3/1/2019

Reaction Mechanisms

Most rxns don't occur in a single step
- there is a series of simpler, elementary steps
  → The Mechanism.

ex: overall rxn: $2O_3(g) \longrightarrow 3O_2(g)$

mechanism: (1) $O_3(g) \longrightarrow O_2(g) + O(g)$
(2) $O(g) + O_3(g) \longrightarrow O_2(g) + O_2(g)$
} elementary steps

the actual collisions that happen!

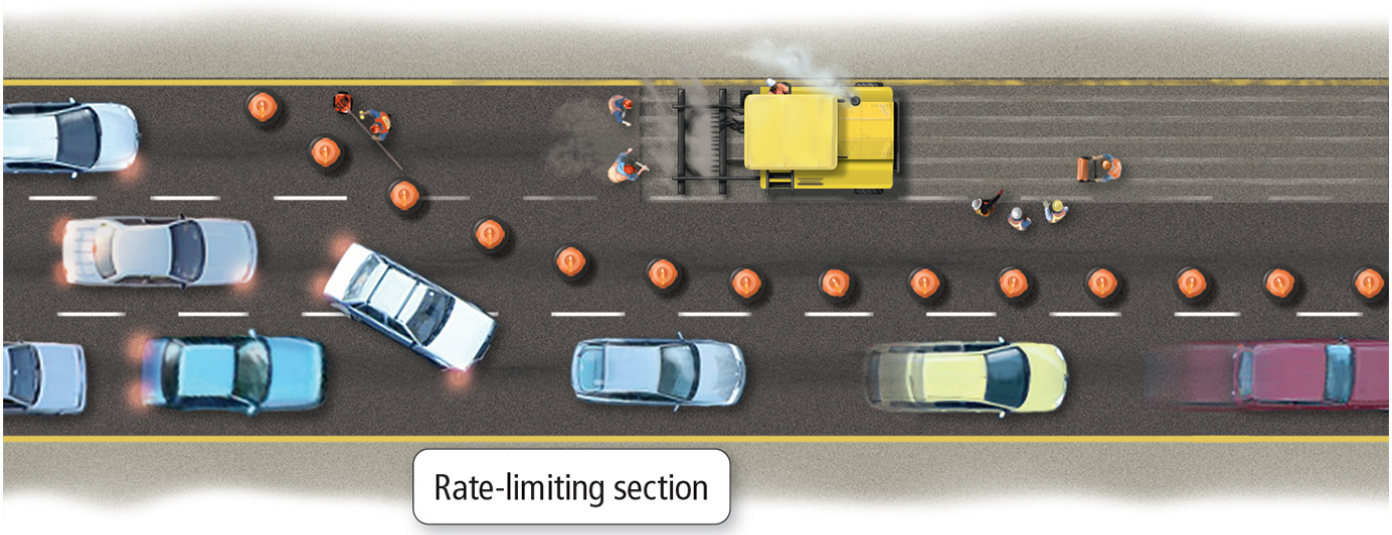
(+)

$2O_3(g) + \cancel{O(g)} \longrightarrow 3O_2(g) + \cancel{O(g)}$
} sum of elem. steps = overall rxn

Rate laws for elementary steps

- Can not write/deduce rate law for overall rxn
- But, we can write rate laws for individual, ELEMENTARY STEPS!

Classify elementary steps according to # molecules colliding
- Molecularity



$A \longrightarrow$ Product UNIMOLECULAR

$A + A \longrightarrow$ Product BIMOLECULAR

$A + B \longrightarrow$ " "

$A + B + C \longrightarrow$ Products TERMOLECULAR

$2A + B \longrightarrow$ "

$3A \longrightarrow$ "

rate $\propto$ conc. of each reactant

ex: $A + B \longrightarrow P$, rate $= K[A][B]$

$\underbrace{2A}_{A+A} \longrightarrow P$, rate $= K[A][A] = K[A]^2$ ~~$= K[2A]$~~

Rate Determining Step (RDS) + Overall rate law

- often, one elementary step is SLOW
  + it determines overall rxn rate. ↑

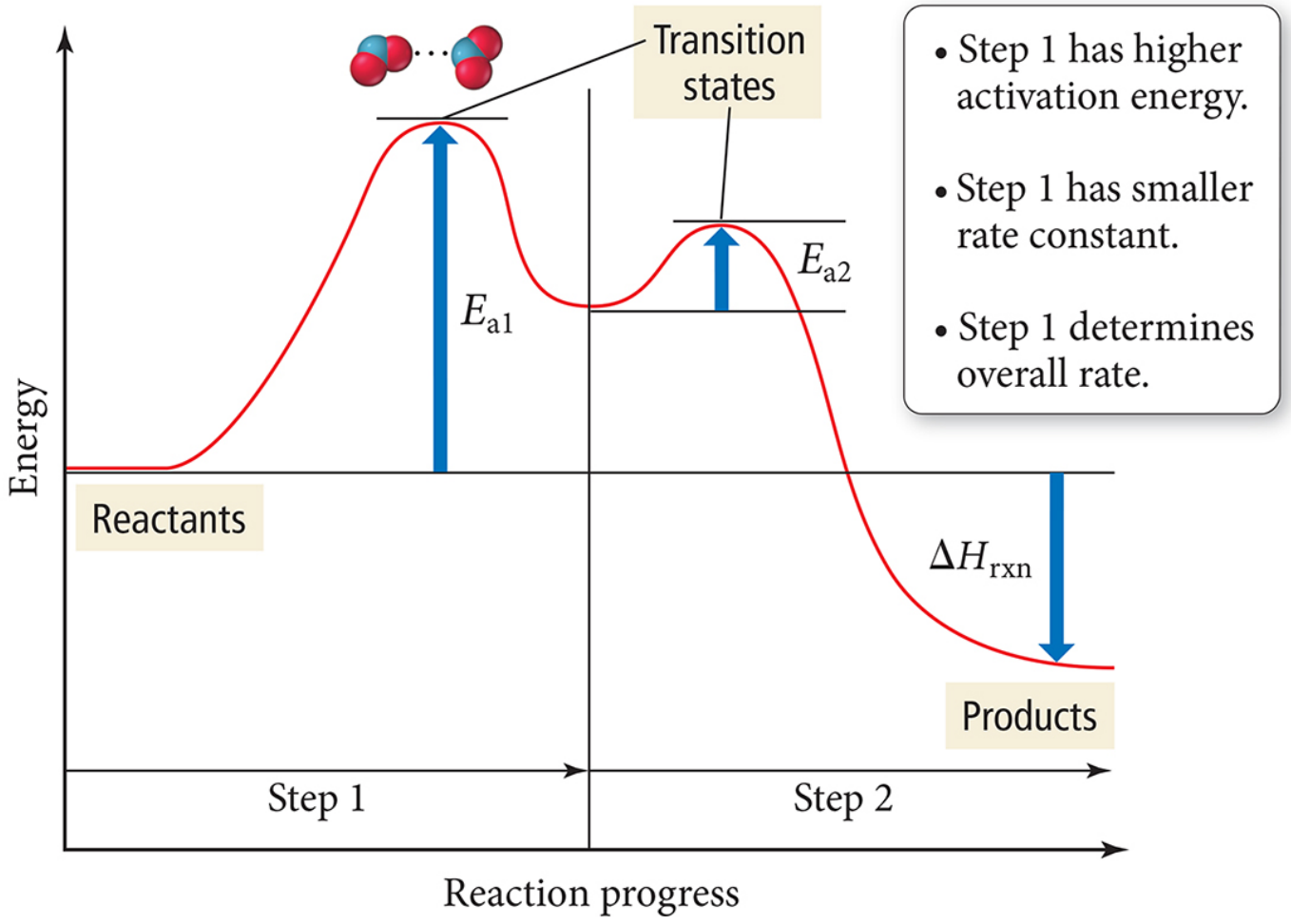
Rate Determining Step.
(bottleneck)

TABLE 14.3 Rate Laws for Elementary Steps

Elementary Step	Molecularity	Rate Law
$A \longrightarrow$ products	1	Rate $= k[A]$
$A + A \longrightarrow$ products	2	Rate $= k[A]^2$
$A + B \longrightarrow$ products	2	Rate $= k[A][B]$
$A + A + A \longrightarrow$ products	3 (rare)	Rate $= k[A]^3$
$A + A + B \longrightarrow$ products	3 (rare)	Rate $= k[A]^2[B]$
$A + B + C \longrightarrow$ products	3 (rare)	Rate $= k[A][B][C]$

Energy Diagram for a Two-Step Mechanism

Because E_a for Step 1 > E_a for Step 2, Step 1 has the smaller rate constant and is rate limiting.



- Step 1 has higher activation energy.
- Step 1 has smaller rate constant.
- Step 1 determines overall rate.

overall: $2O_3(g) \rightarrow 3O_2(g)$; rate $= K[O_3]$ ✗

mechanism:
(1) $O_3(g) \rightarrow O_2(g) + O(g)$ rate $= k_1[O_3]$
(2) $O(g) + O_3(g) \rightarrow 2O_2(g)$ rate $= k_2[O][O_3]$

unimolecular
bimolecular
intermediate

Elem. Step #1 = SLOW (Rate Determining Step)
(XPT) RDS

Overall rate law = rate law for elem. step 1

$\Rightarrow$ **Rate $= K[O_3]$** 1st order

XPTlly: rate $= K[O_3]$ Q: is mech ✓ not necessarily.

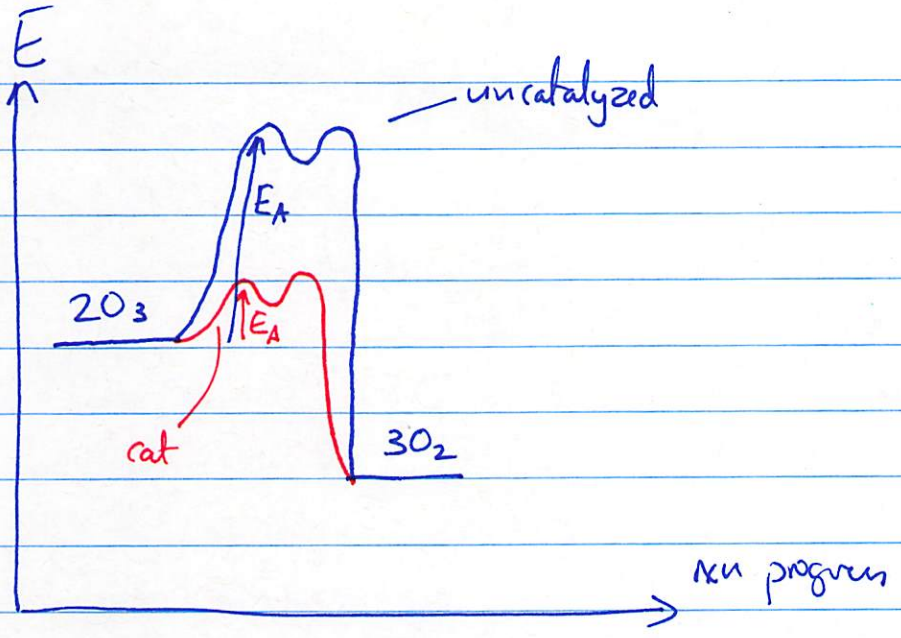
Catalysis

Catalysts - speed up rxn rate, but are not consumed!
- lower E_A by providing alternate mech.

ex: Cl catalyzes decomp of O_3

intermediate

new mech: $Cl + O_3 \rightarrow ClO + O_2$
$ClO + O_3 \rightarrow Cl + 2O_2$


E
uncatalyzed
E_A
$2O_3$
E_A
cat
$3O_2$
rxn progress

Energy Diagram for Catalyzed and Uncatalyzed Pathways