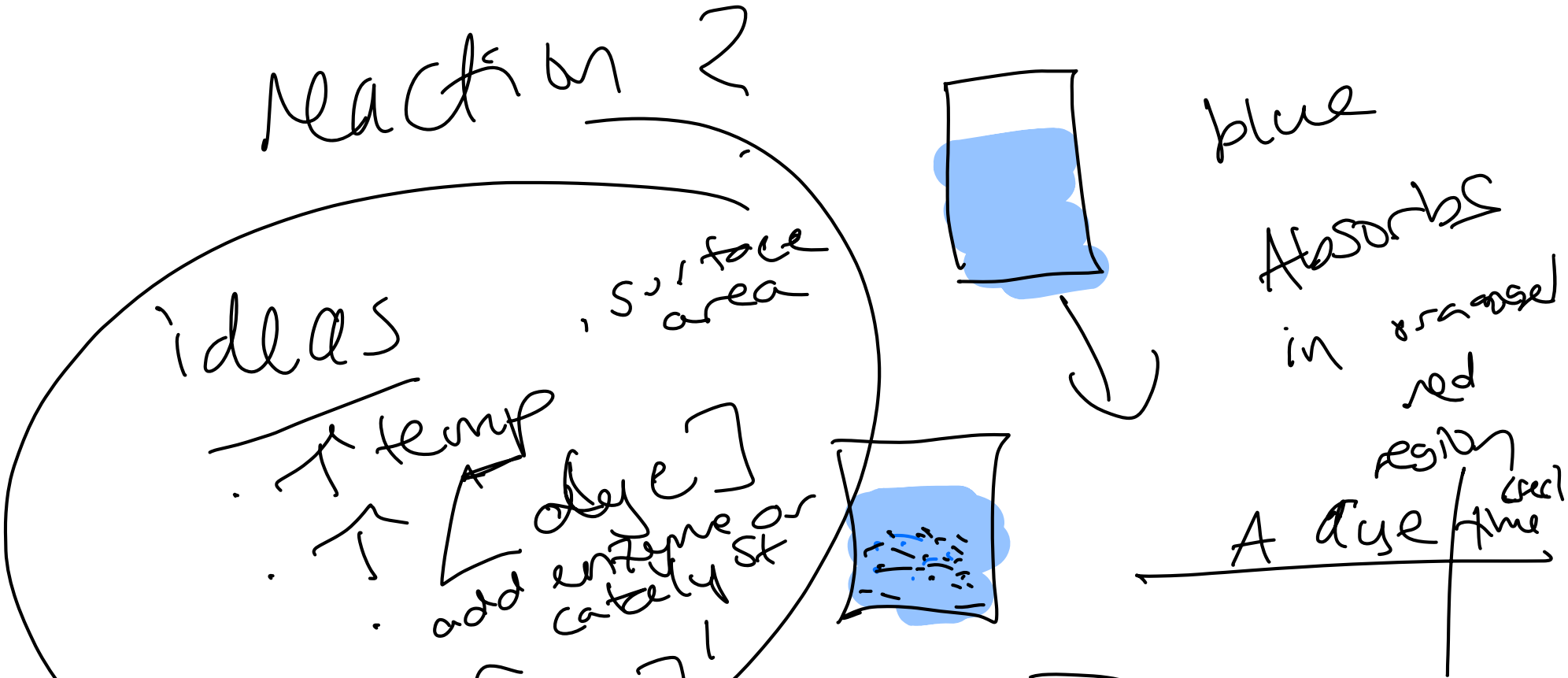
How can ↑ rate of a reaction?

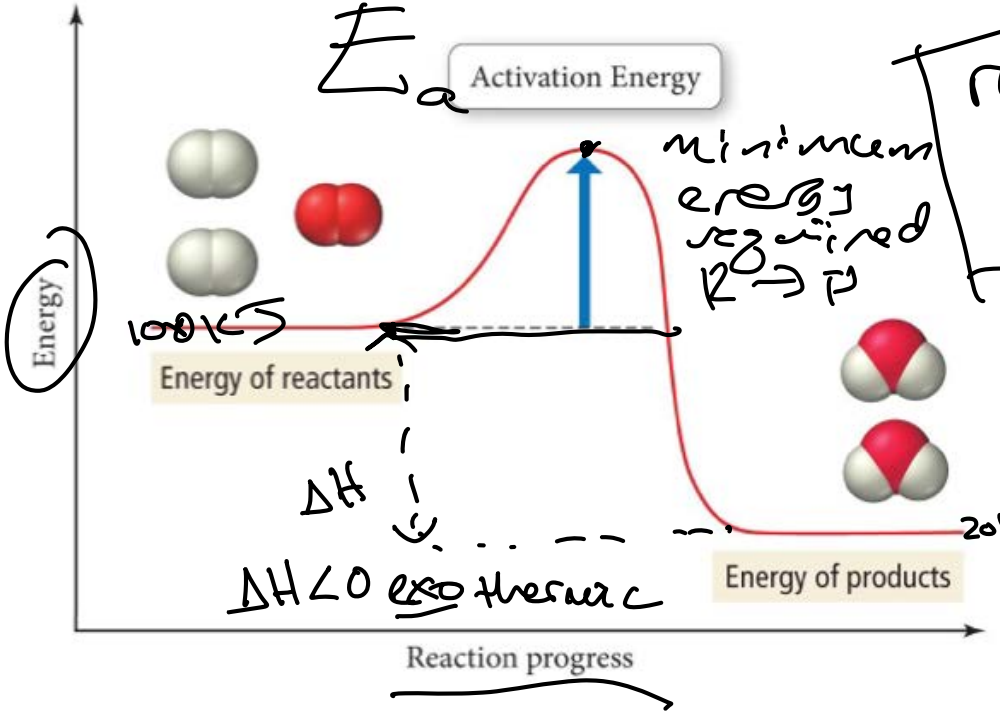


rate = k[dye]

Activation Energy

$$2\,H_2(g) + O_2(g) \rightleftharpoons 2\,H_2O(g)$$

E_a



minimum energy required

100 kJ

ΔH

ΔH < 0 exothermic

200 kJ

rate forward = rate reverse

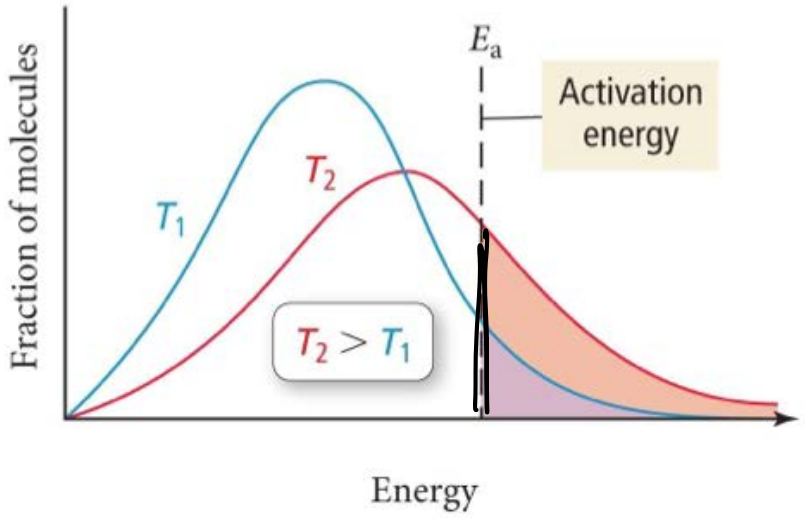
ΔH = Σn Hf products − Σn Hf reactants

ΔH < 0 exothermic

ΔH > 0 endothermic

Thermal Energy Distribution

As temperature increases, the fraction of molecules with enough energy to surmount the activation energy barrier also increases.



↑ temp

↑ reaction rate

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

Ea is activation energy

A → frequency factor

given in the problem

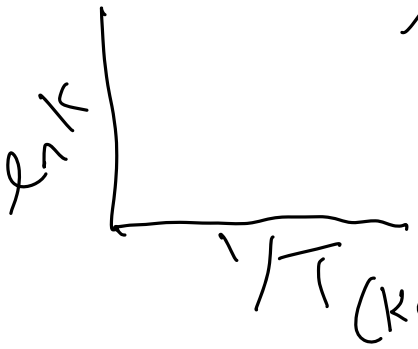
k → rate constant

$$R = 8.314 \frac{J}{mol \cdot K}$$

$$\ln k = \ln\left(A e^{-Ea/RT}\right)$$

$$\ln k = \ln A + \cancel{\ln e^{-Ea/RT}}$$

$$\ln k = \frac{-Ea}{RT} + \ln A$$



"y"

$$\ln k = \frac{-Ea}{R}\left(\frac{1}{T}\right) + \ln A$$

"x"

Arrhenius Plots

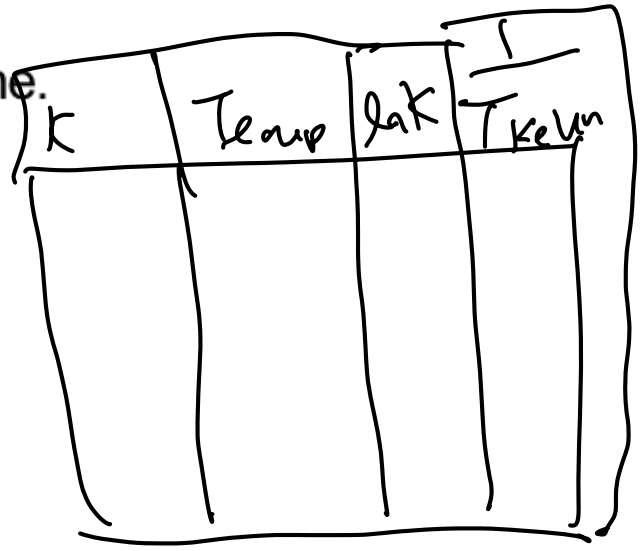
- The Arrhenius equation can be algebraically solved to give the following form:

$$\ln(k) = \frac{-E_a}{R}\left(\frac{1}{T}\right) + \ln(A)$$

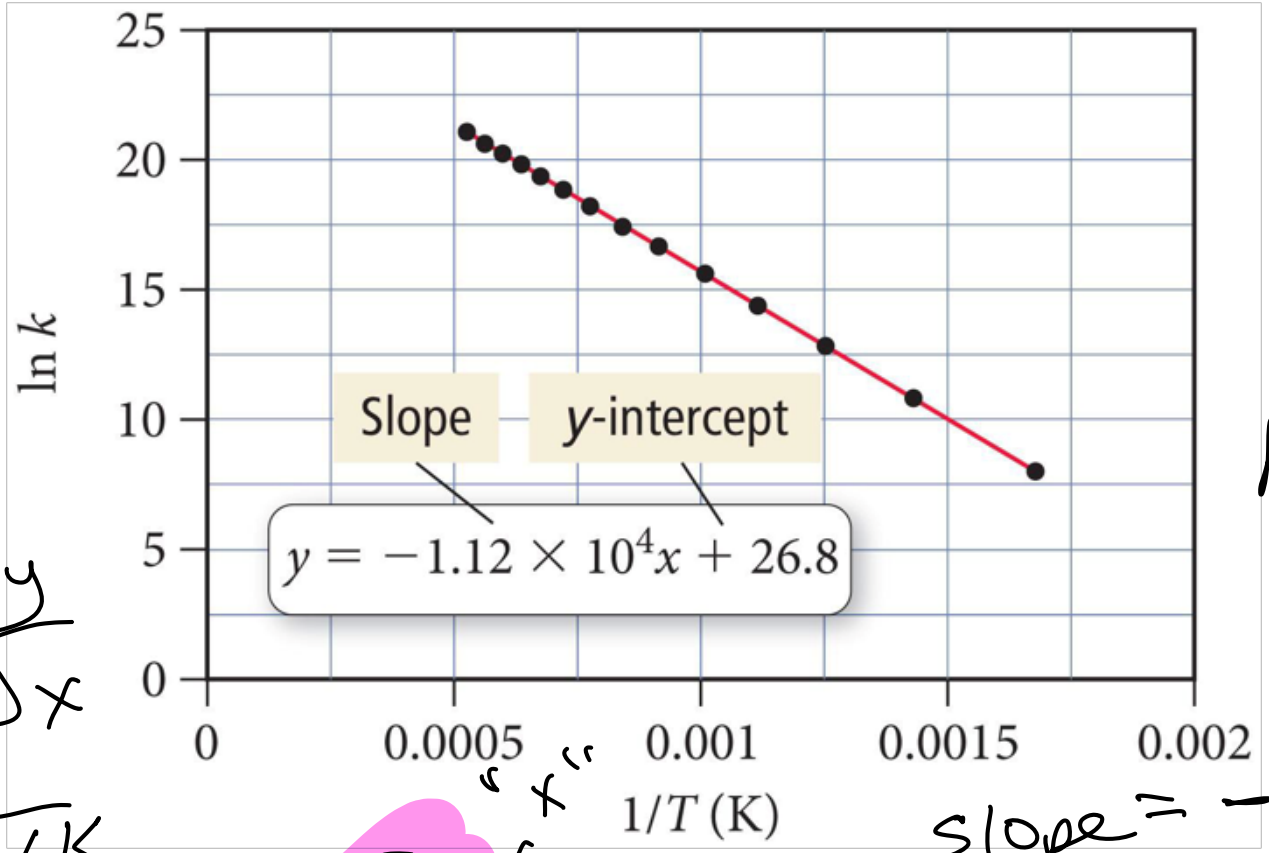
This equation is in the form $y = mx + b$, where $y = \ln(k)$ and $x = (1/T)$.

A graph of $\ln(k)$ versus $(1/T)$ is a straight line.

-Slope (R) = Ea



Determine the activation energy.



$R^2 = 1$

$m = \frac{\Delta y}{\Delta x}$

$m = \frac{1}{1/K}$

"x"

slope $= -1.12 \times 10^4$

$\ln k = -\frac{Ea}{R}\left(\frac{1}{T}\right) + \ln A$

m = " "

Arrhenius Plot Using Excel

$$m = -\frac{Ea}{R}$$

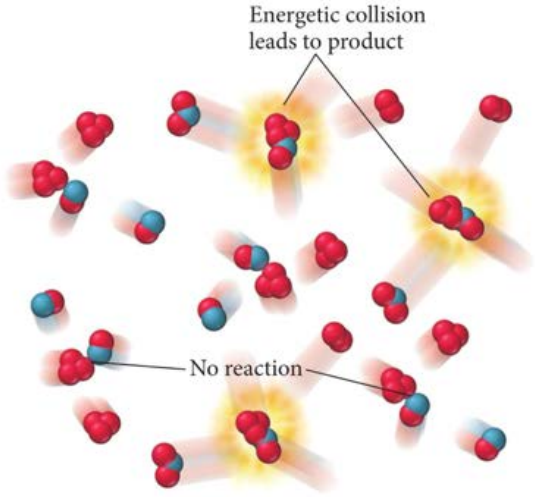
$$-m \times R = Ea$$

$$Ea = -(-1.12 \times 10^{4}\ K) \cdot 8.314\ \frac{J}{mol \cdot K}$$

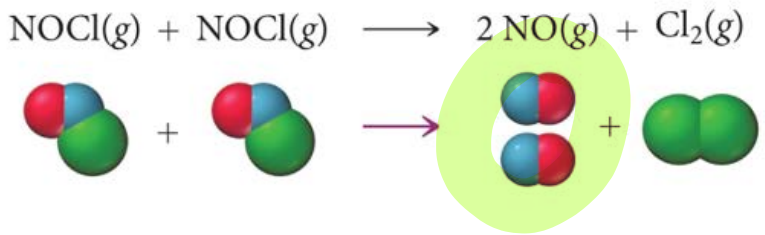
$$Ea = 93,116\ \frac{J}{mol}$$

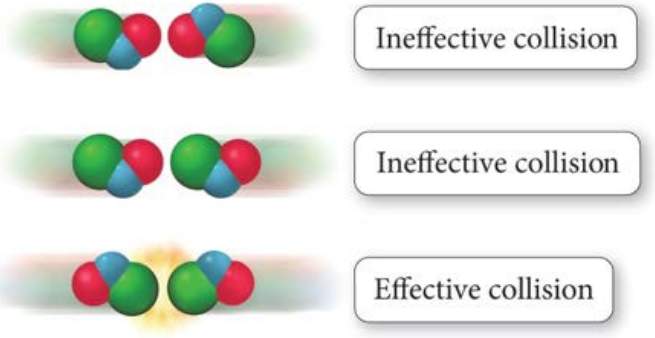
$E_a = 93.1\ kJ/mol$

Effective Collisions: Kinetic Energy Factor

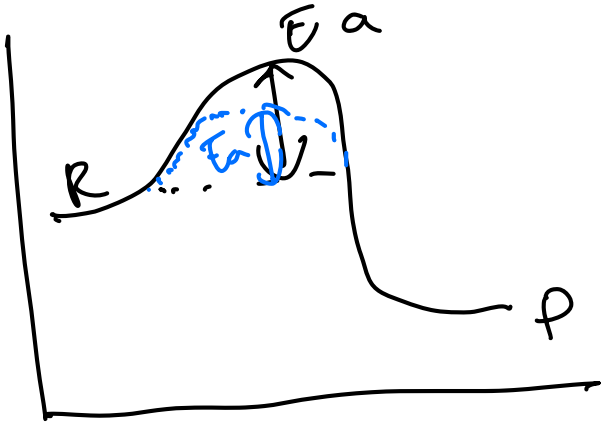


Effective Collisions: Orientation Effect





Time to think…



zero, first, second order

↑ [reactant] for 1st, ↑ rxn rate for 1st and 2nd order only!

- Other factors affecting reaction rate

↑ temp, ↑ rate constant, ↑ rxn. rate

↑ surface area, ↑ rxn rate

add catalyst or enzyme ↑ rxn. rate b/c a catalyst lowers activation energy

Reaction Mechanisms

↓ use elementary steps to determine the rate law for the overall reaction

"elementary step" ⇒ cannot be broken down into smaller ones

⊗ can use stoichiometric coefficients as the order with respect to reactants for an

elementary step

Molecularity

Rate law

rate = $k[A]^1$

rate = $k[A]^2$

rate = $k[A][B]$

rate = $k[A]^3$

unimolecular

A → product

bimolecular

A A → product

A B → product

termolecular

A A A → product

How do we use a reaction mechanism with elementary steps to determine the rate law?

* rate determining step is the slow step in the given mechanism

Validating a Mechanism

To validate (not prove) a mechanism, two conditions must be met:

1. The elementary steps must sum to the overall reaction.
2. The rate law predicted by the mechanism must be consistent with the experimentally observed rate law.

Rate Determining Step is…the slow step

Rate Determining Step

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

$Rate_{obs} = k[NO_2]^2$

bimolecular

Validate the following mechanism

1. $NO_{2(g)} + NO_{2(g)} \rightarrow NO_{3(g)} + NO_{(g)}$ Slow
2. $NO_{3(g)} + CO_{(g)} \rightarrow NO_{2(g)} + CO_{2(g)}$ Fast

bimolecular

What is the intermediate species in this mechanism ?

NO_3 gas

$C_6H_{12}O_6 \xrightarrow{enzyme} CO_2 + CH_3CH_2OH$

$NO_{2(g)} + NO_{2(g)} \rightarrow NO_{3(g)} + NO_{(g)}$

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

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

① Sum of elementary steps = overall rxn.

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

step ① is slow step

$rate = k[NO_2]^2$

$NO_{2(g)} + NO_{2(g)} \rightarrow NO_{3(g)} + NO_{(g)}$

overall reaction

$$2\,O_3(g) \longrightarrow 3\,O_2(g)$$

exp. determined

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

rate law

$$O_3(g) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} O_2(g) + O(g) \qquad \text{Fast}$$

step 1

$$O_3(g) + O(g) \xrightarrow[k_2]{} 2\,O_2(g) \qquad \text{Slow}$$

step 2

1) Is the reaction mechanism consistent with the experimentally determined rate law?

- write a rate law for slow step

$$\text{rate} = k_2[O_3]^1[O]^1$$

"k_1 is the forward rxn. rate constant" 1st step

$$k_1[O_3]^1 = k_{-1}[O_2]^1[O]^1$$

"k_{-1}" is the reverse reaction

$\text{rate}_{for} = \text{rate}_{rev}$

rearrange fast ⇌ rate law to solve for O

$$[O] = \frac{k_1}{k_{-1}}\left(\frac{[O_3]}{[O_2]}\right)$$

$$\text{rate} = k_2[O_3]^1[O]^1$$

plug in $[O] = \frac{k_1}{k_{-1}}\left(\frac{[O_3]}{[O_2]}\right)$

$$k_{new} = \frac{k_2 \cdot k_1}{k_{-1}}$$

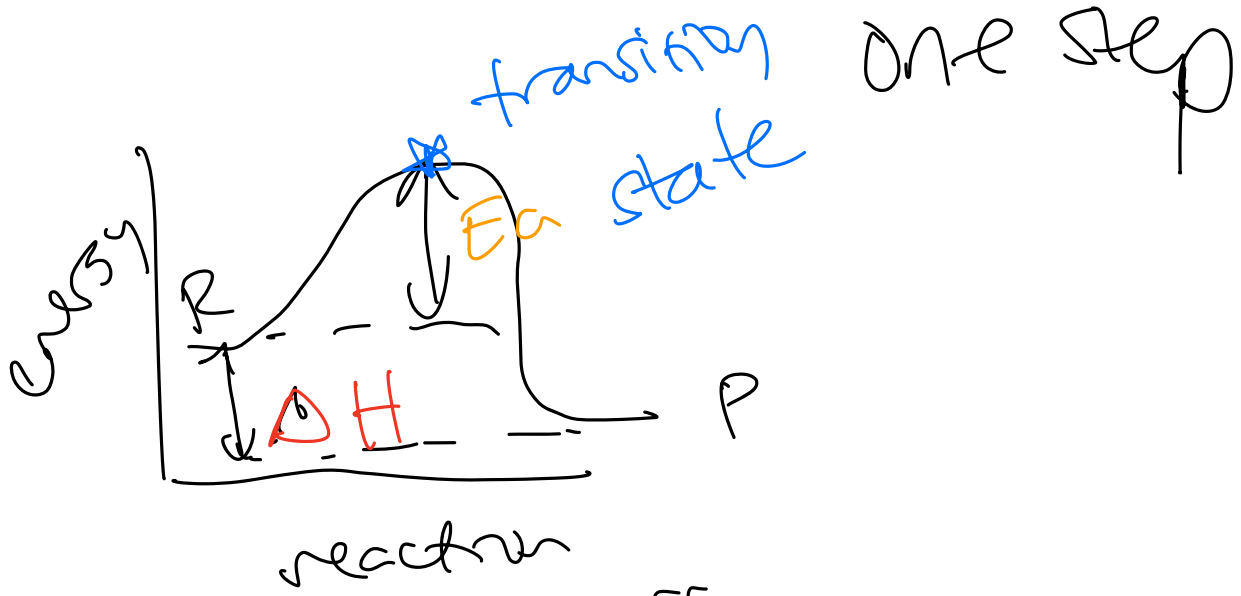
$$\text{rate} = k_{new}[O_3]^1\frac{[O_3]^1}{[O_2]^1}$$

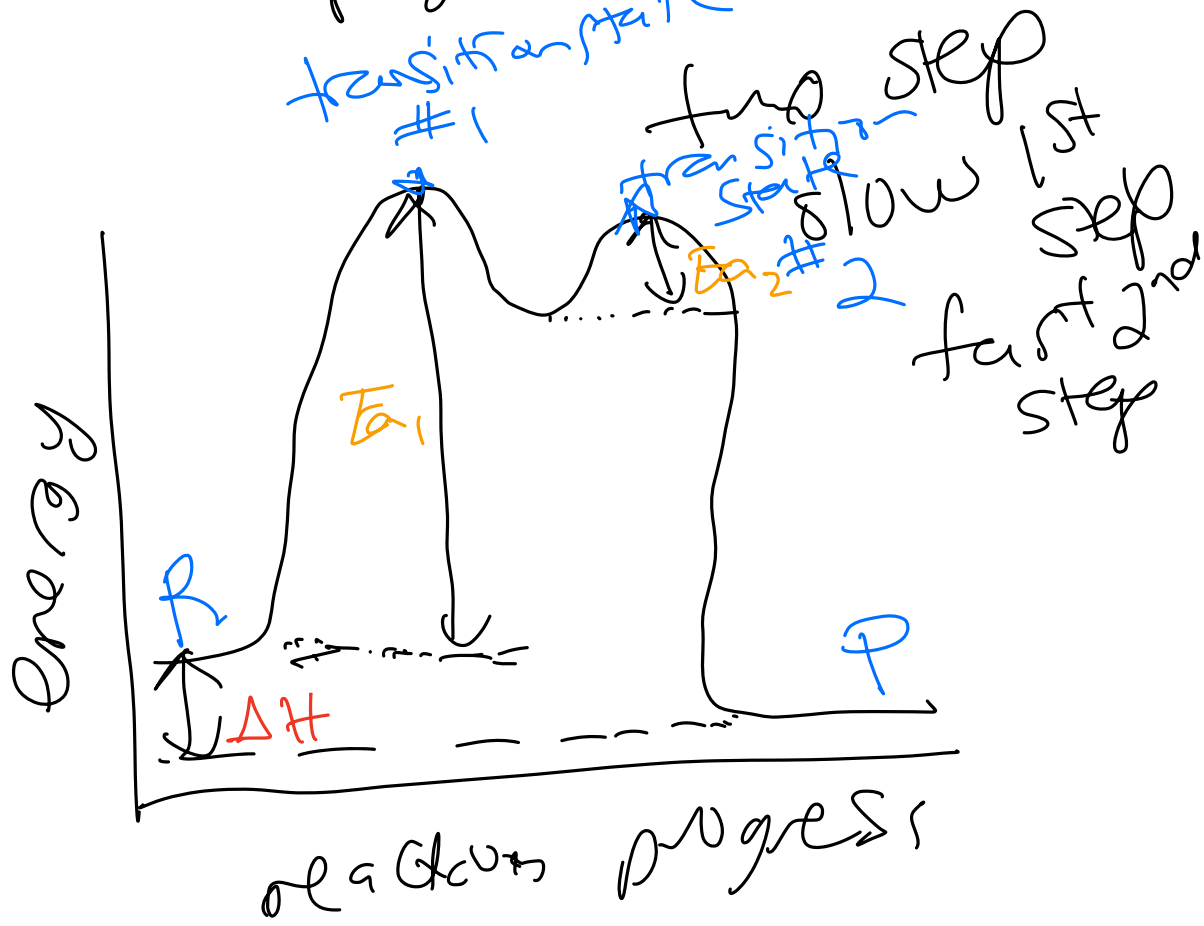
$$\text{rate} = k_{new}[O_3]^2[O_2]^{-1}$$

same as exp rate law

or

$$\text{rate} = k_{new}[O_3]^2\cdot\frac{1}{[O_2]}$$


one step
transition state
Ea
energy
R
ΔH
P
reaction progress


transition state #1
two step
transition state #2
slow 1st step
fast 2nd step
Ea2
Ea1
energy
R
ΔH
P
reaction progress