Kinetics
A molecular look!!
Take out worksheet!!!

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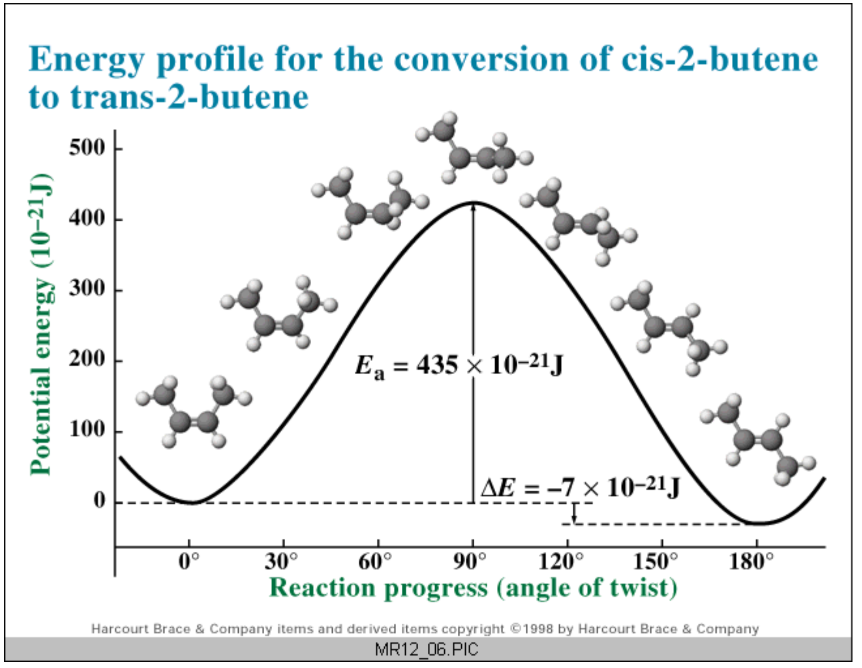
03/03/2003

unimolecular

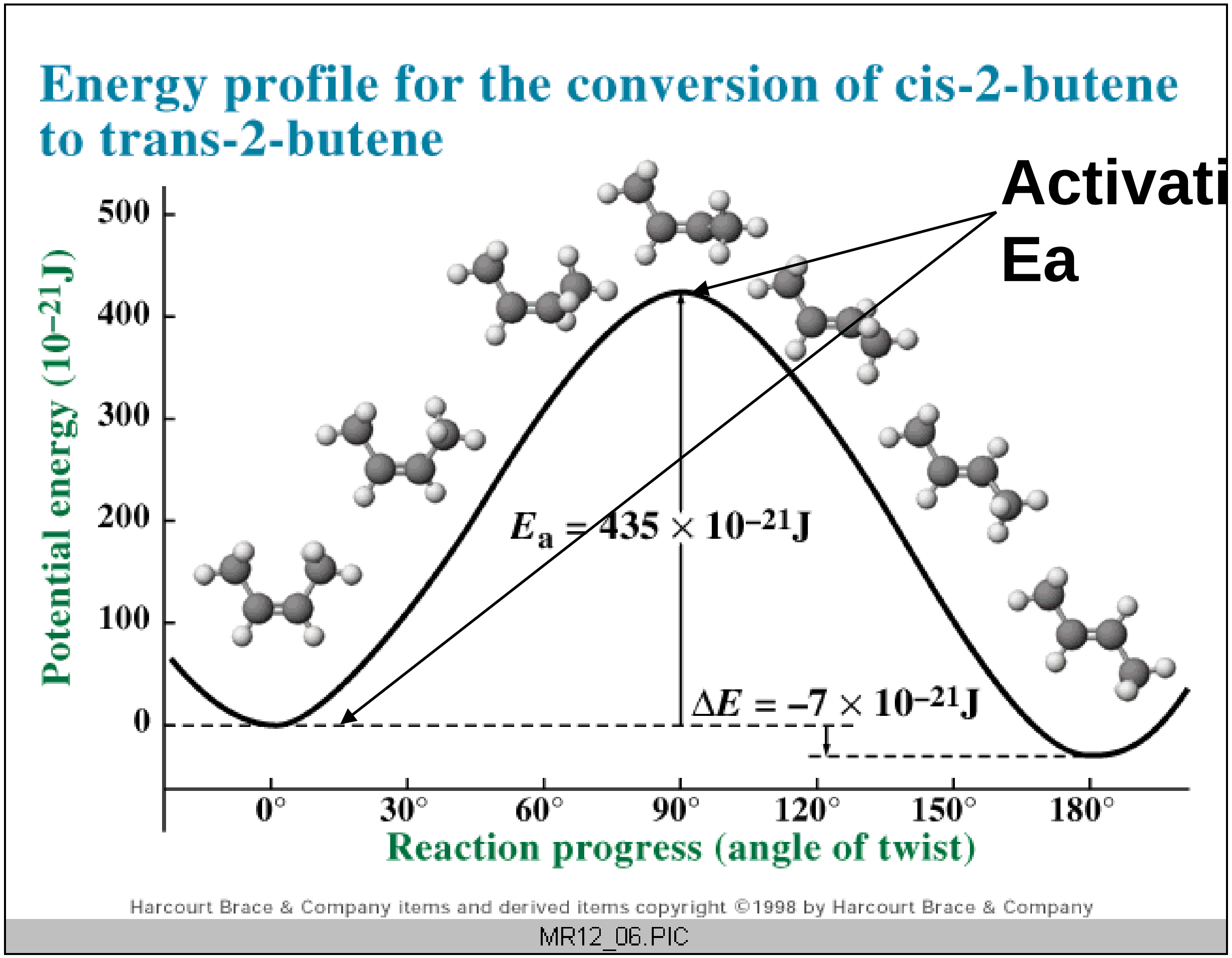
- unimolecular - rearrangement of a molecule

unimolecular

- Is reaction exothermic or endothermic
- ΔH = ?
- ΔEa = ?



Unimolecular
Energy of activation

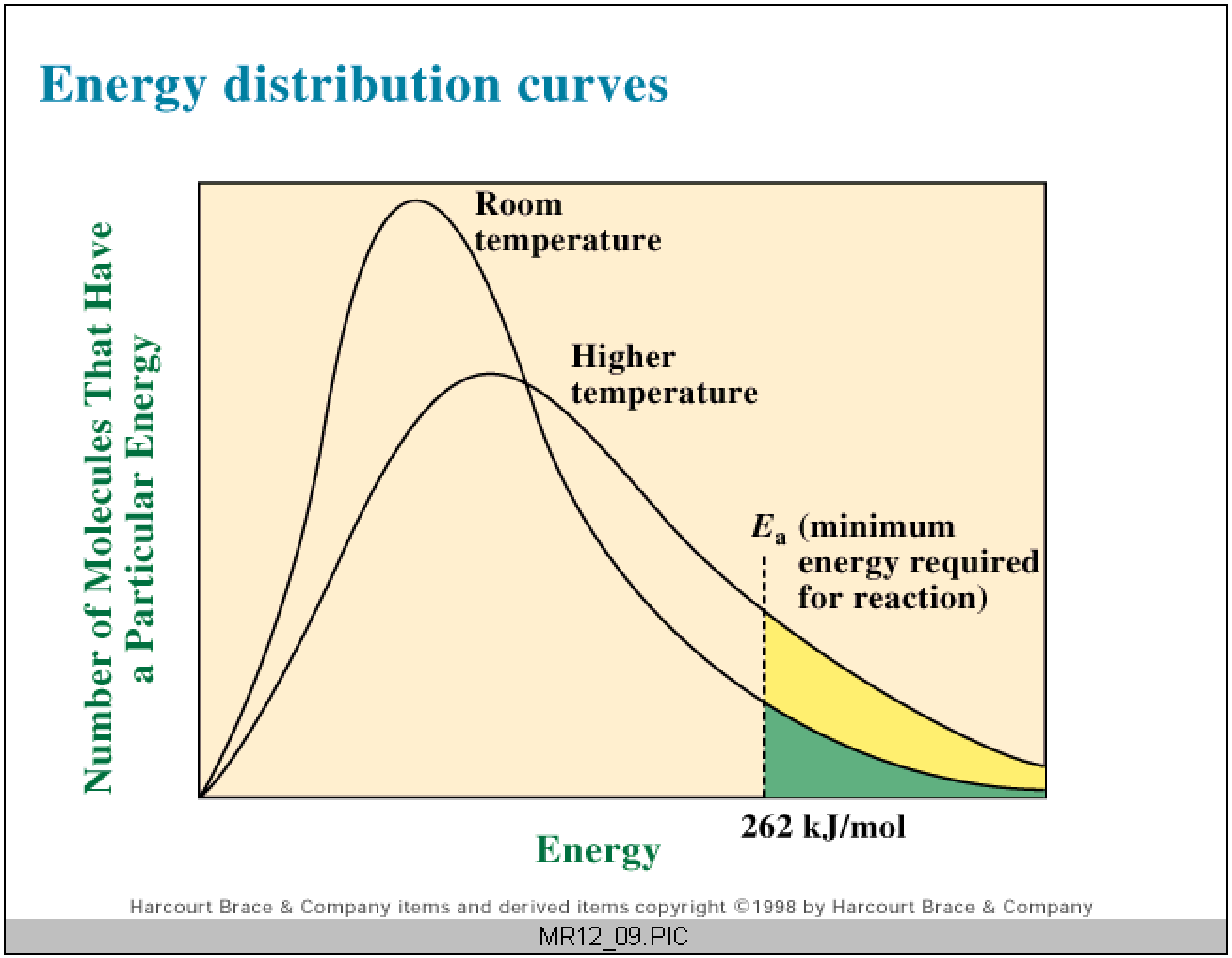


Activation energy Ea

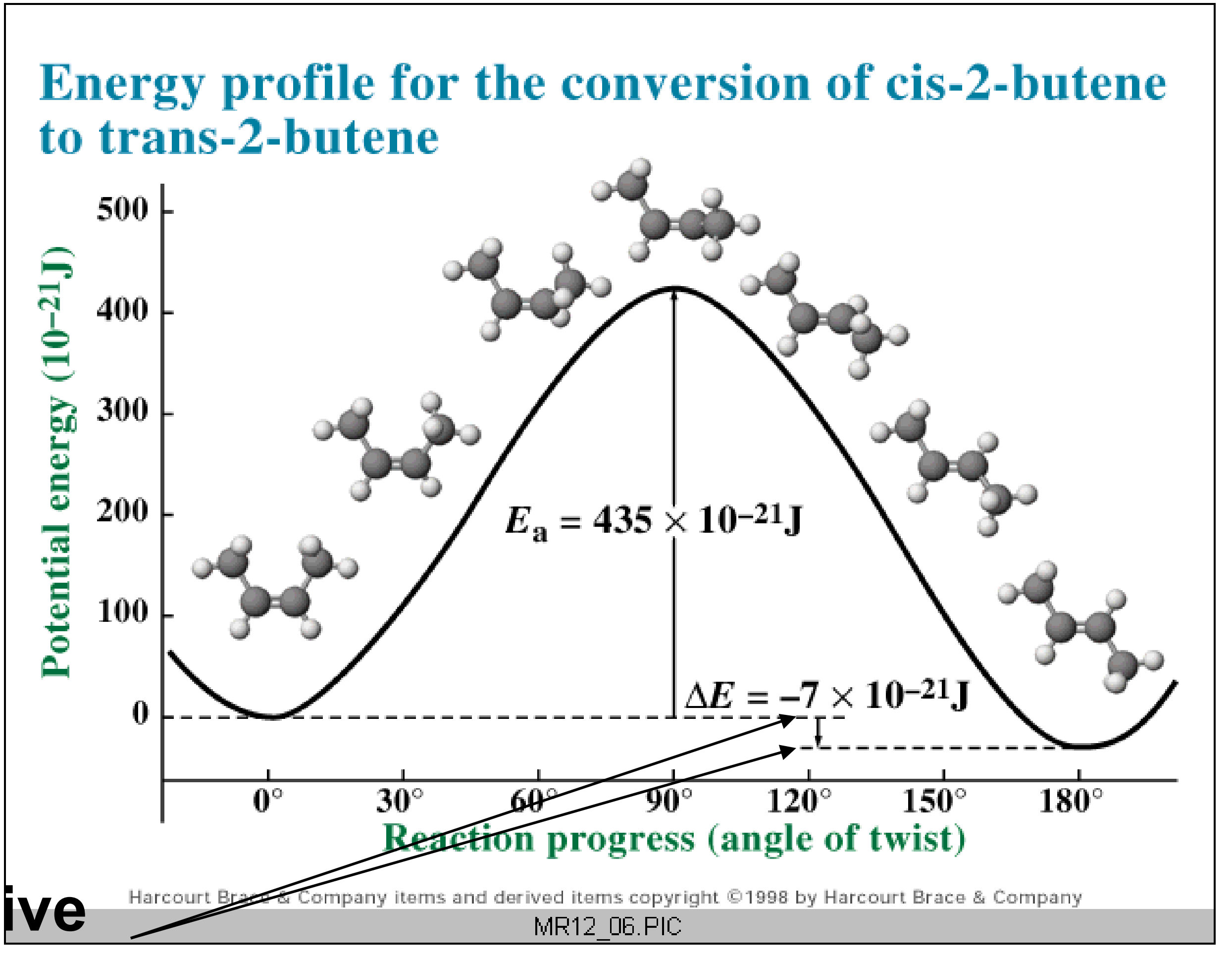
Energy of Activation

- Energy needed to start a Reaction
- The higher the energy of reaction the slower the rate.
- Graphically
  - Start to peak energy
- Catalyst- Speed up reactions by lowering activation energy

Temperature & Reaction Rate Maxwell's distribution



Unimolecular
Change in Heat energy
ΔH



ΔH = negative exothermic

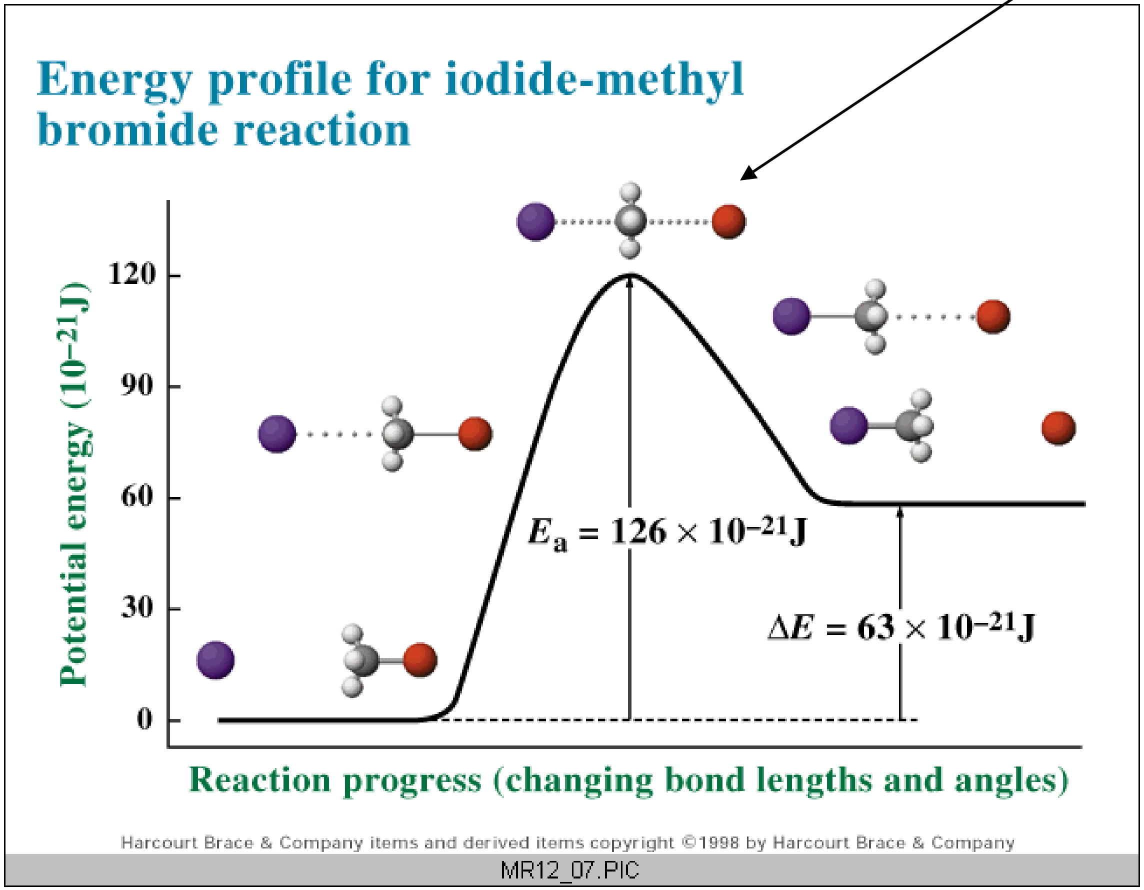
Change in energy
ΔH

1. Energy can not be created nor destroyed
2. What ever energy is lost will be gained with the reverse reaction and vise-versa
3. ΔH measures change in heat. Which is thermal energy. Since most of our reactions do not give off nuclear any other significant forms of energy heat can usually represent all energy.
4. -ΔH = exothermic; system loosing energy to the surrounding
5. + ΔH = endothermic; system taking energy from surroundings

bimolecular

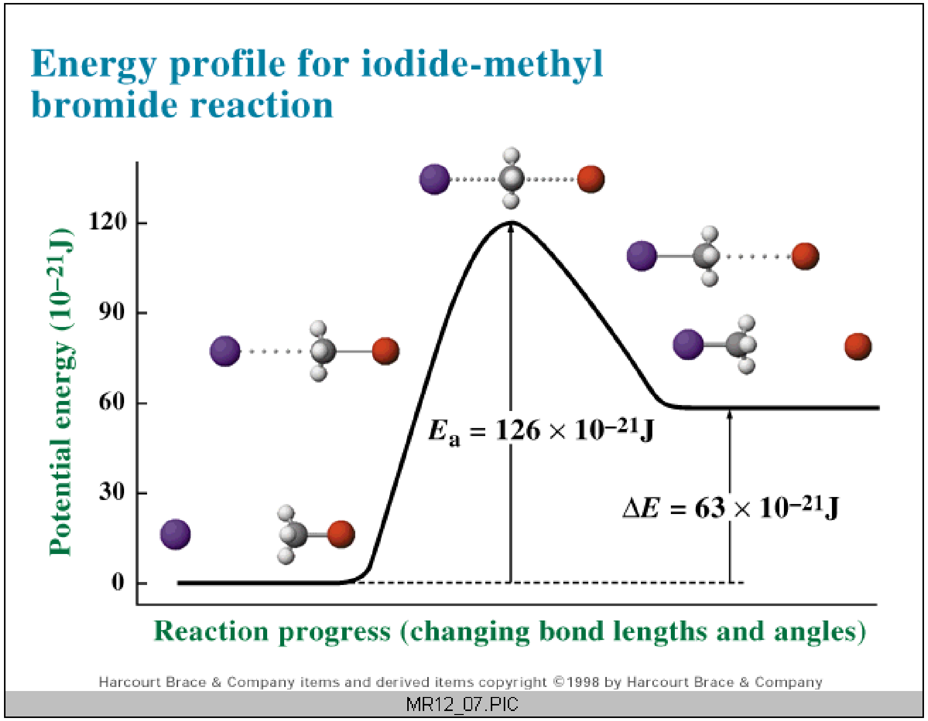
- bimolecular - reaction involving the collision of two particles

Intermediate



bimolecular

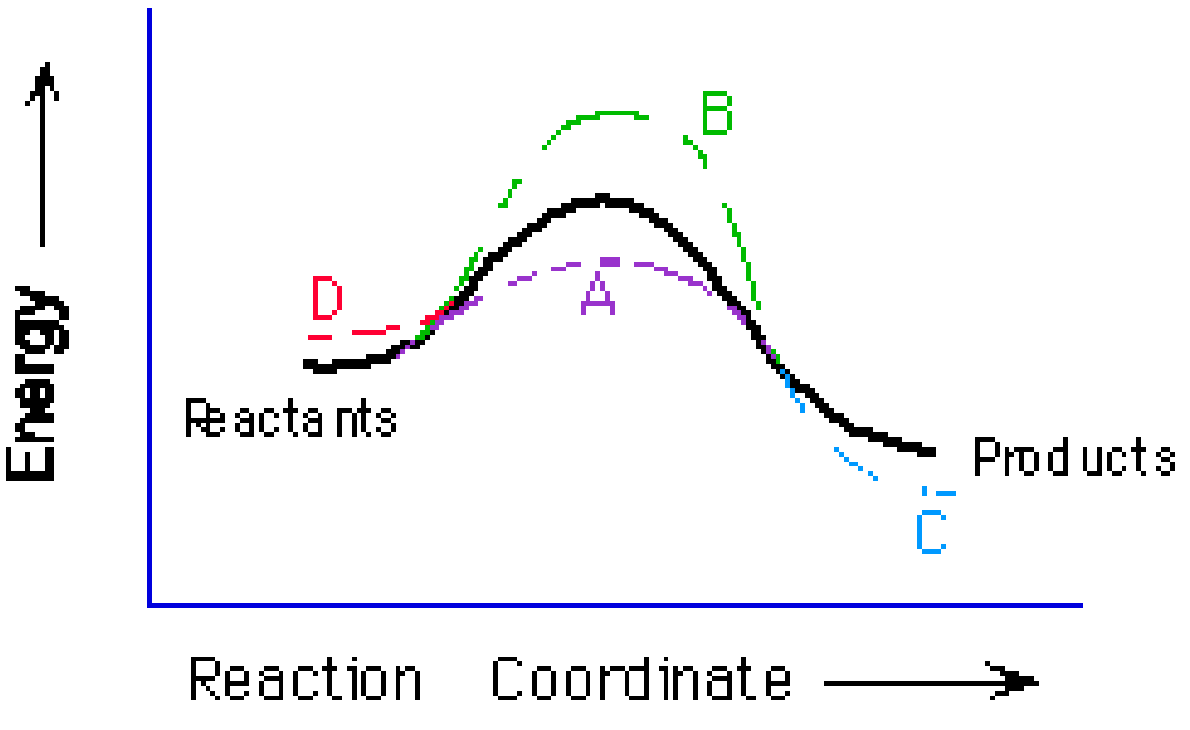
- Doubling concentration of each substance will cause reaction rate to double.
- bimolecular



termolecular

- termolecular - reaction involving the collision of three particles
- In order for a reaction to be termolecular 3 substances will need to collide instantaneously.

Which reaction is the fastest?



Catalyst
Lower activation energy

- substance which speeds up the rate of a reaction while not being consumed

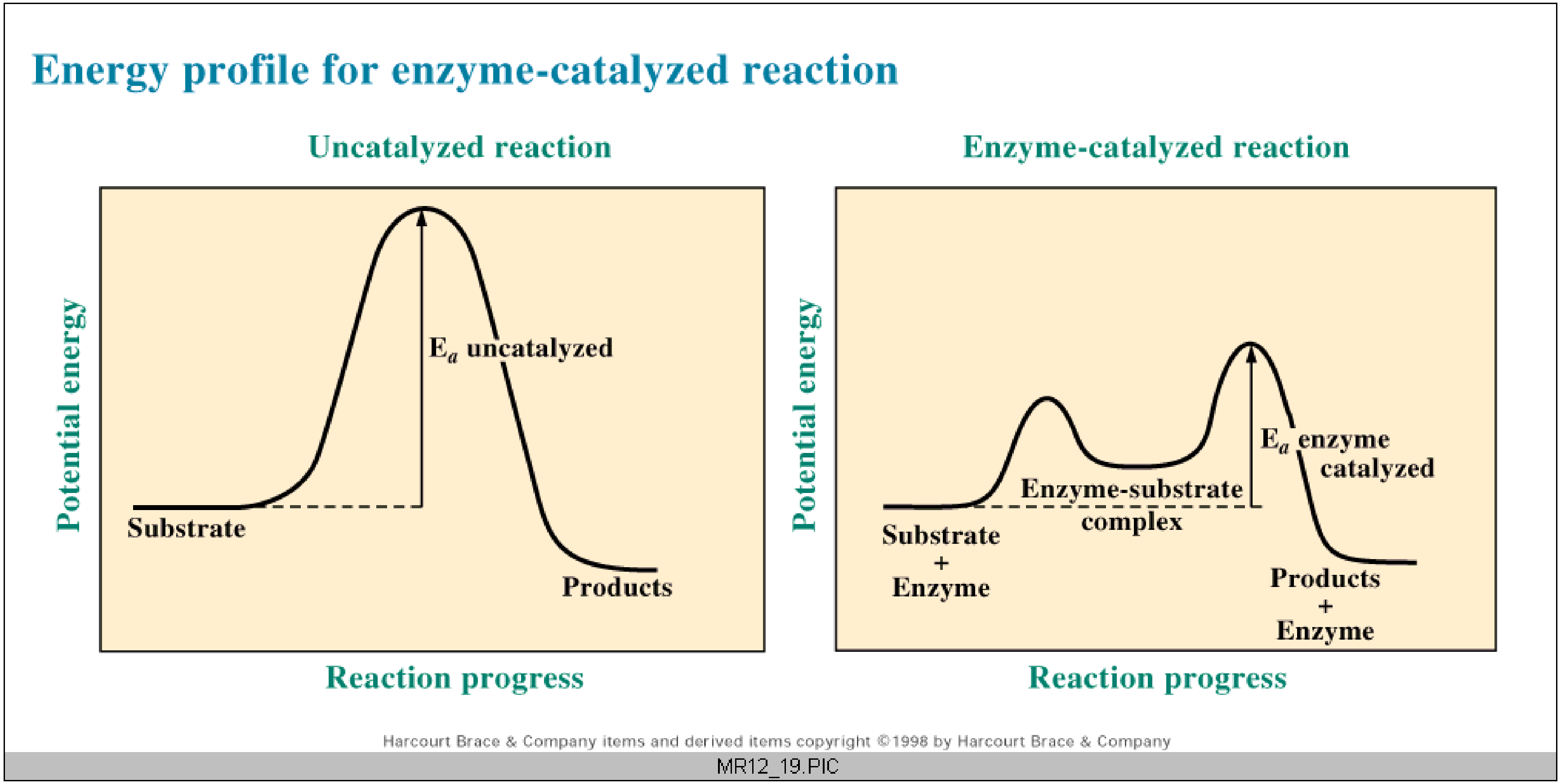
Homogeneous Catalysis - a catalyst which is in the same phase as the reactants

Heterogeneous Catalysis - a catalyst which is in the different phase as the reactants

catalytic converter

– solid catalyst working on gaseous materials

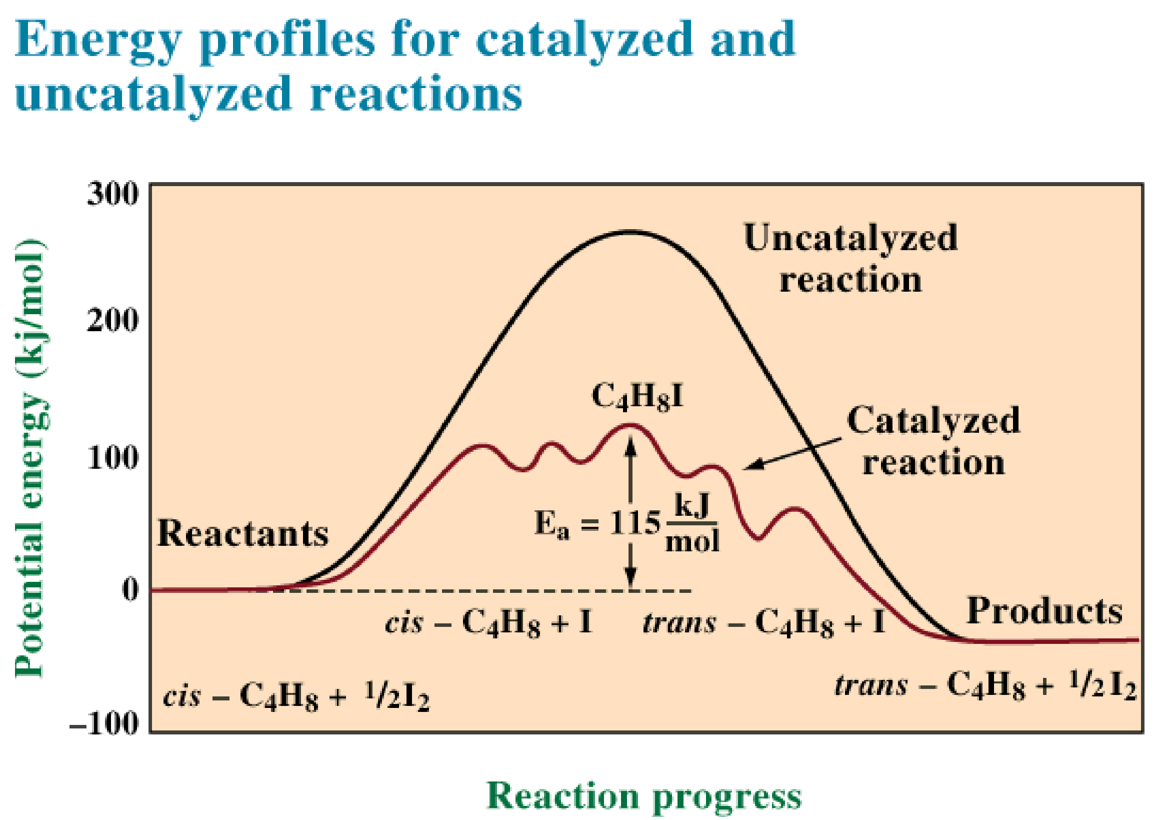
Un-catalyzed vs. Catalyzed Note: each bump stands for a reaction



Reaction Mechanism

- A set of elementary reactions which represent the overall reaction
- Catalyst: Are not consumed and will not show up in overall reaction
- Intermediate: Species produced and consumed with in a reaction. Will not show up in overall reaction.
- ΔH and Keq values add as well.

How many elementary steps ?



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Reaction mechanisms and rate of reaction.

- The slowest rate controls the rate of reaction.
- Example: Hwy. 45 at either 7:40am or 3:15pm. What controls rate of traffic.
- Actual time or rate = limiting rate + any time after.

Rate equation for elementary reaction

- $A \rightarrow B + C$
- Doubling concentration of A will double reaction rate
- Rate = $k[A]$

Rate equation for elementary reaction

- $A + B \rightarrow C + D$

- Rate = $k[A][B]$
- Each individual is 1st order but the reaction is second order overall.
- Doubling the concentration of each will quadruple the rate.

Rate equation for elementary reaction

- $A + B + C \rightarrow D + E$
- Rate = k[A][B][C]
- Each individual is 1st order but the reaction is 3rd order overall.

Rate equation for rate determining step

- $NO_2 + F_2 \rightarrow NO_2F + F$ (slow step)
- $F + NO_2 \rightarrow NO_2F$ (Fast)
- --
- $2NO_2 + F_2 \rightarrow 2NO_2F$

*Rate equation can be written from rate determining step.

Rate = $k[NO_2][F_2]$

* Any NO_2 add for second reaction will not affect rate.

Practice

- $O_3 + NO_2 \rightarrow NO_3 + O_2$ (slow)
- $NO_3 + NO_2 \rightarrow N_2O_5$ (fast)
- Overall reaction please
- $O_3 + 2NO_2 \rightarrow N_2O_5 + O_2$
- Please write Rate law
- Rate = $k[O_3][NO_2]$

Practice,
write the rate equation!

- $2N_2O_5 \leftrightarrow 2NO_2 + 2NO_3$ (fast, equilibrium)
- $NO_2 + NO_3 \rightarrow NO + NO_2 + O_2$ (slow)
- $\underline{NO_3 + NO \rightarrow 2NO_2 \text{ (fast)}}$

- Determine rate equation
- *** you can not use intermediate in reaction equation***

Practice, write the rate equation!

- $2N_2O_5 \leftrightarrow 2NO_2 + 2NO_3$ (fast, equilibrium)
- $NO_2 + NO_3 \rightarrow NO + NO_2 + O_2$ (slow)
- $\underline{NO_3 + NO \rightarrow 2NO_2 \text{ (fast)}}$
- $2N_2O_5 \rightarrow 4NO_2 + O_2$
- Determine rate equation
- *** you can not use intermediate in reaction equation***
- Rate = $K[N_2O_5]^2$

1st practice question #4

$Br2(g) \to 2Br(g)$	fast
$Br(g) + H2(g) \to HBr(g) + H(g)$	slow
$H(g) + Br(g) \to HBr(g)$	fast

Write overall equation, indicate intermediates and write the rate law.

Write overall equation

$Br2(g) \rightarrow 2Br(g)$ fast

$Br(g) + H2(g) \rightarrow HBr(g) + H(g)$ slow

$H(g) + Br(g) \rightarrow HBr(g)$ fast

$Br2(g) + 2Br(g) + H2(g) + H(g) \rightarrow 2Br(g) + HBr(g) + H(g) + HBr(g)$

Put all reactants and all products on one equation. Combining like terms.

$Br_2(g) + H2(g) \rightarrow 2HBr(g)$

Write overall equation

Br2(g) → 2Br(g) fast

Br(g) + H2(g) → HBr(g) + H(g) slow

H(g) + Br(g) → HBr(g) fast

$Br_2(g) + H2(g) \rightarrow 2HBr(g)$

Write a rate law. Add all reactants.

Rate = k $[Br]^?[H_2]^?$

If reactant is zero order it is quite often left off the rate law.

Write overall equation

$\underline{Br2(g)} \rightarrow 2Br(g)$ fast

$Br(g) + \underline{H2(g)} \rightarrow HBr(g) + H(g)$ slow

$H(g) + Br(g) \rightarrow HBr(g)$ fast

$$Br_2(g) + H2(g) \rightarrow 2HBr(g)$$

Rate = k $[Br]^1 [H_2]^1$

What are the orders (?) The slow reaction and anything that feeds the slow reaction is what determines orders.

What do we have?

$$5Br^-_{(aq)} + BrO_3^-{}_{(aq)} + 6H^+_{(aq)} \rightarrow 3Br_{2(l)} + 3H_2O_{(l)}$$

$$\text{Rate} = k[Br^-][BrO_3^-][H^+]^2$$

One proposed reaction mechanism has three steps up to and including the slow step. The 1st step of this reaction is:

$$Br^- + H^+ \rightarrow Int_1$$

Which of the following could be the next two steps in the mechanism?

a. $Int_1 + H^+ \rightarrow Int_2$: $Int_2 + Br^- \rightarrow Int_3$

b. $Int_1 + BrO_3^- \rightarrow Int_2$: $Int_2 + H^+ \rightarrow Int_3$

c. $Int_1 + H^+ \rightarrow Int_2$: $Br^- + BrO_3^- \rightarrow Int_3$

d. $Int_1 + BrO_3^- \rightarrow Int_2$: $Int_2 + Br^- \rightarrow Int_3$

e. $Int_1 + Br^- \rightarrow Int_2$: $Int_2 + BrO_3^- \rightarrow Int_3$

$$5Br^-_{(aq)} + BrO_3^-{}_{(aq)} + 6H^+_{(aq)} \rightarrow 3Br_{2(l)} + 3H_2O_{(l)}$$
$$\text{Rate} = k[Br^-][BrO_3^-][H^+]^2$$

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$$5Br^-_{(aq)} + BrO_3^-{}_{(aq)} + 6H^+_{(aq)} \rightarrow 3Br_{2(l)} + 3H_2O_{(l)}$$

$$\text{Rate} = k[Br^-][BrO_3^-][H^+]^2$$

The overall order of this reaction is

a. 2

b. 3

c. 4

d. 6

e. 12

$$5Br^{-}_{(aq)} + BrO_3^{-}{}_{(aq)} + 6H^{+}_{(aq)} \rightarrow 3Br_{2(l)} + 3H_2O_{(l)}$$

$$Rate = k[Br^-][BrO_3^-][H^+]^2$$

The overall order of this reaction is

a. 2

b. 3

c. 4

d. 6

e. 12

$$5Br^-_{(aq)} + BrO_3^-{}_{(aq)} + 6H^+_{(aq)} \rightarrow 3Br_{2(l)} + 3H_2O_{(l)}$$

$$\text{Rate} = k[Br^-][BrO_3^-][H^+]^2$$

- What is the effect of increasing $[H^+]$ in this reaction system?

a. The value of the rate constant increases.
b. The potential energy of the products decreases.
c. The potential energy of the activated complex decreases.
d. The number of collisions between H^+ and Br^- ions increases.
e. The effectiveness of collisions between H^+ and Br^- ions increases.

$$5Br^{-}_{(aq)} + BrO_3^{-}{}_{(aq)} + 6H^{+}_{(aq)} \rightarrow 3Br_{2(l)} + 3H_2O_{(l)}$$

$$\text{Rate} = k[Br^-][BrO_3^-][H^+]^2$$

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$$5Br^{-}_{(aq)} + BrO_3^{-}{}_{(aq)} + 6H^{+}_{(aq)} \rightarrow 3Br_{2(l)} + 3H_2O_{(l)}$$

$$\text{Rate} = k[Br^-][BrO_3^-][H^+]^2$$

What is the effect of adding $Br_2(l)$ to the system?

I. The mass of the system increases.

II. The rate of the reduction of BrO_3^- increases.

III. The rate of the oxidation of Br^- decreases.