UNIT7-DAY7-LaB1230pm

Wednesday, April 03, 2013
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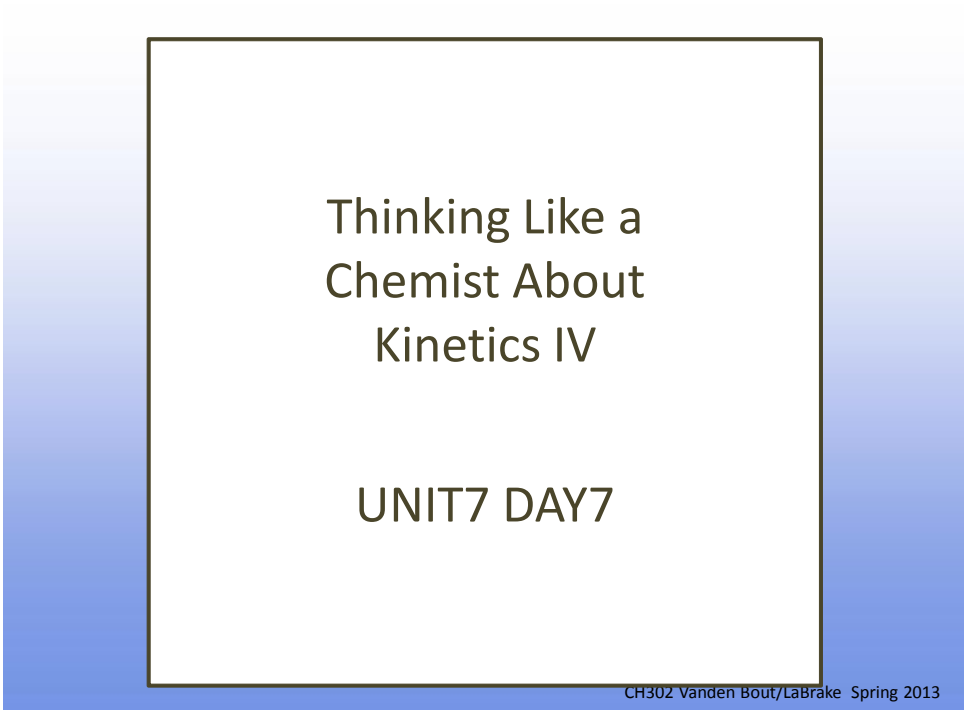

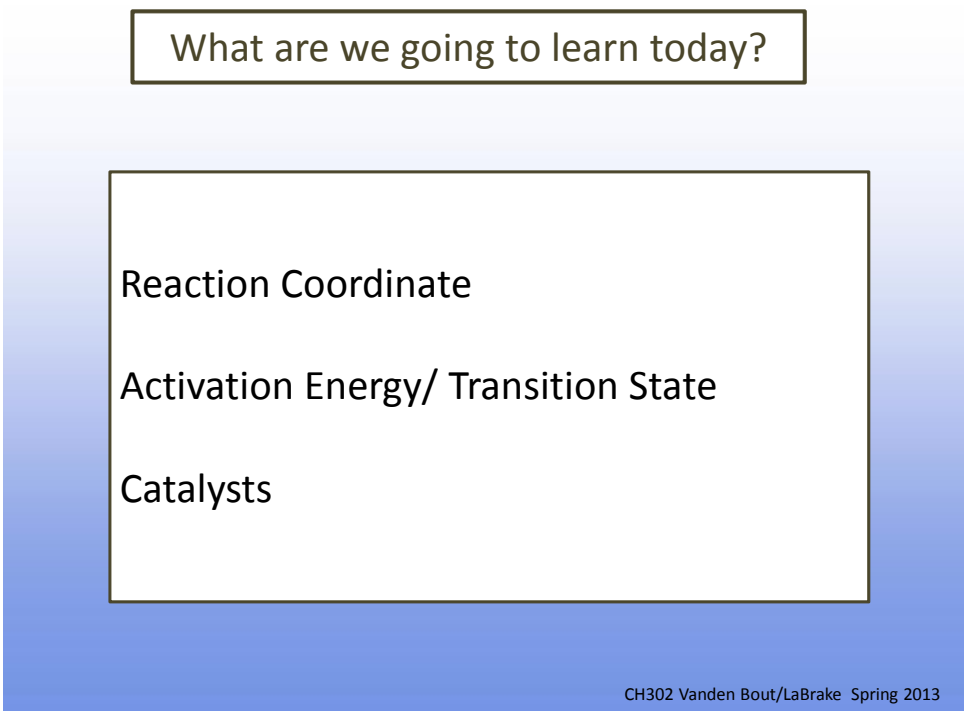

IMPORTANT INFORMATION

HW10 due Tue 9 AM

Quiz: Clicker Question 1

Write the overall reaction and the rate expressions that correspond to the following mechanisms. Be sure to eliminate intermediates from the answers.

1. A + B ←→ C (fast, equilibrium)
2. C + B ←→ F (fast, equilibrium)
3. F → G (slow)

a) Rate = k[F]

b) Rate = k[C][B]

c) Rate = k[A][B]^2

d) Rate = k[A]^2[B]^2

intermediate need to solve for intermediate

A + 2B → G

What factors affect the speed of a reaction?
Nuclear Change vs Chemical Change

Look at some demos!

CONCENTRATION/AMOUNT - remember 3m HCl w/ chalk vs. 0.1M HCl

MEDIUM - remember – crushed vs. whole chalk

CATALYSTS – later today

TEMPERATURE - now Room temp – faster Cold – slower

Principles of Chemistry II

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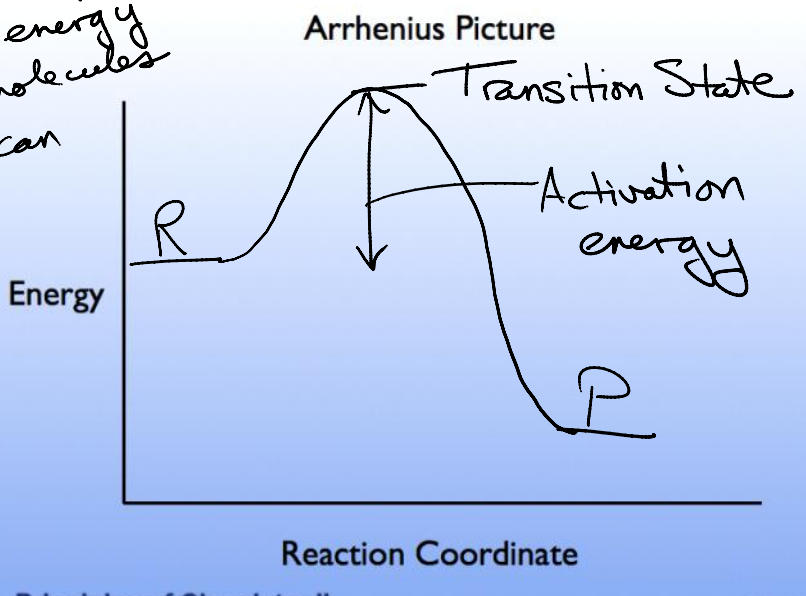
inc temp inc energy of molecules more can reach



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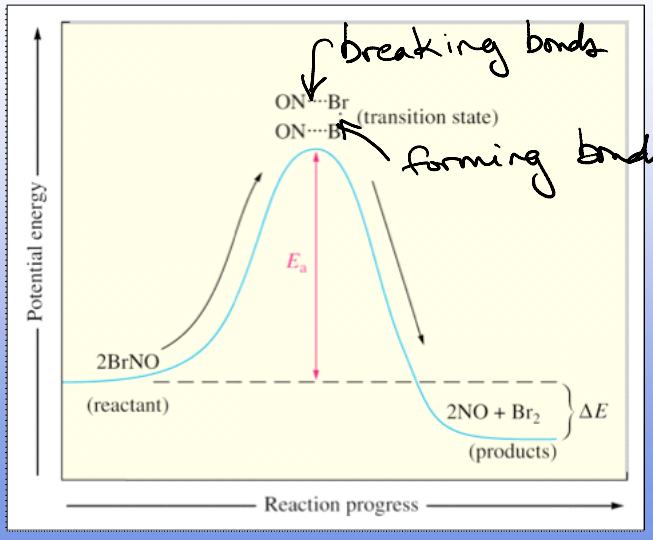
Collision Matters



At a given temperature the molecules in a sample

A. all have the same energy

B. have a distribution of energies

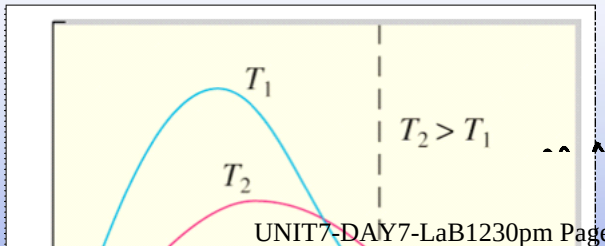
C. have one of several fixed energies

very important to have in your mind

Evaporation...

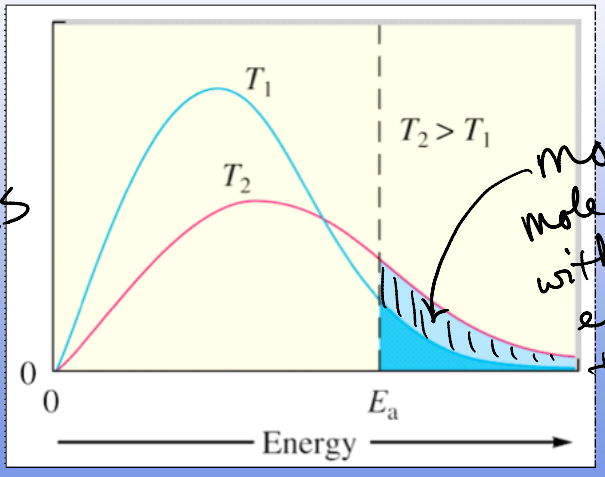
How many molecules have enough energy to get over the barrier?

#



...are

get over the barrier?



# of molecules

more molecules with enough energy to cross Ea barrier

Arrhenius Law

The rate constant k is a function of temperature

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

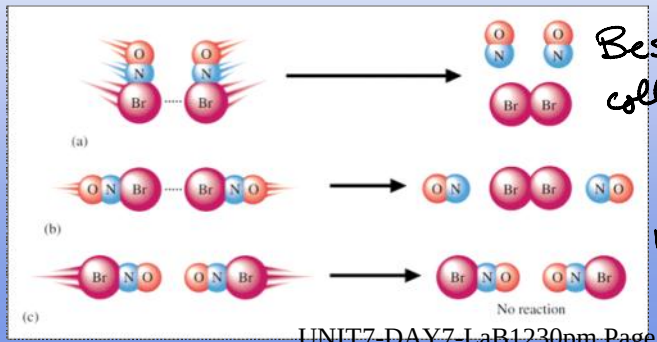
energy barrier affects rate

pre exponential factor → constant assuming proper orientation & medium

The higher the temperature the more molecules that have enough energy to make it over the barrier

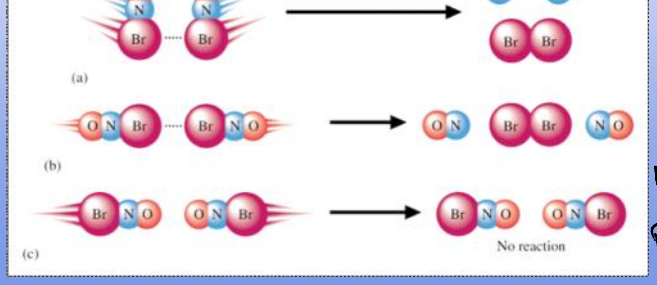
What is A? → pre exponential factor

This is the rate at infinite temperature
(not all interactions between the molecules even with sufficient energy will lead to products)



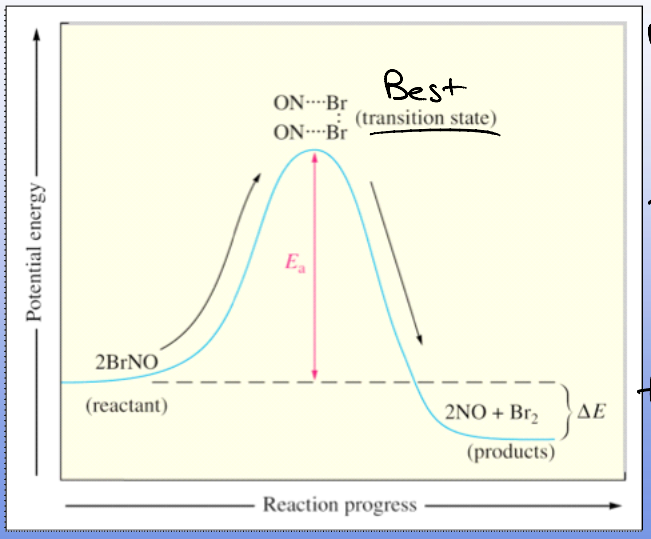
Best collision

not



not productive

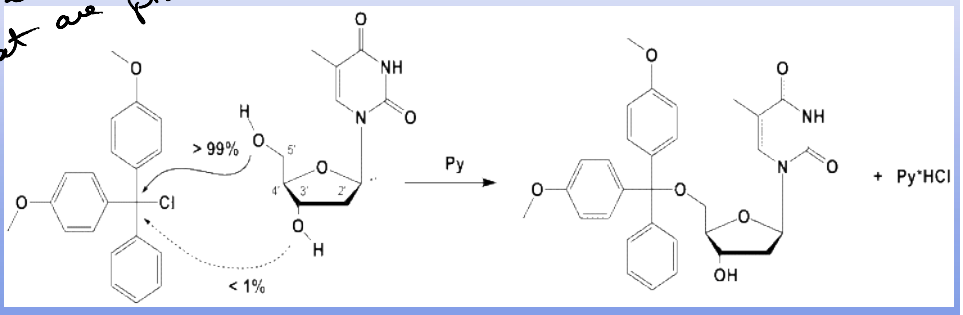
Collision Matters



must have both
-orientation
-enough energy to overcome E_a

Engineer molecules and control reactions by limiting orientations that are productive

Very important in organic chemistry
"steric effect"
"steric hindrance"
"steric protection"
putting a big unreactive part of the molecule
"in the way"
to slow (or stop) the reaction



$1/\ln A$

One equation many forms

$k = A e^{-Ea/RT}$

$\ln k = \ln A - E_a/RT$

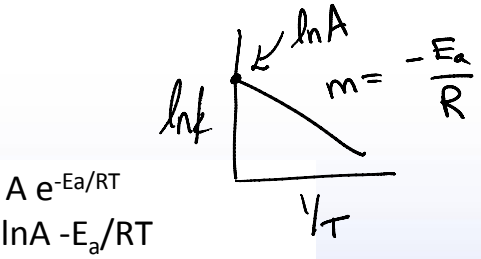
$\ln k = \ln A - \frac{E_a}{R} \cdot \frac{1}{T}$

let's look at two temperatures

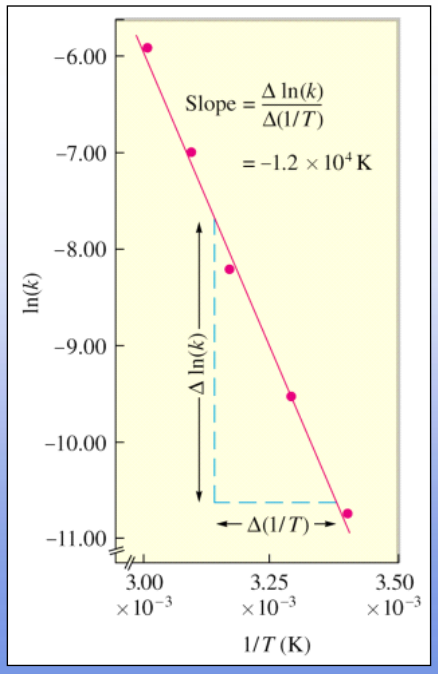
$\ln k_1 = \ln A - E_a/RT_1$

$\ln k_2 = \ln A - E_a/RT_2$

$\ln k_2 - \ln k_1 = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$



in lab can measure A & E_a!



Poll: Clicker Question

What is the activation energy for this reaction?

$R = 8.314\ J/molK$

A. -1.2 x 10^4 K
B. 1 x 10^5 J mol^{-1}
C. 1.2 x 10^4 J mol^{-1}
D. 1 x 10^5 K
E. -1 x 10^2 kJ mol^{-1}

$m = -1.2 \times 10^4 = -\frac{E_a}{R}$

$E_a = (1.2 \times 10^4)(8.314)$

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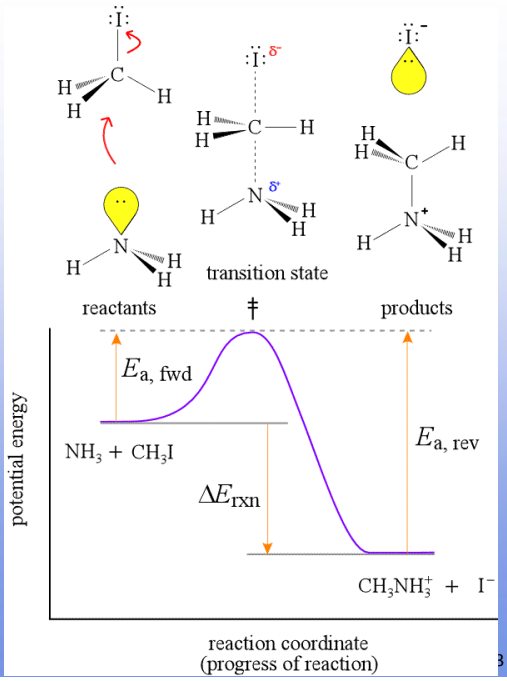
Why are reactions faster at higher temperatures?

More molecules have sufficient energy to get over the barrier.
BIG EFFECT
More molecules have collisions (but this is a very small effect) that is ignored in Arrhenius view

THIS AN IMPORTANT POINT!!

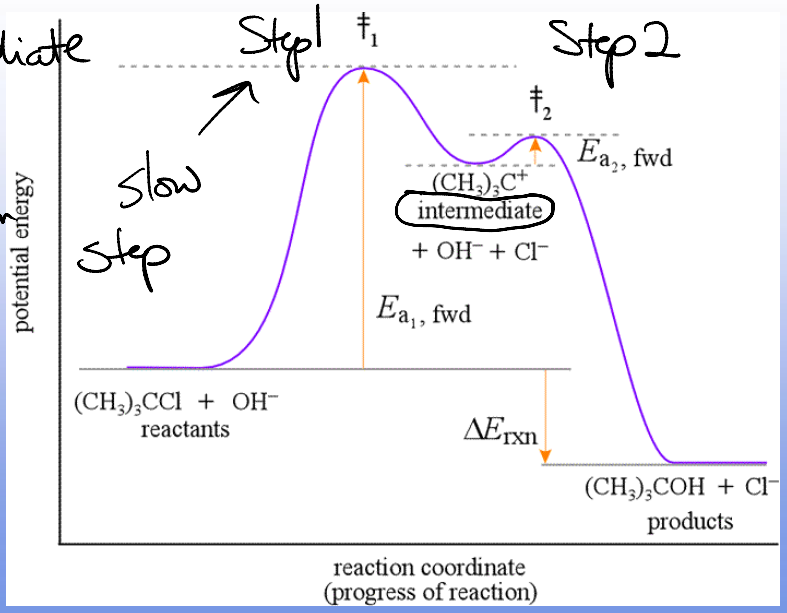
Transition State Theory



transition state vs intermediate

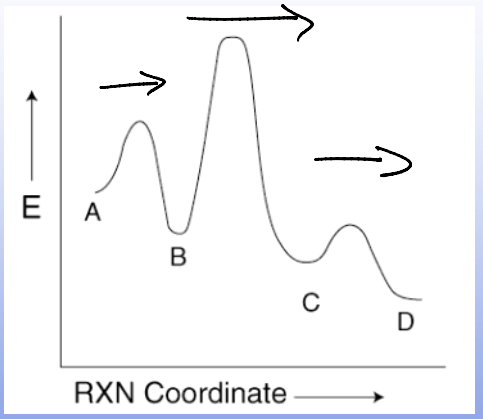
2 step mechanism

Transition State Theory



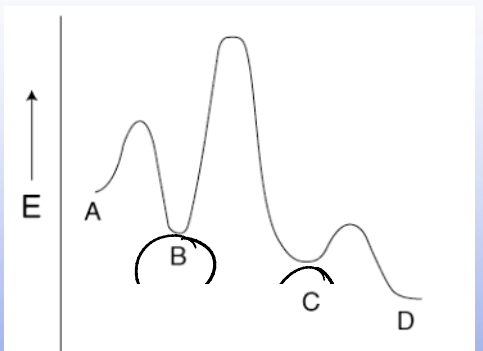
Transition State Theory

Look at the following graph:
The mechanism will have ___ steps:
a)1
b)2
c)3
d)4

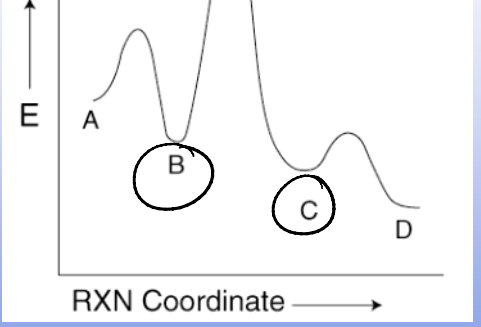


Transition State Theory

Look at the following graph:
The reaction will have ____ intermediates:
a)1
b)2
c)3
d)4



a)1
b)2
c)3
d)4

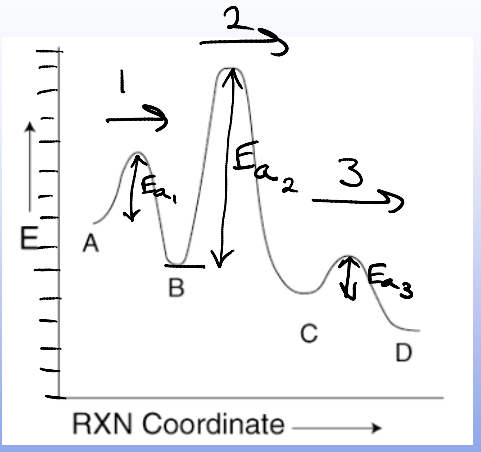


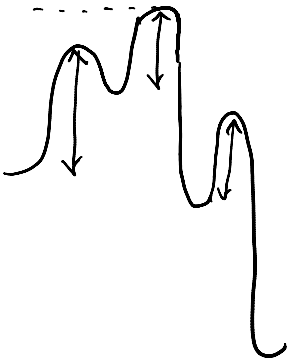
Transition State Theory

Look at the following graph:
The slow step will be ____:

a)1
b)2
c)3
d)4

3 different activation energies





Poll: Clicker Question 3

Which of the following factors that affect the rate of a reaction do so by changing the activation energy?

A. Increasing the temperature of the reaction mixture
more molecules overcome same E_a

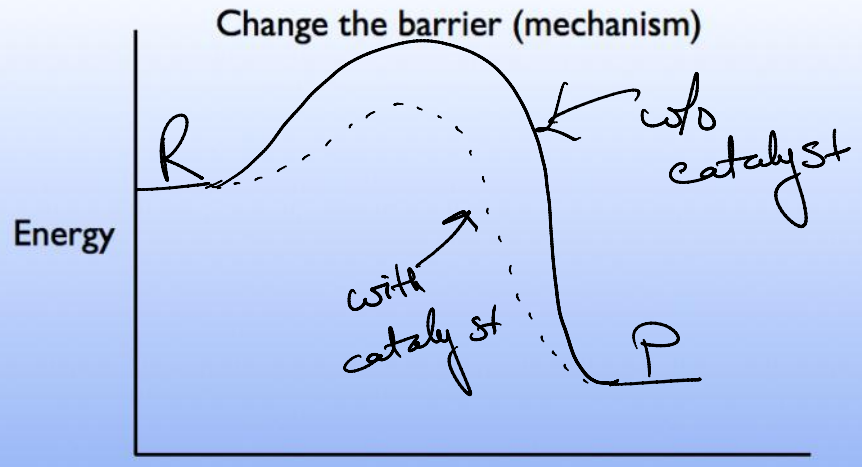
B. Increasing the surface area of a reactant
↳ pre exponential factor

C. Increasing the concentration of a reactant
↳ rate (not rate constant)

D. Adding a catalyst to the reaction mixture
new mechanism!

How else can affect k?

Change the barrier (mechanism)



DEMONSTRATION

Decomposition of Hydrogen Peroxide

$$H_2O_2(l) \longrightarrow O_2(g) + H_2O(l)$$

This reaction is very slow at room temperature
(thus you can get a bottle of H_2O_2 at the store)

What happens when I add the catalyst

$$H_2O_2 + MnO_2 + 2H^+ \longrightarrow Mn^{2+} + 2H_2O + O_2$$

new mechanism

$$Mn^{2+} + 2H_2O_2 \longrightarrow Mn(OH)_2 + 2H^+$$

$$Mn(OH)_2 + H_2O_2 \longrightarrow MnO_2 + 2H_2O$$

What happens when I add the catalyst

$$H_2O_2 + MnO_2 + 2H^+ \rightarrow Mn^{2+} + 2H_2O + O_2$$

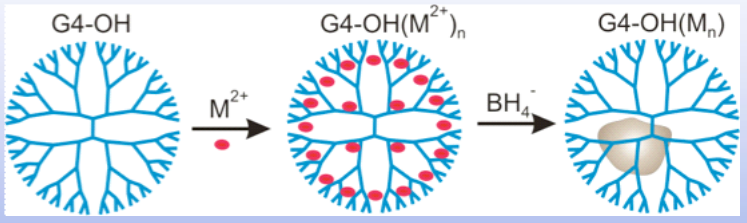
$$Mn^{2+} + 2H_2O_2 \rightarrow Mn(OH)_2 + 2H^+$$

$$Mn(OH)_2 + H_2O_2 \rightarrow MnO_2 + 2H_2O$$

new mechanism

Note: During the reaction the catalyst changes. But at the end it is back to the same compound!

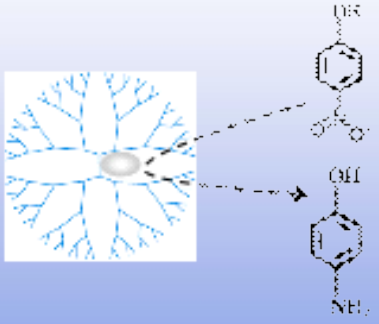
Freshman Research Initiative Project
Nanomaterials



Dendrimer encapsulated nanoparticle

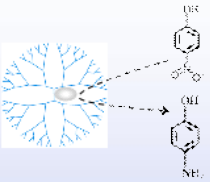
small metal particle can be made of a variety of materials (Au,Ag, Pd, Pt, Cu, Pt/Cu, Pd/Cu,....)

How good is the catalyst? Measure the kinetics.
Do the worksheet……



nitrophenol goes faster if nanoparticle catalyst

aminophenol



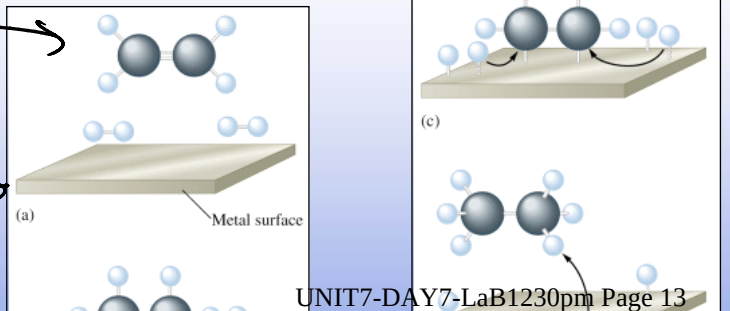
REPORT OUT ANSWERS!!

How do many catalysts work?

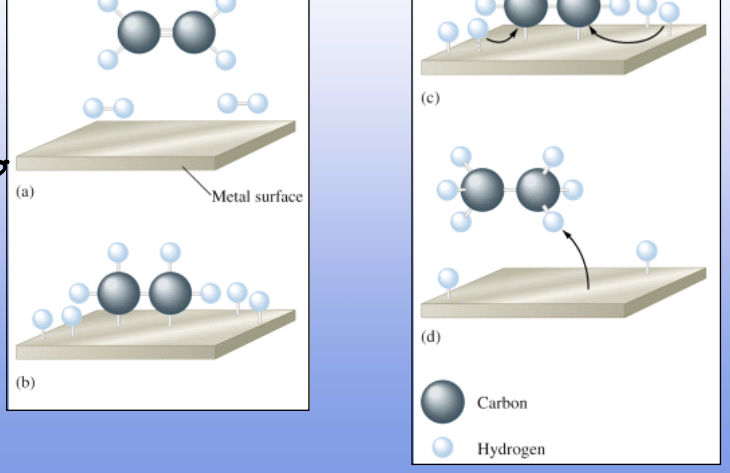
C_2H_4??

gas

solid



What is an example of a catalyst in everyday life?



Solid →

a catalyst in everyday life? Solid heterogeneous? in your car...

Catalytic Converter

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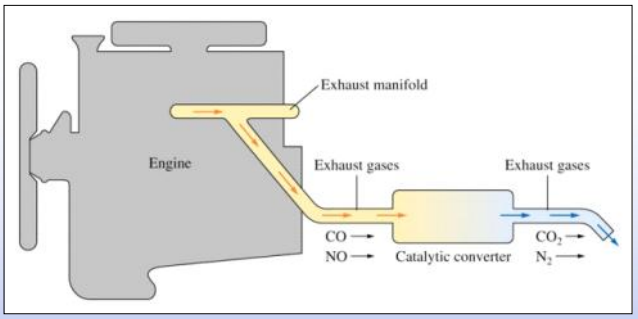

Catalyzes three chemical reactions

$2NO_x \rightarrow xO_2 + N_2$

$2CO + O_2 \rightarrow 2CO_2$

$2C_xH_y + (2x+y/2)O_2 \rightarrow 2xCO_2 + yH_2O$

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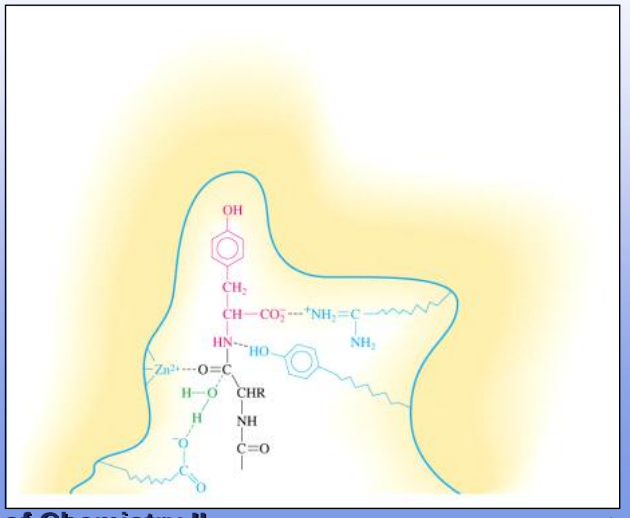
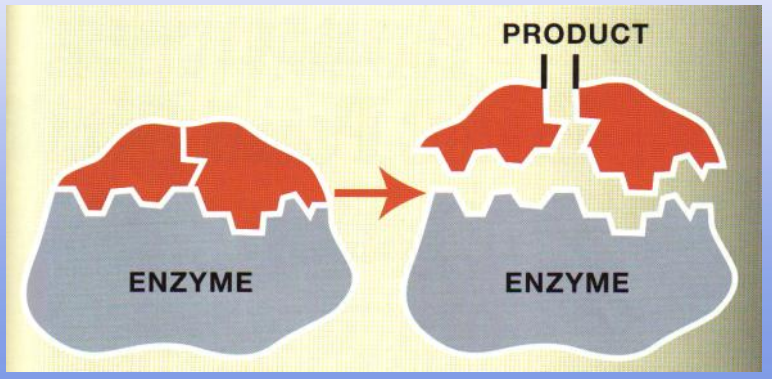
Enzymes
Biological Catalysts



Substrate + Enzyme = Complex = Product + Enzyme

S + E = [SE] = P + E



What did we learn today?

Recall and explain why certain factors such as concentration, temperature, medium and presence of catalyst will affect the speed of a chemical change.
Interpret a reaction coordinate diagram and determine if such a diagram Supports a given mechanism, including the concept of the transition state and the reaction intermediate
Understand the concept of activation energy in the context of the transition State and be able to calculate the activation energy given some experimental data
Recall, manipulate and properly employ the Arrhenius Law to determine various unknowns, including reaction running at different temperature and vice versa.
Explain the function of a catalysts.