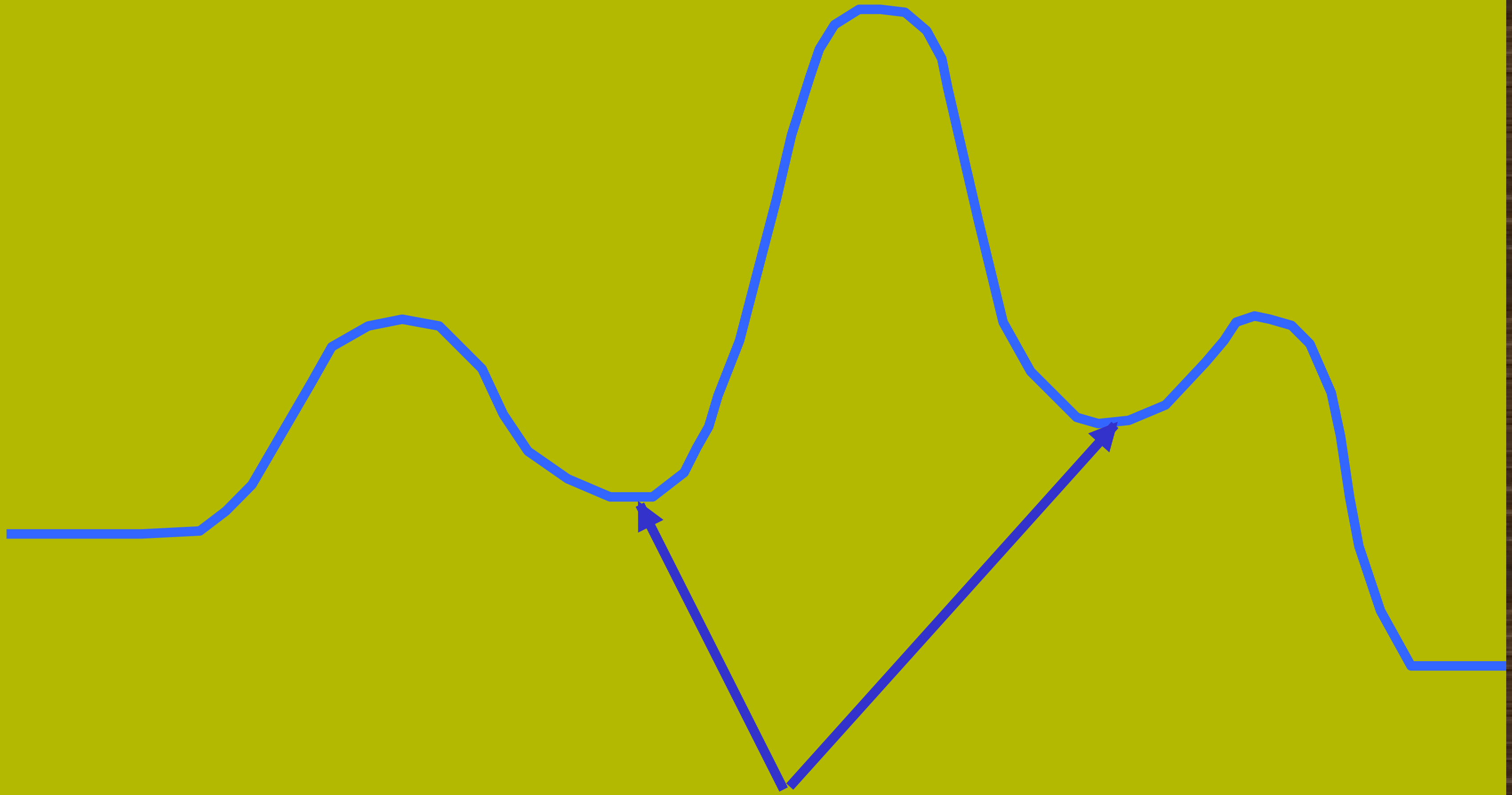
Second step is slow

High activation energy

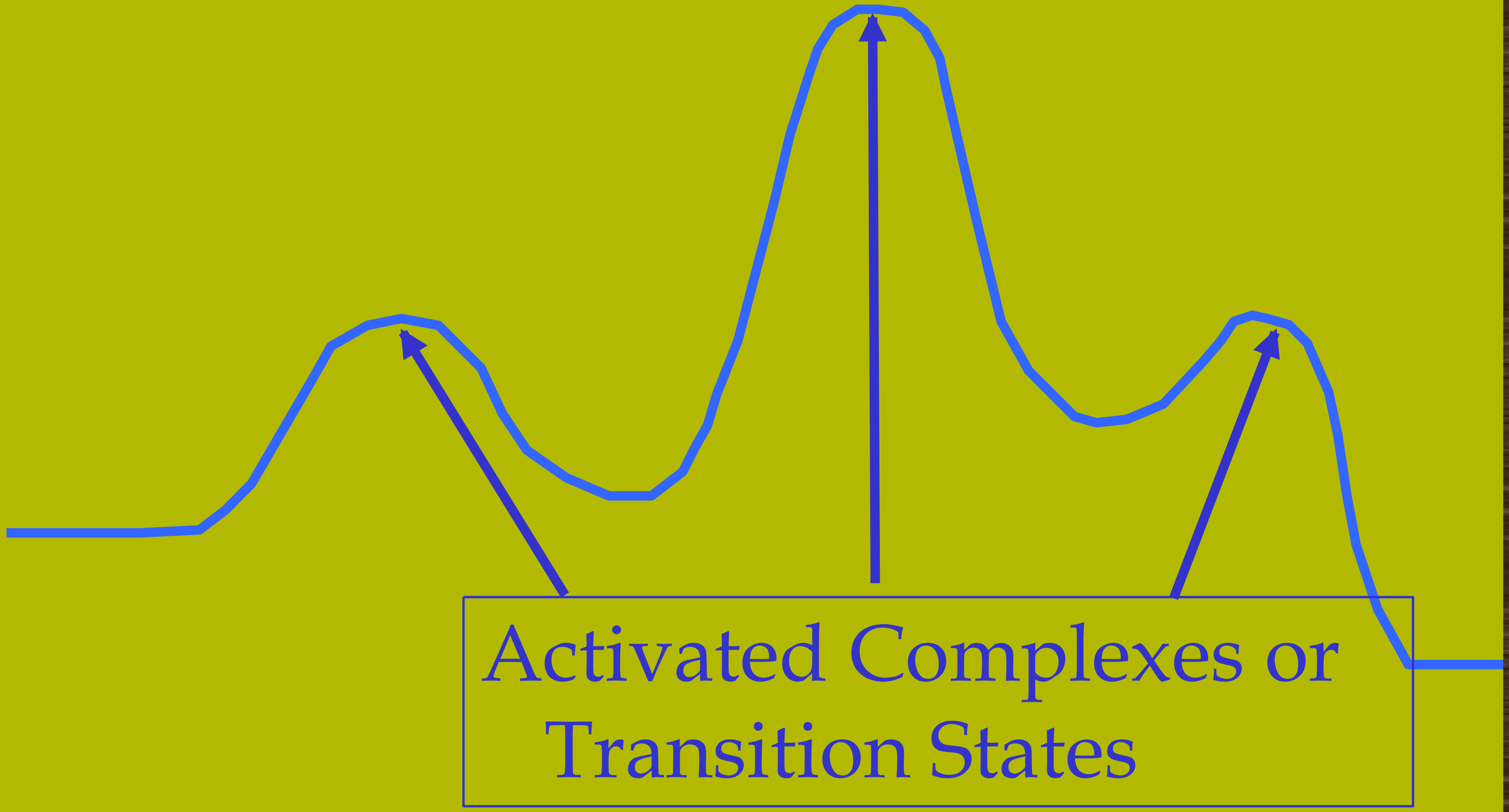


Third step is fast

Low activation energy



Intermediates are present



Activated Complexes or
Transition States

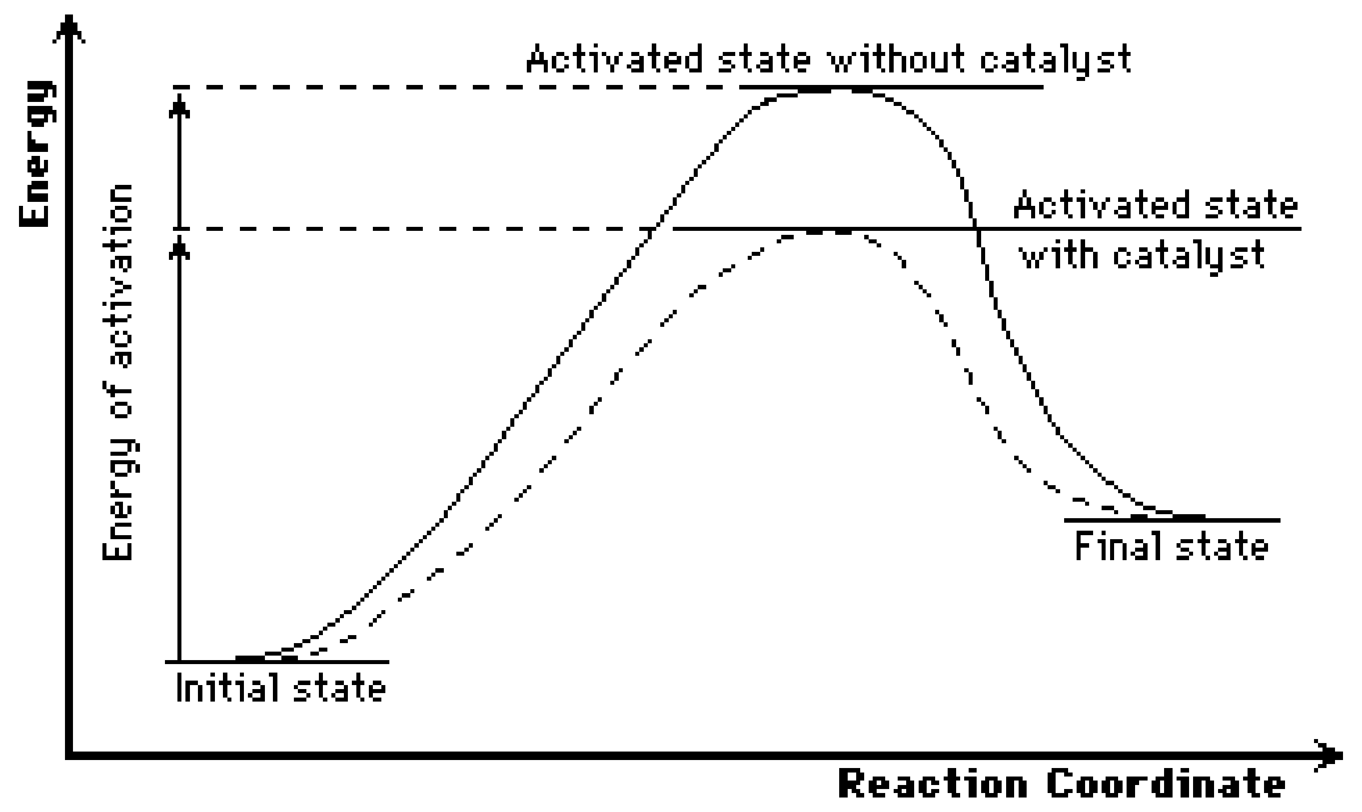
Catalysts

- Speed up a reaction without being used up in the reaction.
- Enzymes are biological catalysts.
- Homogenous Catalysts are in the same phase as the reactants.
- Heterogeneous Catalysts are in a different phase as the reactants.

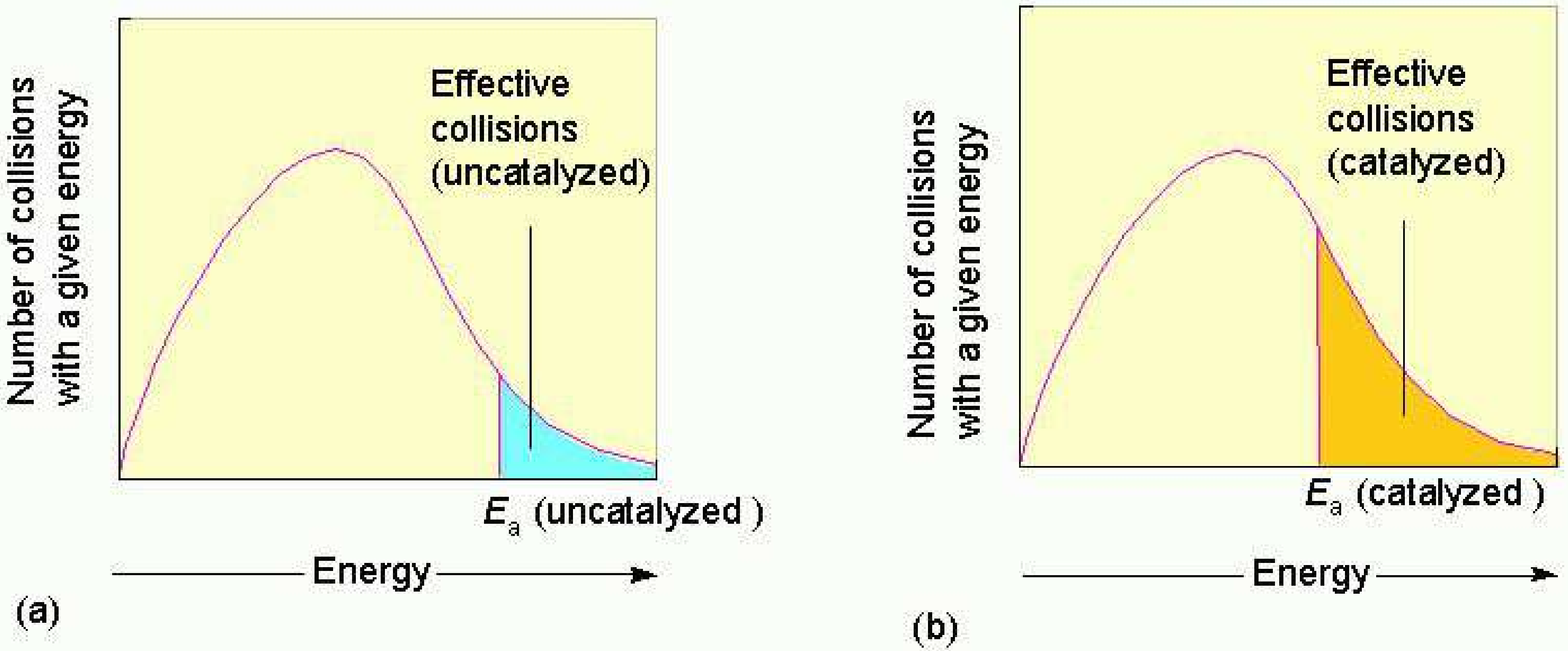
How Catalysts Work

- Catalysts allow reactions to proceed by a different mechanism - a new pathway.
- New pathway has a lower activation energy.
- More molecules will have this activation energy.
- Do not change ΔE

Lowering of Activation Energy by a Catalyst



Catalysts Increase the Number of Effective Collisions



Homework

- #53-56