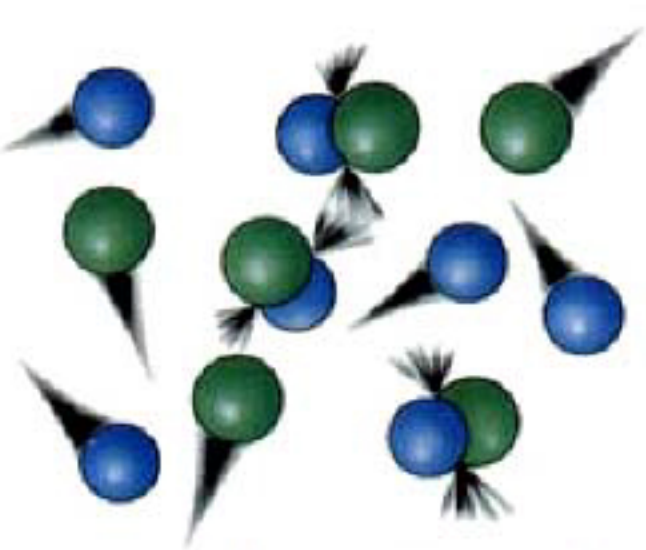
Module 8

Chemical Kinetics

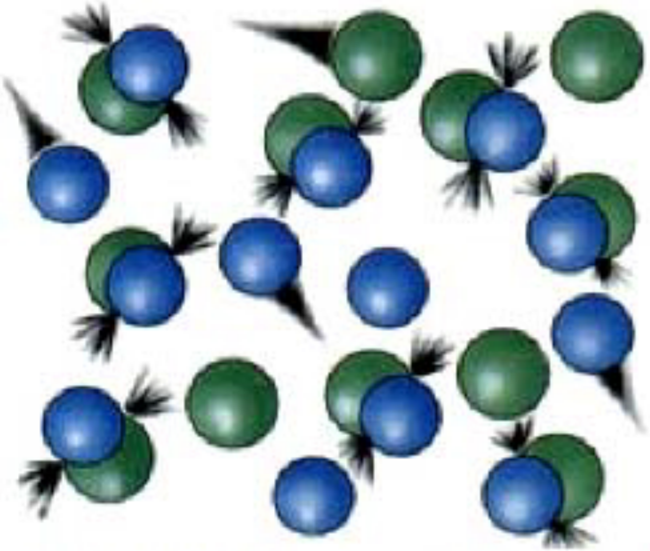
Session Slides with Notes

Chemical Kinetics

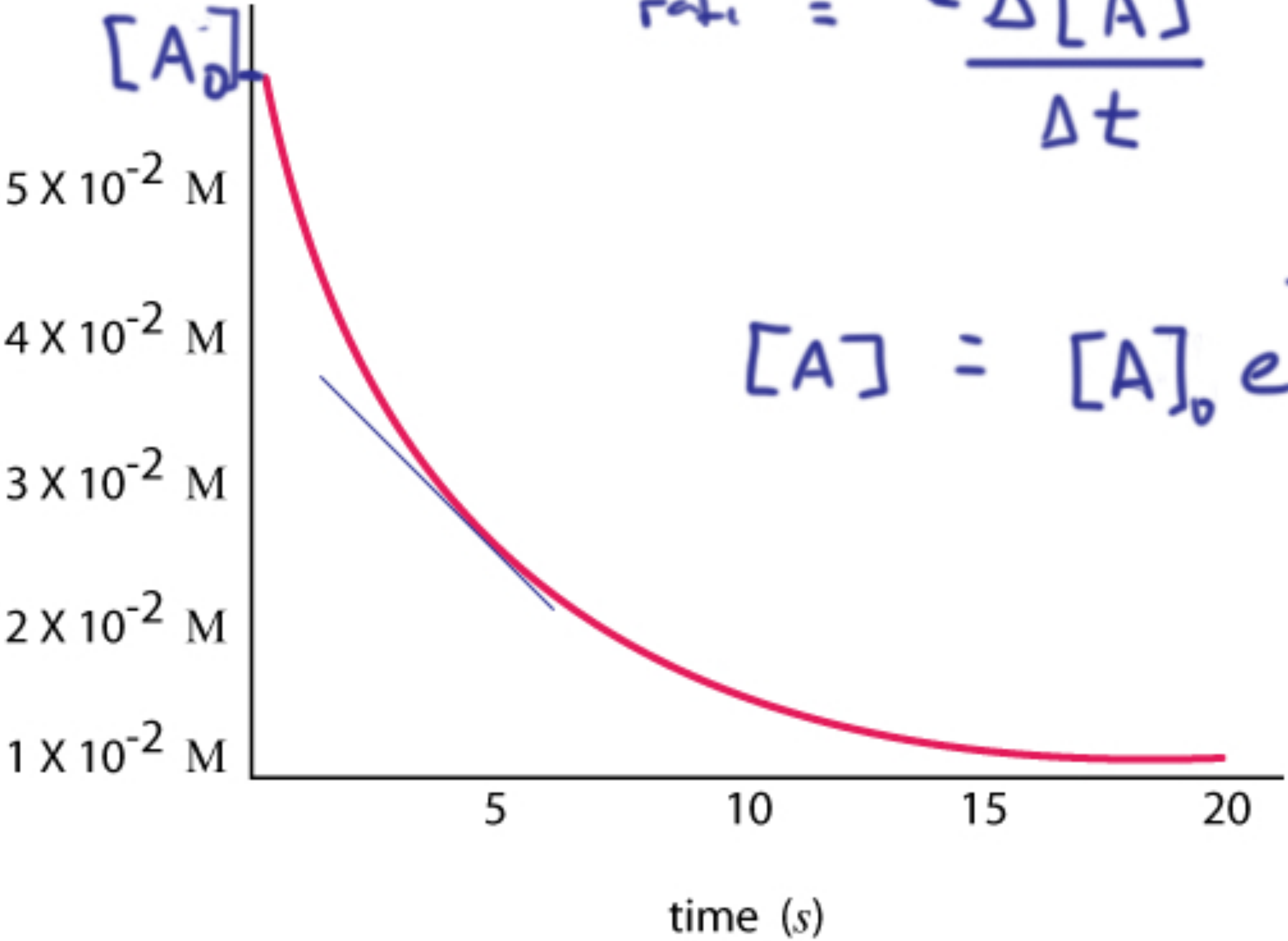
Collision Theory



Low concentration = Few collisions



High concentration = More collisions



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

$$[A] = [A]_0 e^{-kt}$$

$$n_a\,A \quad + \quad n_b\,B \quad \longrightarrow \quad n_p\,P \quad + \quad n_q\,Q$$

$$Rate = \frac{\textit{concentration change}}{\textit{time interval}}$$

normalize the rate

$$v = \frac{-1}{n_a}\frac{\Delta[A]}{\Delta t} = \frac{-1}{n_b}\frac{\Delta[B]}{\Delta t} = \frac{1}{n_p}\frac{\Delta[P]}{\Delta t} = \frac{1}{n_q}\frac{\Delta[Q]}{\Delta t}$$

$$v = \frac{-1}{n_a}\frac{\Delta[A]}{\Delta t} = \frac{-1}{n_b}\frac{\Delta[B]}{\Delta t} = \frac{1}{n_p}\frac{\Delta[P]}{\Delta t} = \frac{1}{n_q}\frac{\Delta[Q]}{\Delta t}$$

$$v = k\ f([A], [B], \ldots)$$

only from experiment
(or if you know the
actual mechanism)

$$v = k\,[A]^a[B]^b$$

a rate
expression

rate
constant

$$2\,HI\,(g) \longrightarrow H_2\,(g) + I_2\,(g)$$

$$\frac{\Delta[I_2]}{\Delta t} = k\,[HI]^2 \longleftarrow$$

2nd order
rate expression
(sum of the
exponents)

Choose the correct rate expression for the reaction below

$$2\text{MgO} + \text{Si} \longrightarrow 2\text{Mg} + \text{SiO}_2$$

A. $\text{rate} = k\,[\text{MgO}]\,[\text{Si}]$
B. $\text{rate} = k\,[\text{MgO}]^2\,[\text{Si}]$
C. $\text{rate} = 2k\,[\text{MgO}][\text{Si}]$
[✓ **D.**] impossible to detemine from given information

If the reaction rate is quadrupled by doubling the concentration of a reactant, the order of the reaction with respect to that reactant is

A. 1
[✓ **B.**] 2
C. 4
D. cannot be determined except by experiment

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

3rd order reaction that is 2nd order with respect to A.

$CH_3CH_2Br + NaOCH_3 \longrightarrow CH_3CH_2OCH_3 + NaBr$

SN2

Rate = *k* [CH_3CH_2Br] [$NaOCH_3$]

Total order: 2

$CH_3CHBrCH_3 + NaSH \longrightarrow CH_3CHSHCH_3 + NaBr$

SN1

Rate = *k* [$CH_3CHBrCH_3$]

Total order: 1

$$A + 3B + C \longrightarrow$$

practice!

rate expression?

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

Experiment	1	2	3	4
[A]	0.5 M	1.0 M	1.0 M	0.5 M
[B]	0.5 M	0.5 M	1.0 M	0.5 M
[C]	0.5 M	0.5 M	0.5 M	1.0 M
rate	0.2 M/s	1.6 M/s	1.6 M/s	0.4 M/s

$x = 3$

$y = 0$

$z = 1$

some number N here is N^3 what about $(2N)^3 = 8N^3$

rate = k [A]

1st Order

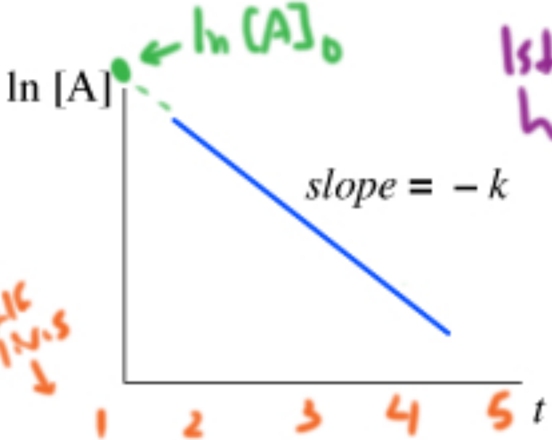
$$-\frac{\Delta[\mathrm{A}]}{\Delta t} = k\,[\mathrm{A}]$$

exponential decay →

$$[\mathrm{A}] = [\mathrm{A}]_o\, e^{(-k\,t)}$$

$$\ln[\mathrm{A}] = \ln[\mathrm{A}]_o - k\,t$$

$$y = b + mx$$



half lives ↓

1	2	3	4	5
$\frac{1}{2}$	$\frac{1}{4}$	$\frac{1}{8}$	$\frac{1}{16}$	$\frac{1}{32}$

1st order reactions have a half life

$$\text{half life} = \frac{\ln(2)}{k}$$

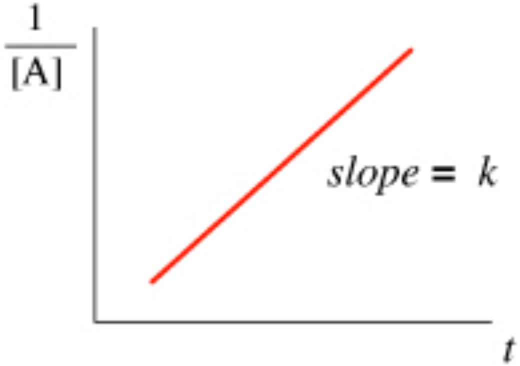
$$\ln(2) = .69$$

$$t_{\frac{1}{2}} = \frac{0.69}{k}$$

2nd Order

$$-\frac{\Delta[\mathrm{A}]}{\Delta t} = k\,[\mathrm{A}]^2$$

$$\frac{1}{[\mathrm{A}]} - \frac{1}{[\mathrm{A}]_o} = k\,t$$



$$\text{half life} = \frac{1}{k\,[\mathrm{A}]_o}$$

The decomposition of N_2O_5 in carbon tetrachloride can be represented

$$N_2O_5 \longrightarrow 4NO_2 + O_2$$

The reaction rate equation was found to be

rate = $(6.9 \times 10^{-4}\ \mathrm{M\ s^{-1}})\ [N_2O_5]$

If we begin with 30 g of N_2O_5 in solution, approximately how much time elapses before only 1 g remains?

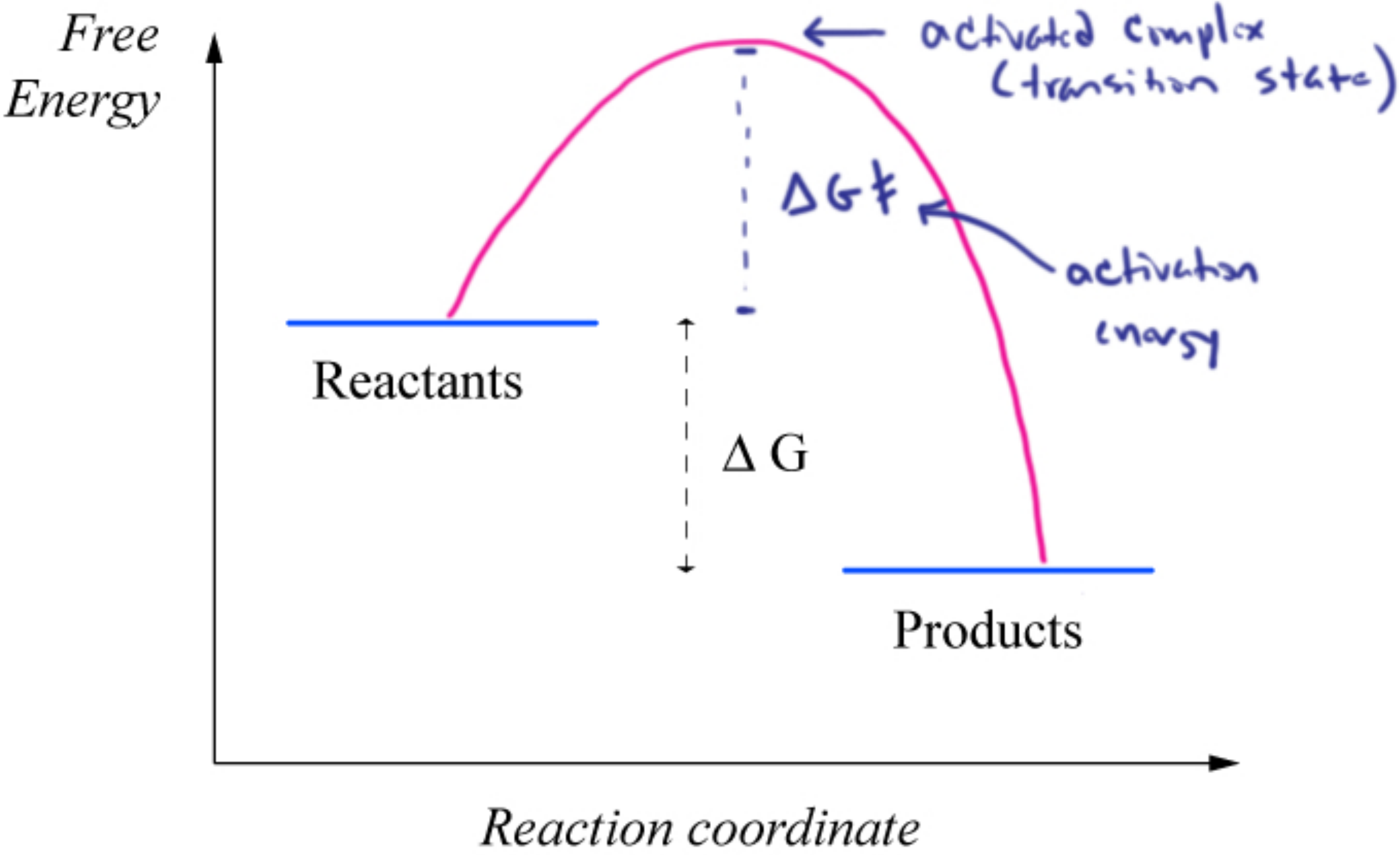
[✓ **A.**] 5.0×10^3 s
B. 4.0×10^4 s
C. 2.0×10^4 s
D. 1.4×10^4 s

$$t_{\frac{1}{2}} = \frac{0.69}{k}$$

$$t_{\frac{1}{2}} = \frac{6.9 \times 10^{-1}}{6.9 \times 10^{-4}}$$

$$= 1 \times 10^3$$

1	2	3	4	5
$\frac{1}{2}$	$\frac{1}{4}$	$\frac{1}{8}$	$\frac{1}{16}$	$\boxed{\frac{1}{32}}$

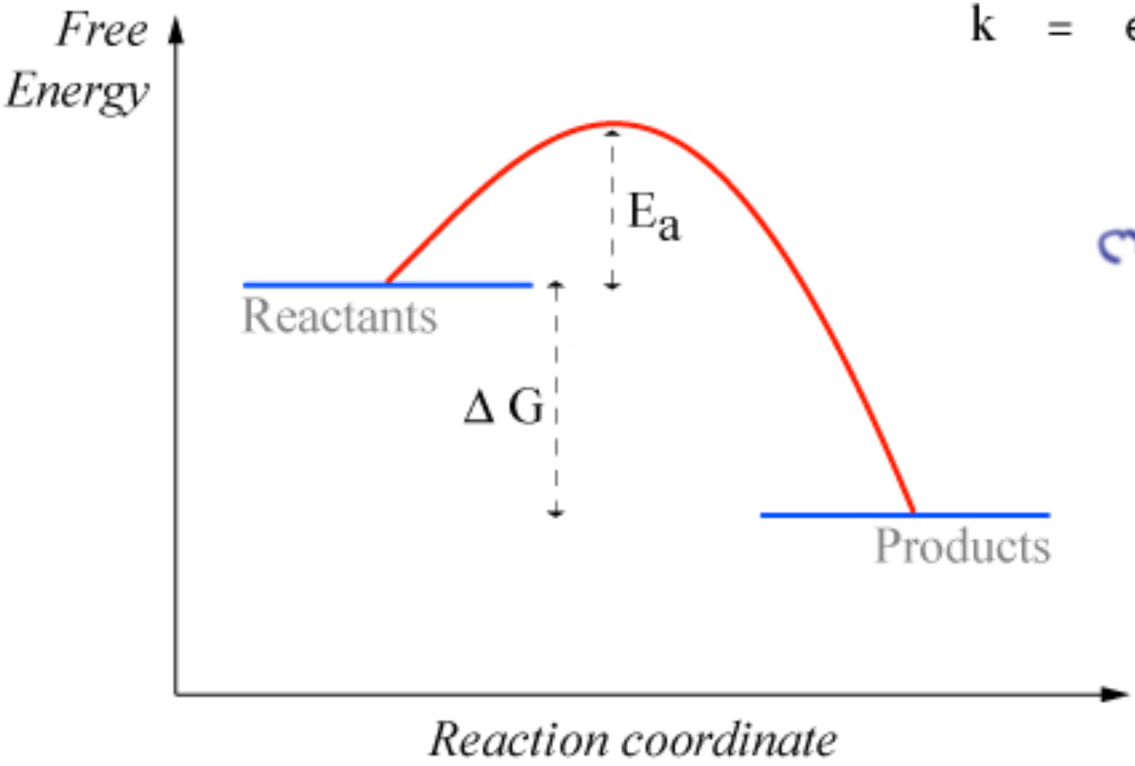

Free Energy
activated complex (transition state)
$\Delta G^\ddagger$
activation energy
Reactants
ΔG
Products
Reaction coordinate

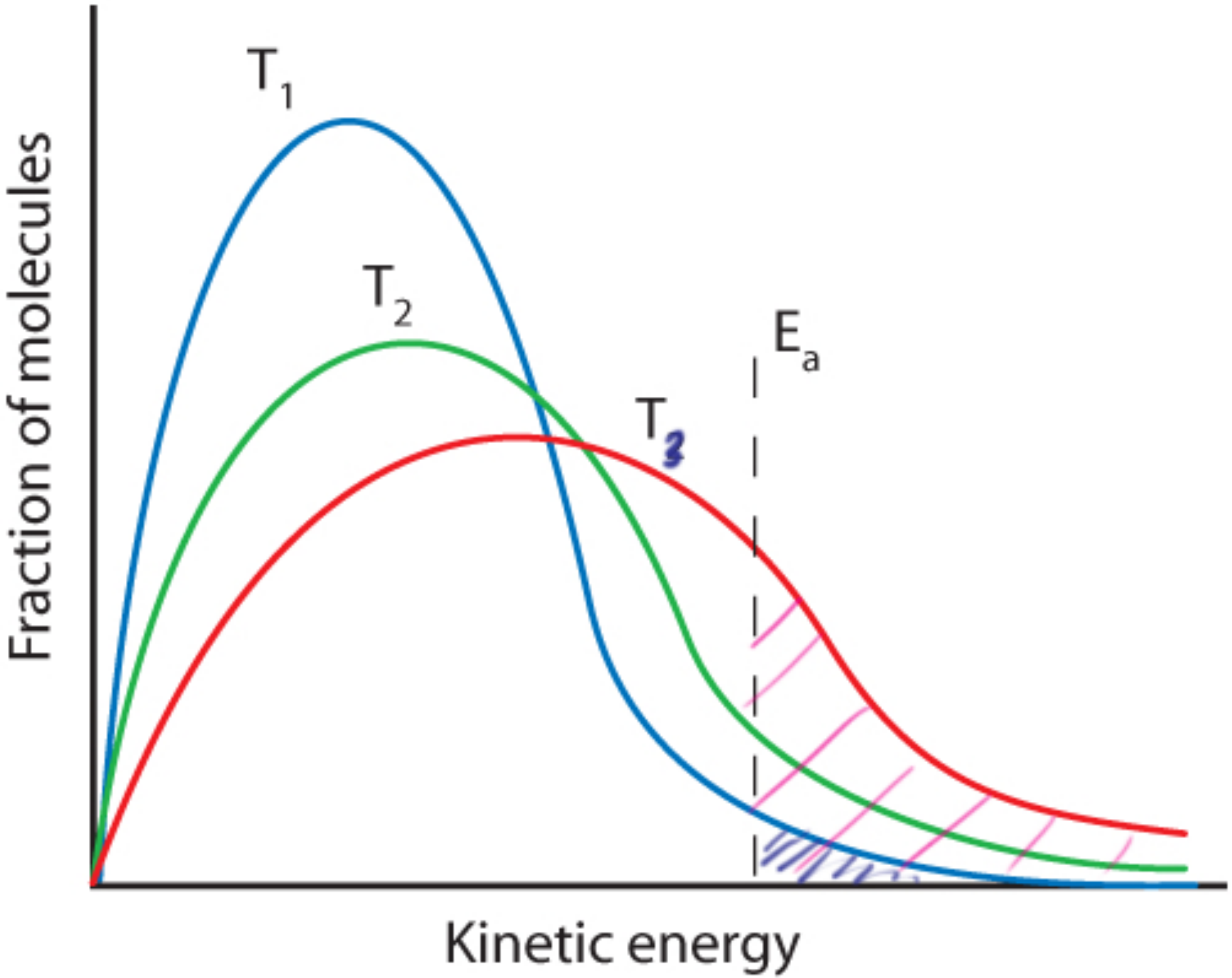
$$v = k\,[A]^a[B]^b$$

$$k = e^{\left(\frac{-E_a}{RT}\right)}$$

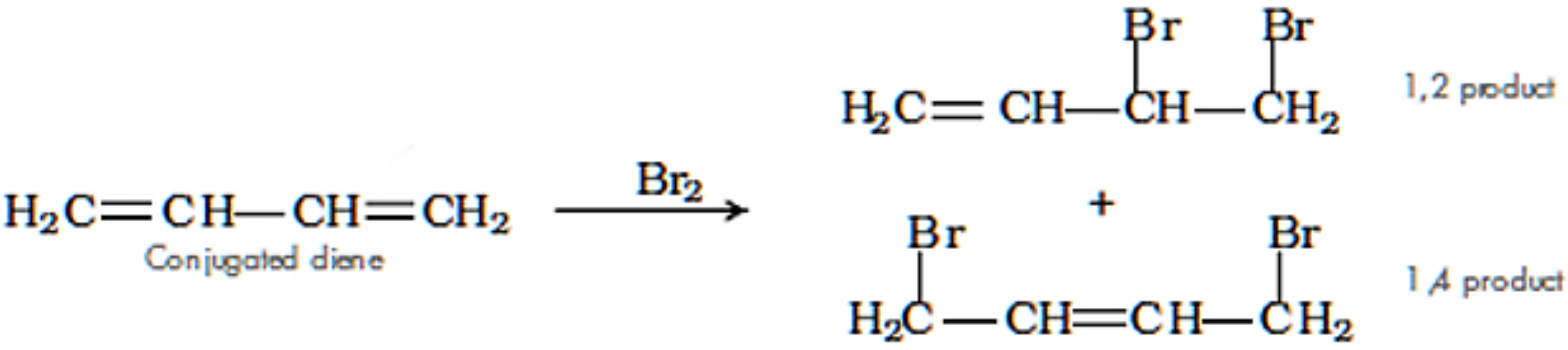
← Arrhenius equation

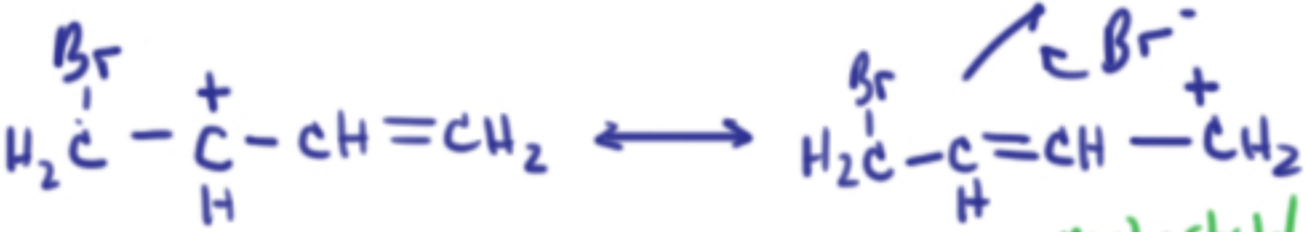
↑ rate increases exponentially with temperature




T$_1$
T$_2$
T$_3$
E$_a$
Fraction of molecules
Kinetic energy

Kinetic vs Thermodynamic Control

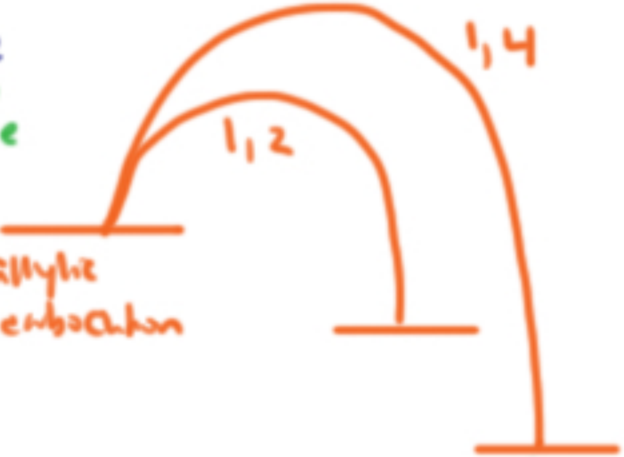


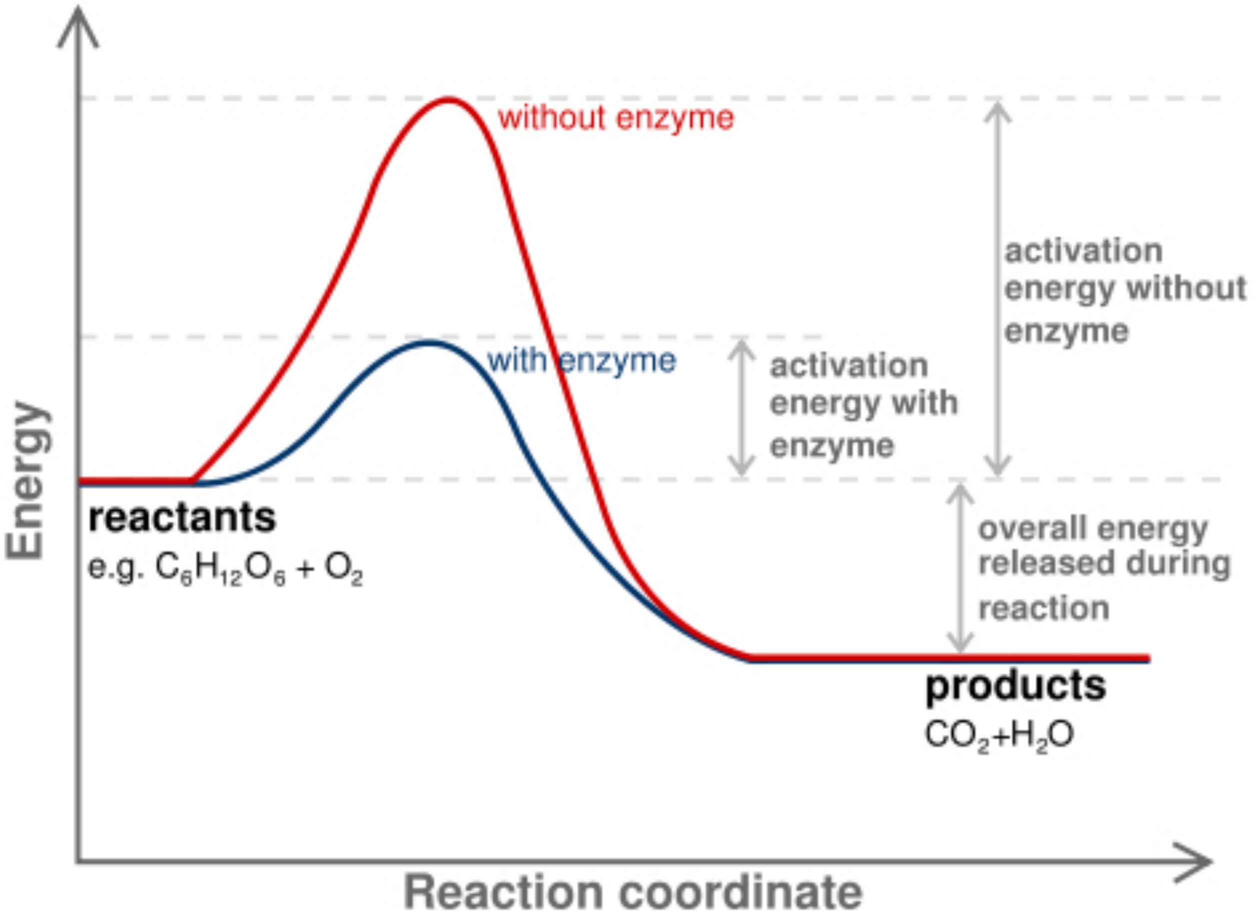


metastable

1,2 ⇒ kinetic product
favored at low T

1,4 ⇒ thermodynamic product
favored at high T





Catalysts

- lowers activation energy

In the presence of a catalyst

I. Effective collisions among reactant molecules become more likely to occur.
~~II.~~ Chemical equilibrium will shift toward the products.
III. The activation energy for the reaction is lowered.

A. I
[✓ **B.**] I and III
C. II and III
D. I, II, and III