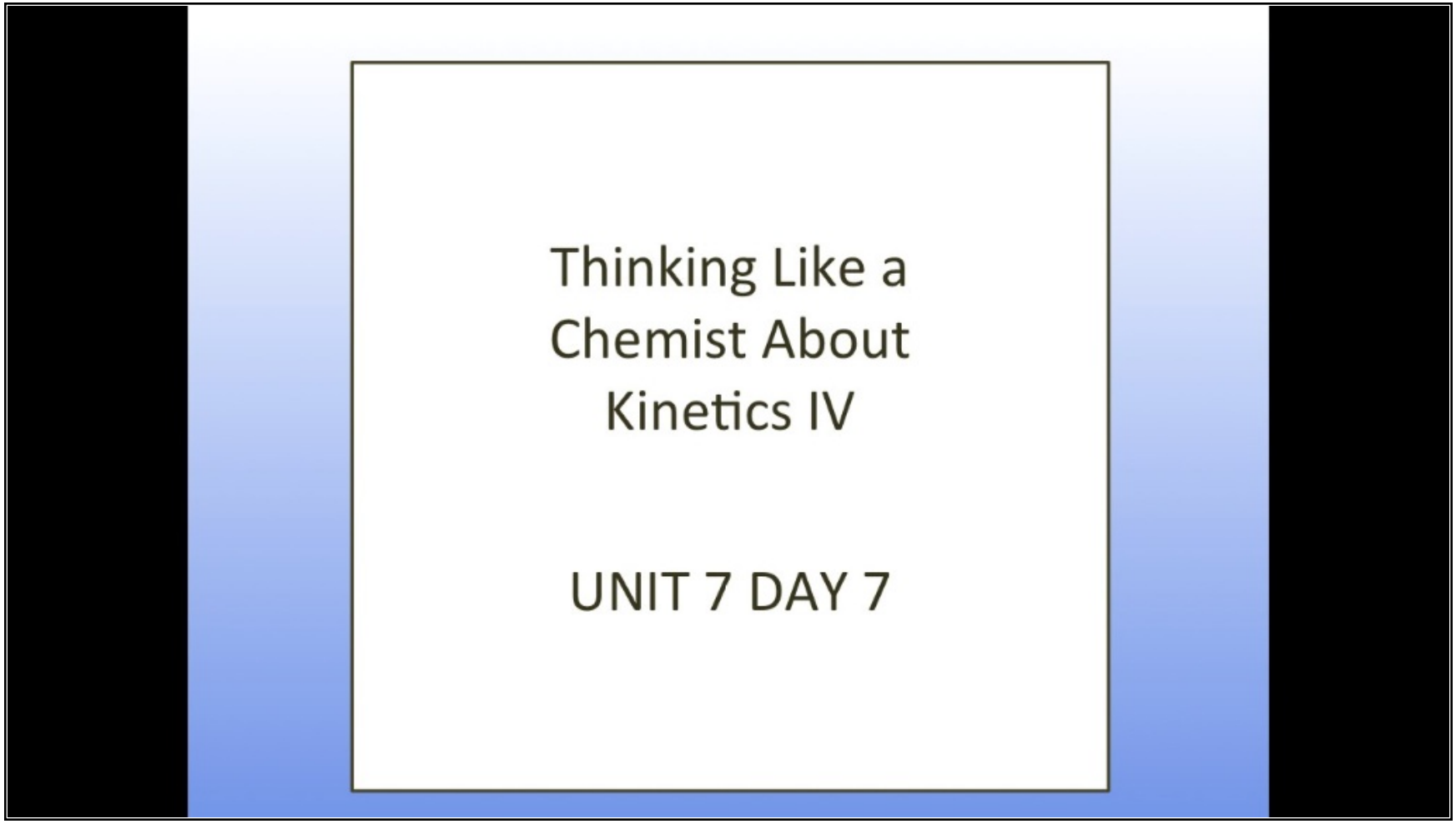
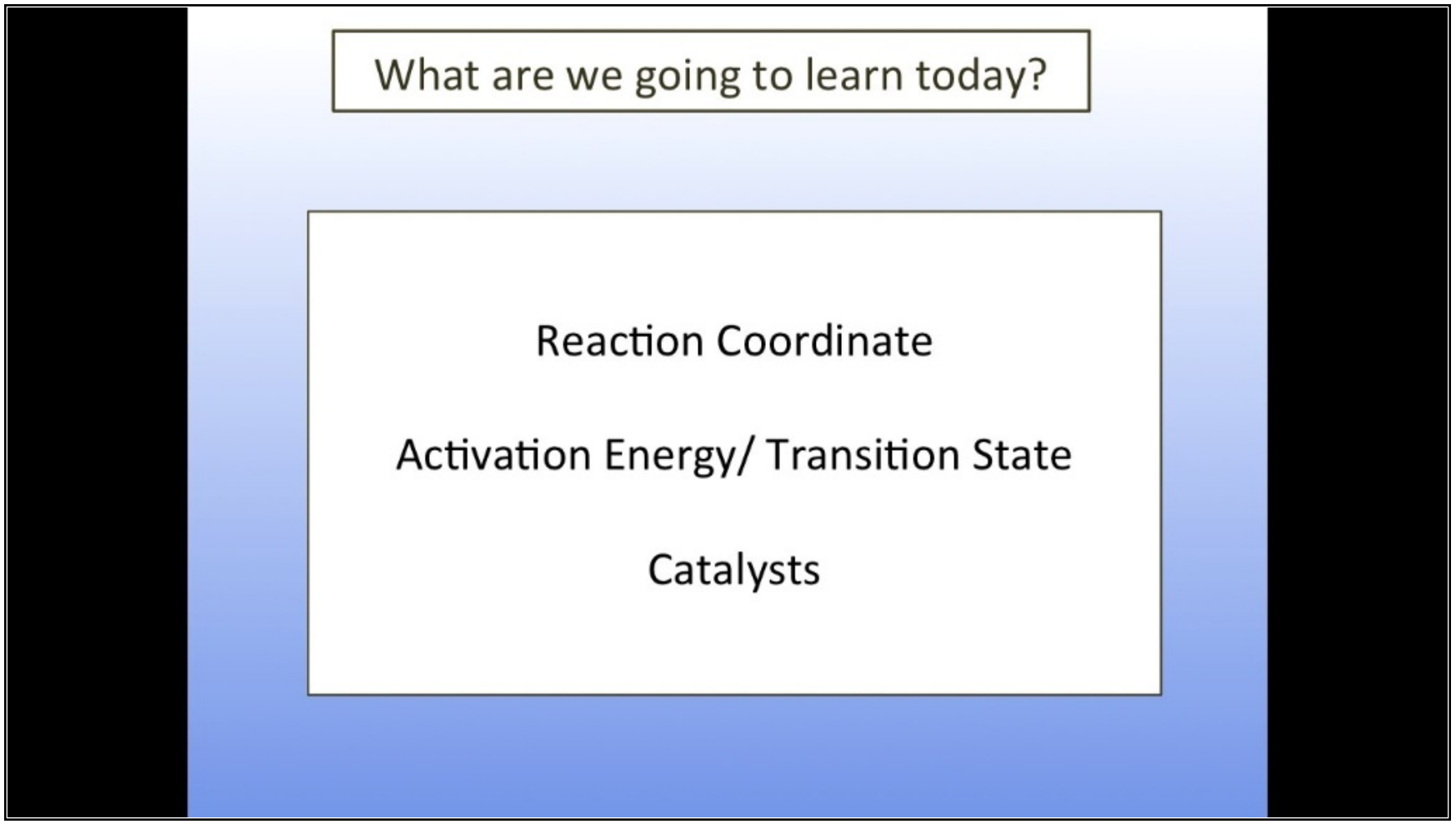
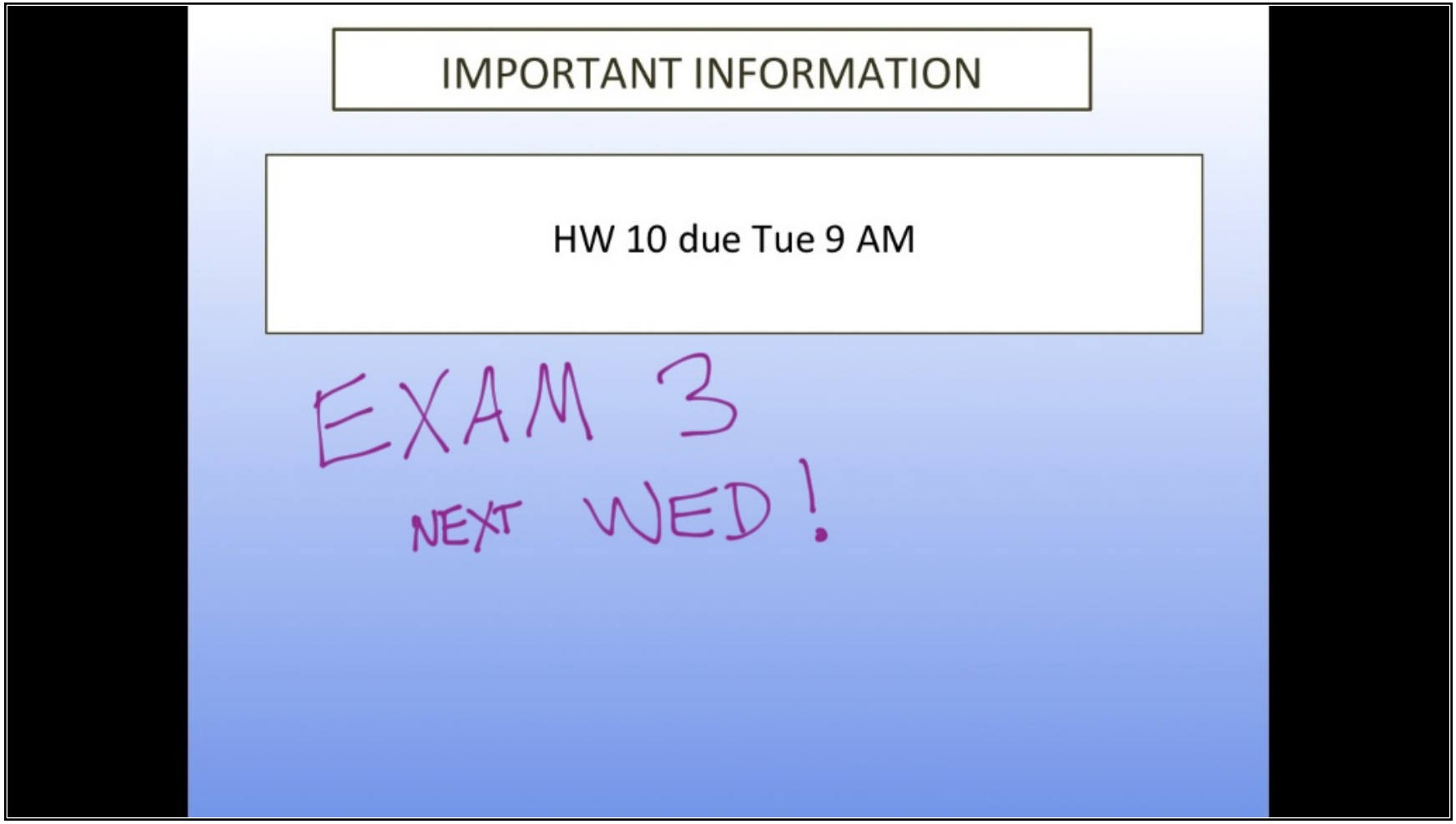
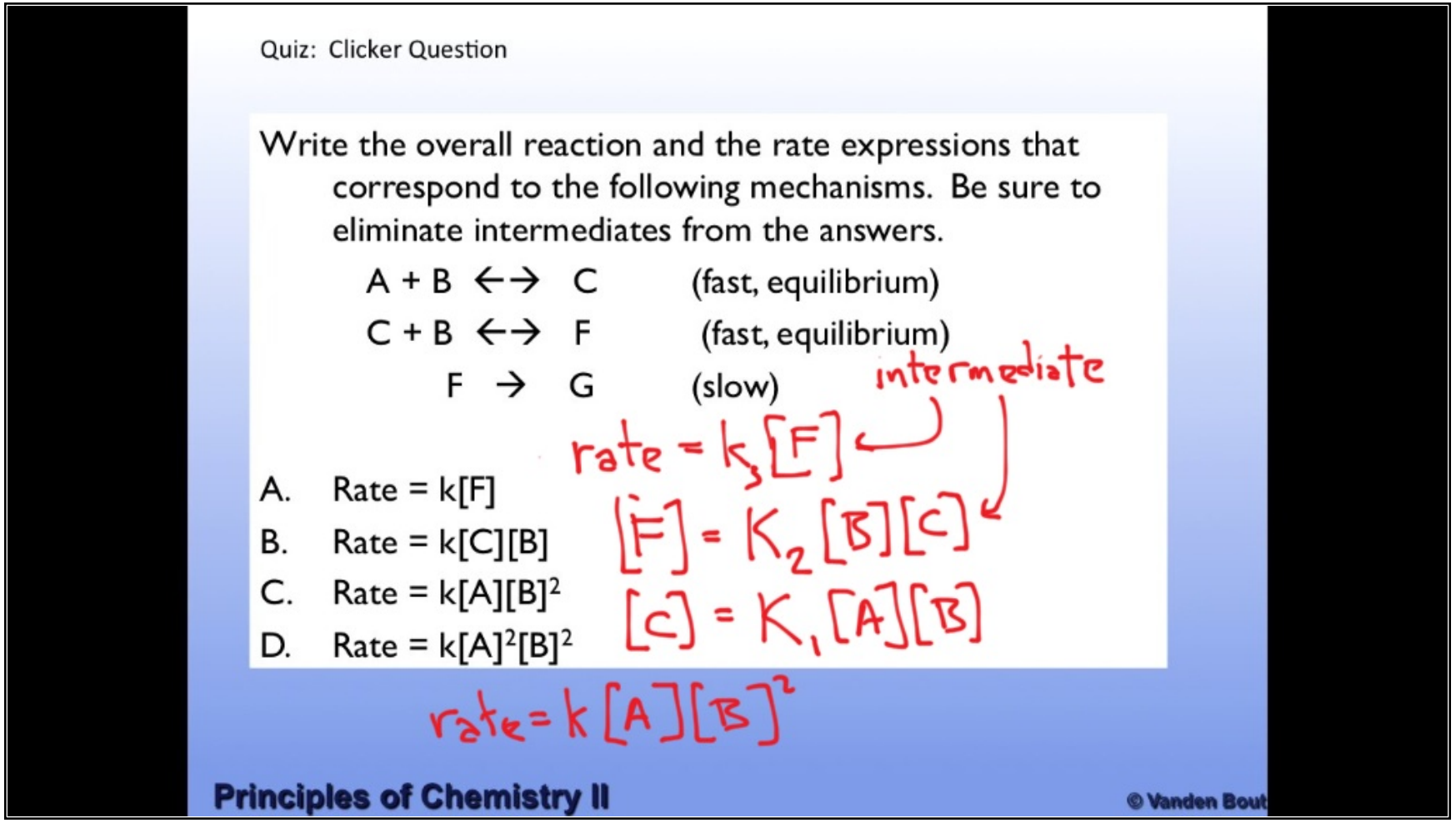

Thinking Like a
Chemist About
Kinetics IV
UNIT 7 DAY 7


What are we going to learn today?
Reaction Coordinate
Activation Energy/ Transition State
Catalysts


IMPORTANT INFORMATION
HW 10 due Tue 9 AM
EXAM 3
NEXT WED!


Quiz: Clicker Question
Write the overall reaction and the rate expressions that correspond to the following mechanisms. Be sure to eliminate intermediates from the answers.
A + B ←→ C (fast, equilibrium)
C + B ←→ F (fast, equilibrium)
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
rate = k₃[F]
[F] = K₂[B][C]
[C] = K₁[A][B]
rate = k[A][B]²
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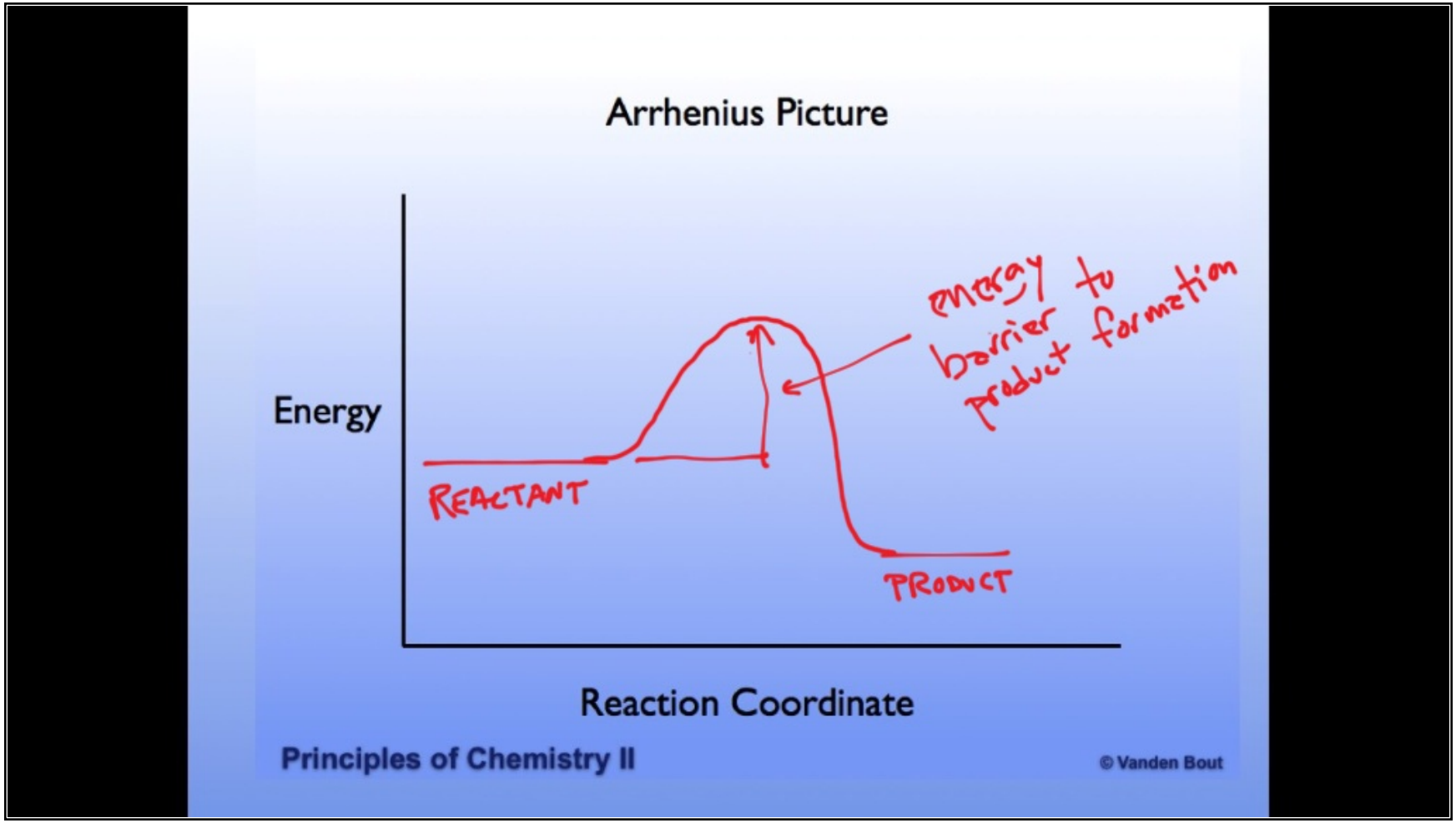
Arrhenius Picture
Energy
energy to barrier to product formation
REACTANT
PRODUCT
Reaction Coordinate
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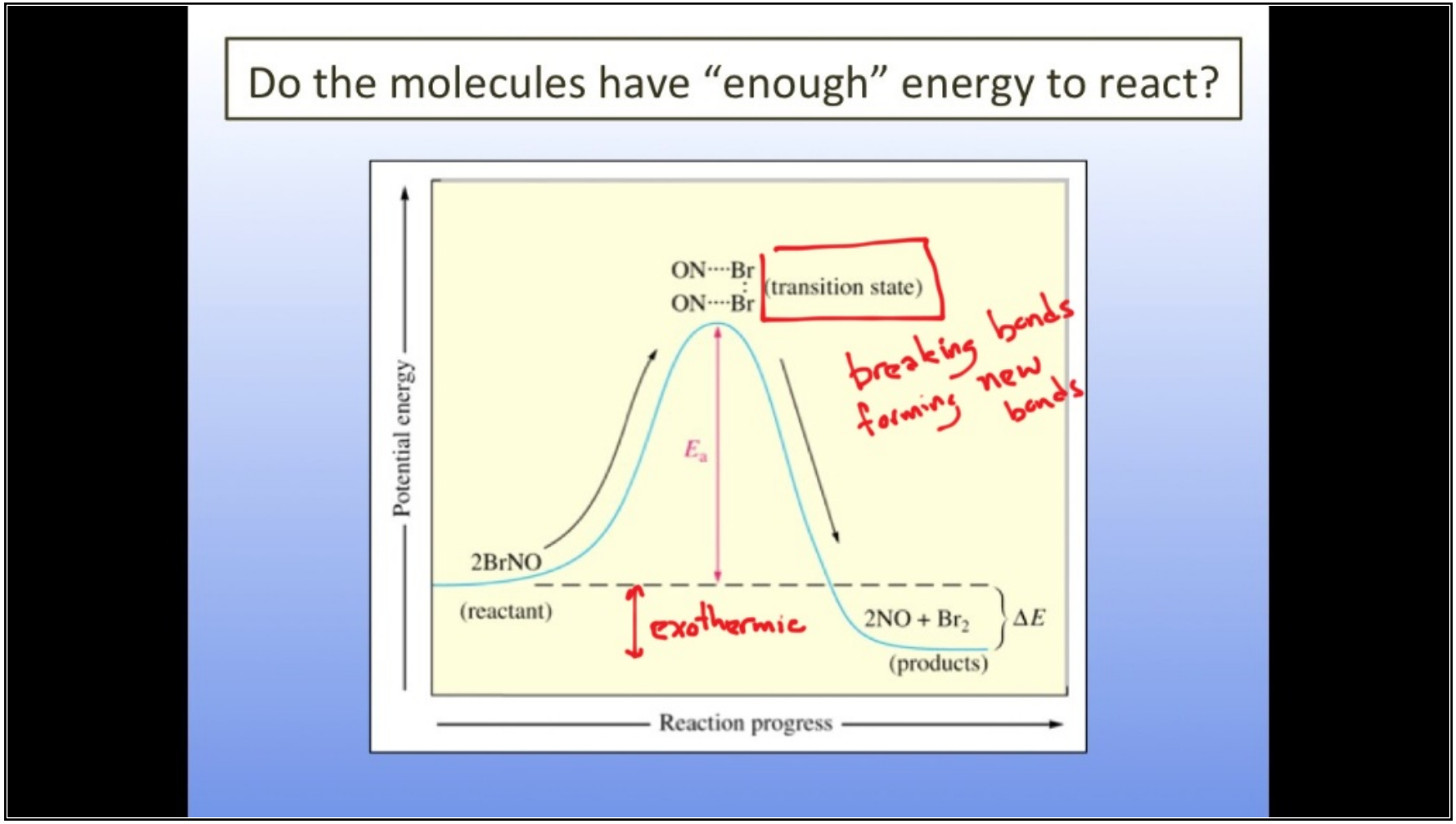
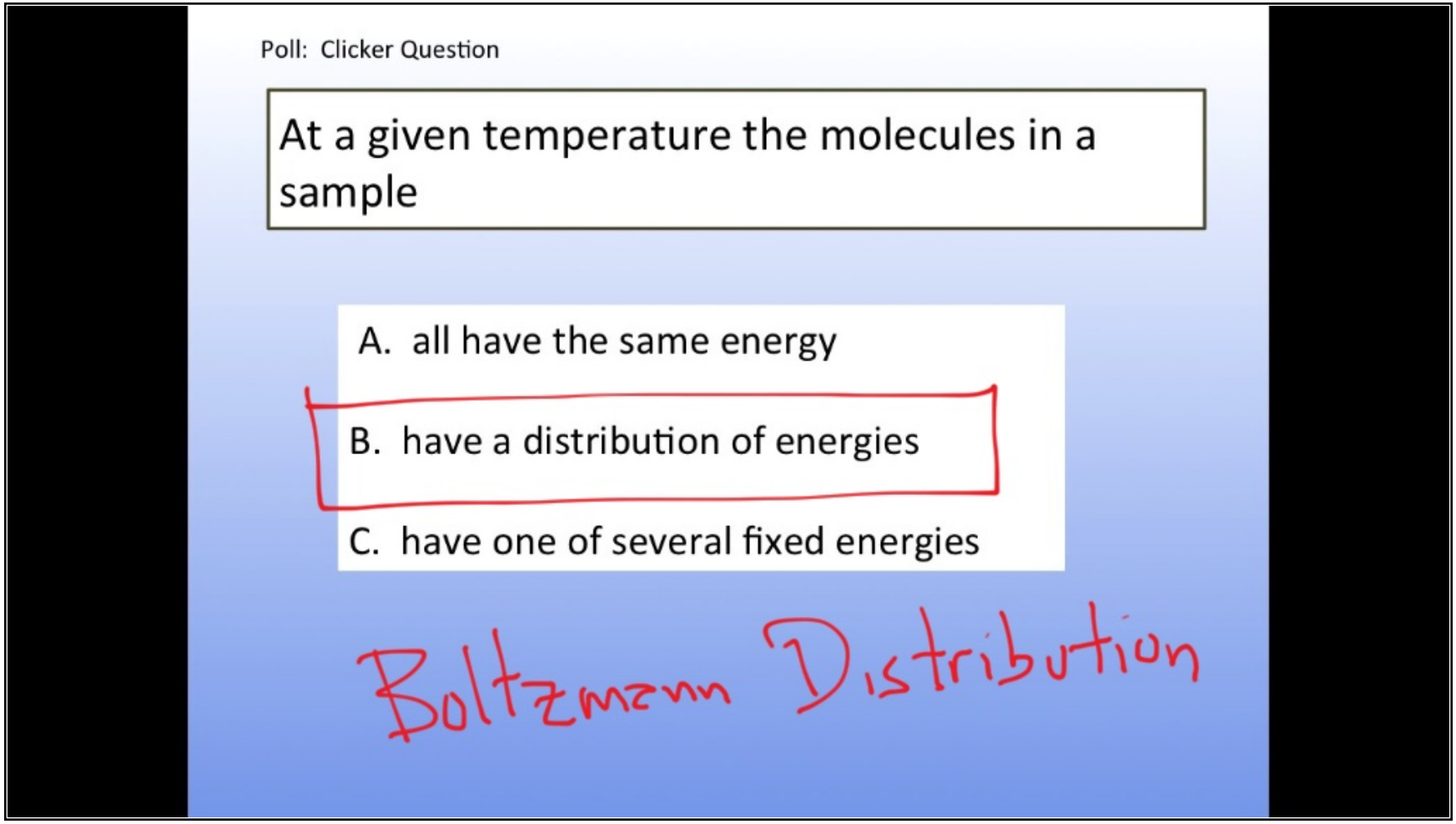
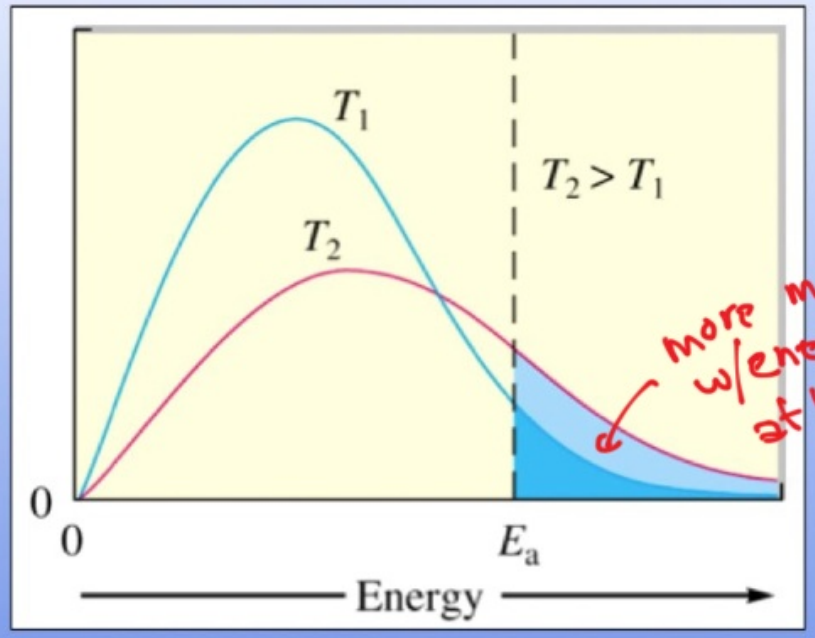
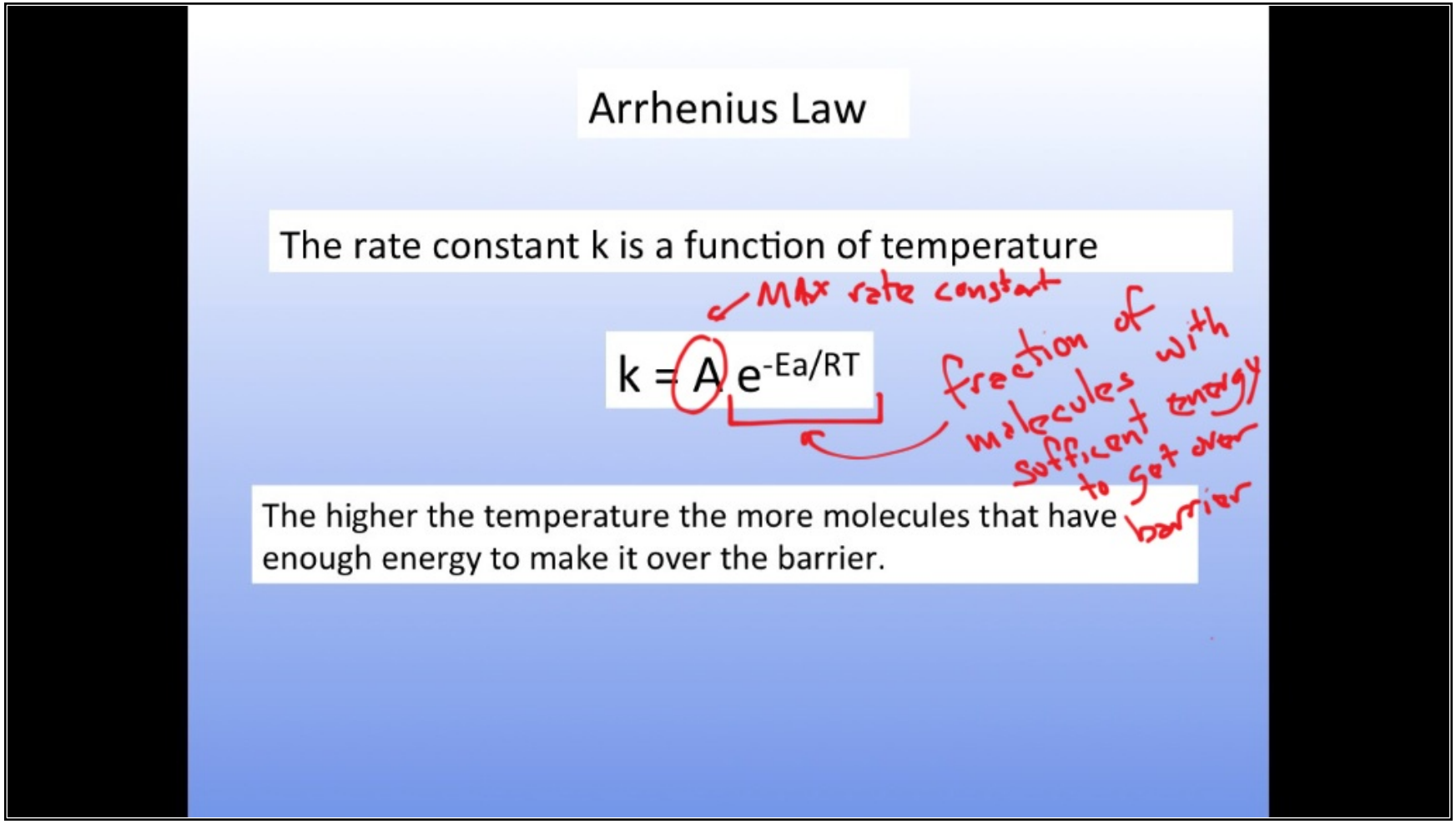

Do the molecules have "enough" energy to react?
ON····Br
ON····Br
(transition state)
breaking bonds
forming new bonds
Potential energy
E_a
2BrNO
(reactant)
exothermic
2NO + Br_2
(products)
ΔE
Reaction progress


Poll: Clicker Question
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
Boltzmann Distribution

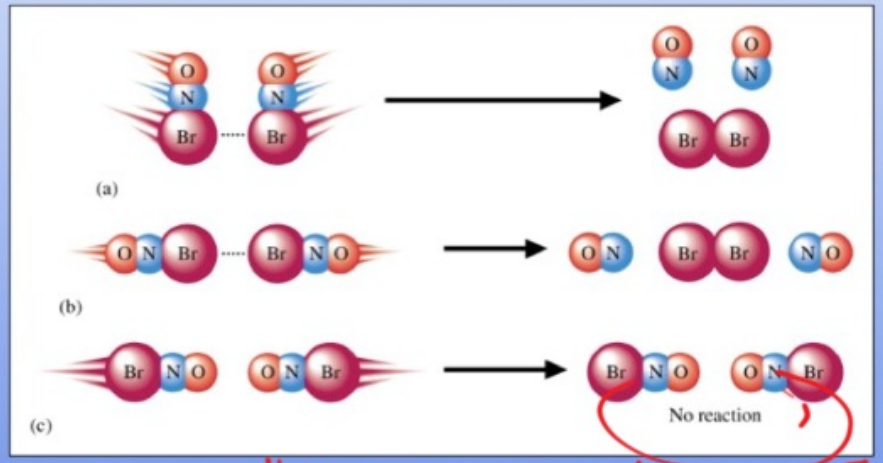
How many molecules have enough energy to get over the barrier?




Arrhenius Law
The rate constant k is a function of temperature
Max rate constant
$k = A e^{-Ea/RT}$
fraction of molecules with sufficient energy to get over barrier
The higher the temperature the more molecules that have enough energy to make it over the barrier.

What is A?

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



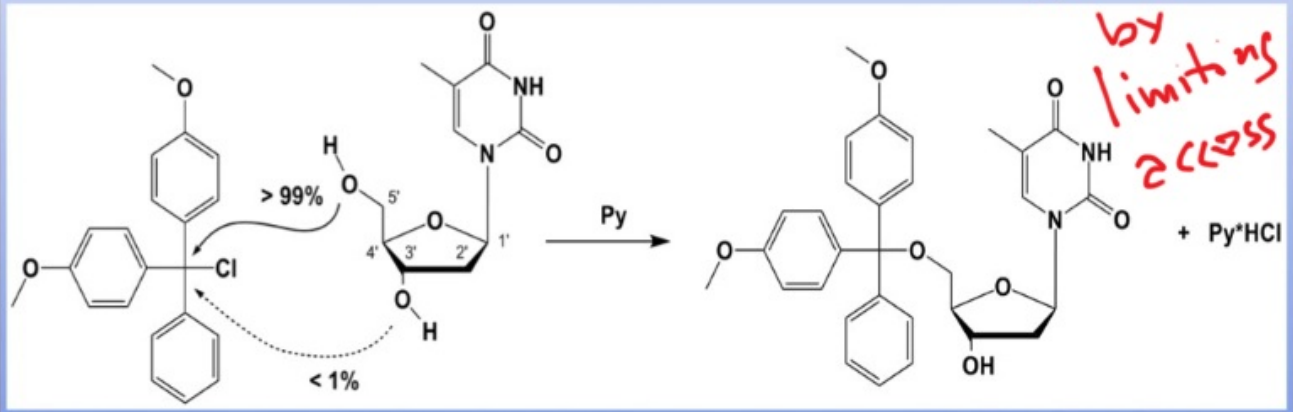
Some collisions = no reaction even $E > E_a$

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

Useful idea

Control chemistry by limiting access



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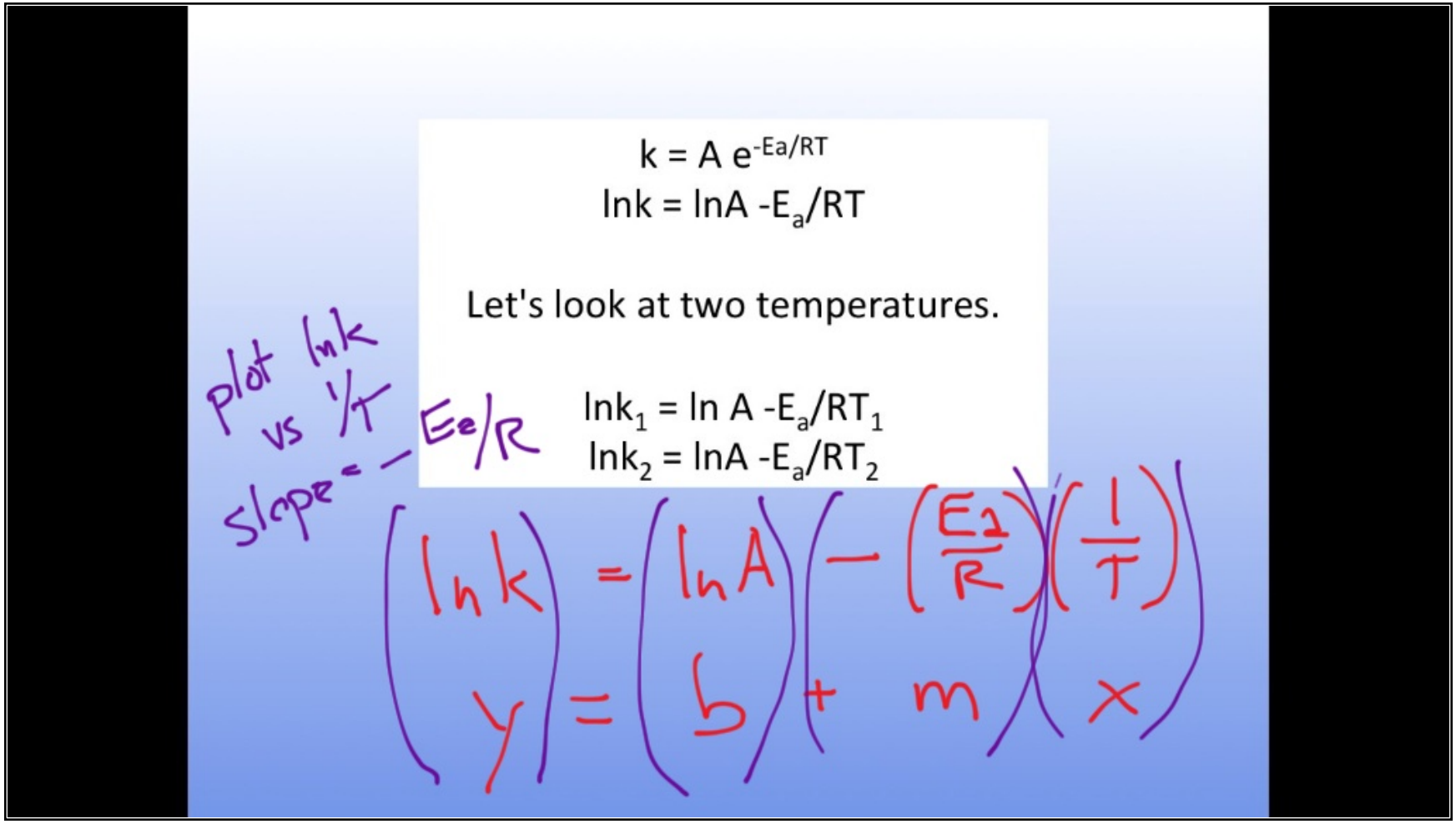
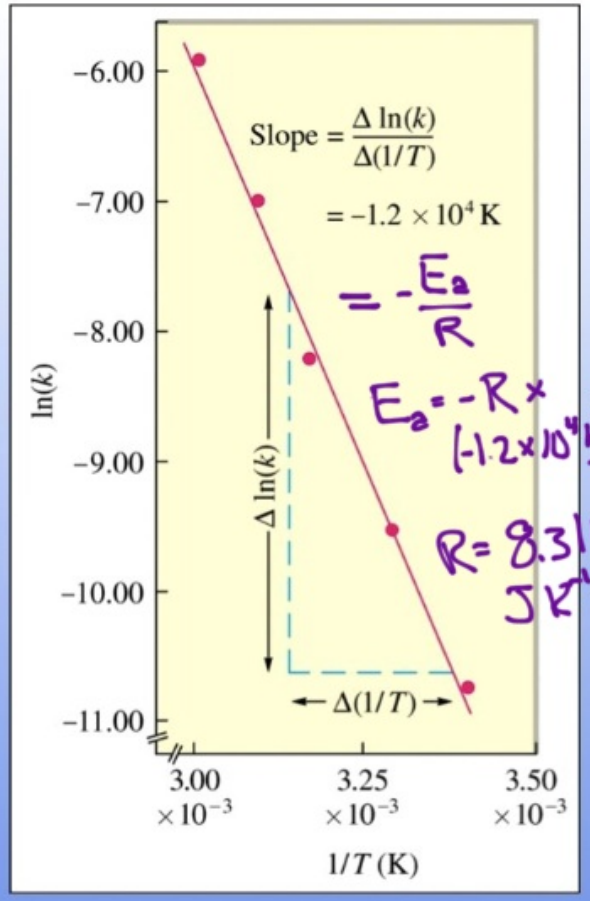

$k = A\, e^{-Ea/RT}$
$\ln k = \ln A - E_a/RT$
Let's look at two temperatures.
$\ln k_1 = \ln A - E_a/RT_1$
$\ln k_2 = \ln A - E_a/RT_2$
plot lnk vs 1/T
slope = $-E_a/R$
$(\ln k) = (\ln A) - \left(\frac{E_a}{R}\right)\left(\frac{1}{T}\right)$
$y = b + m\,x$



Poll: Clicker Question

What is the activation energy for this reaction?

$= -\frac{E_a}{R}$

$E_a = -R \times (-1.2 \times 10^4\ K)$

$R = 8.314\ J\ K^{-1}\ mol^{-1}$

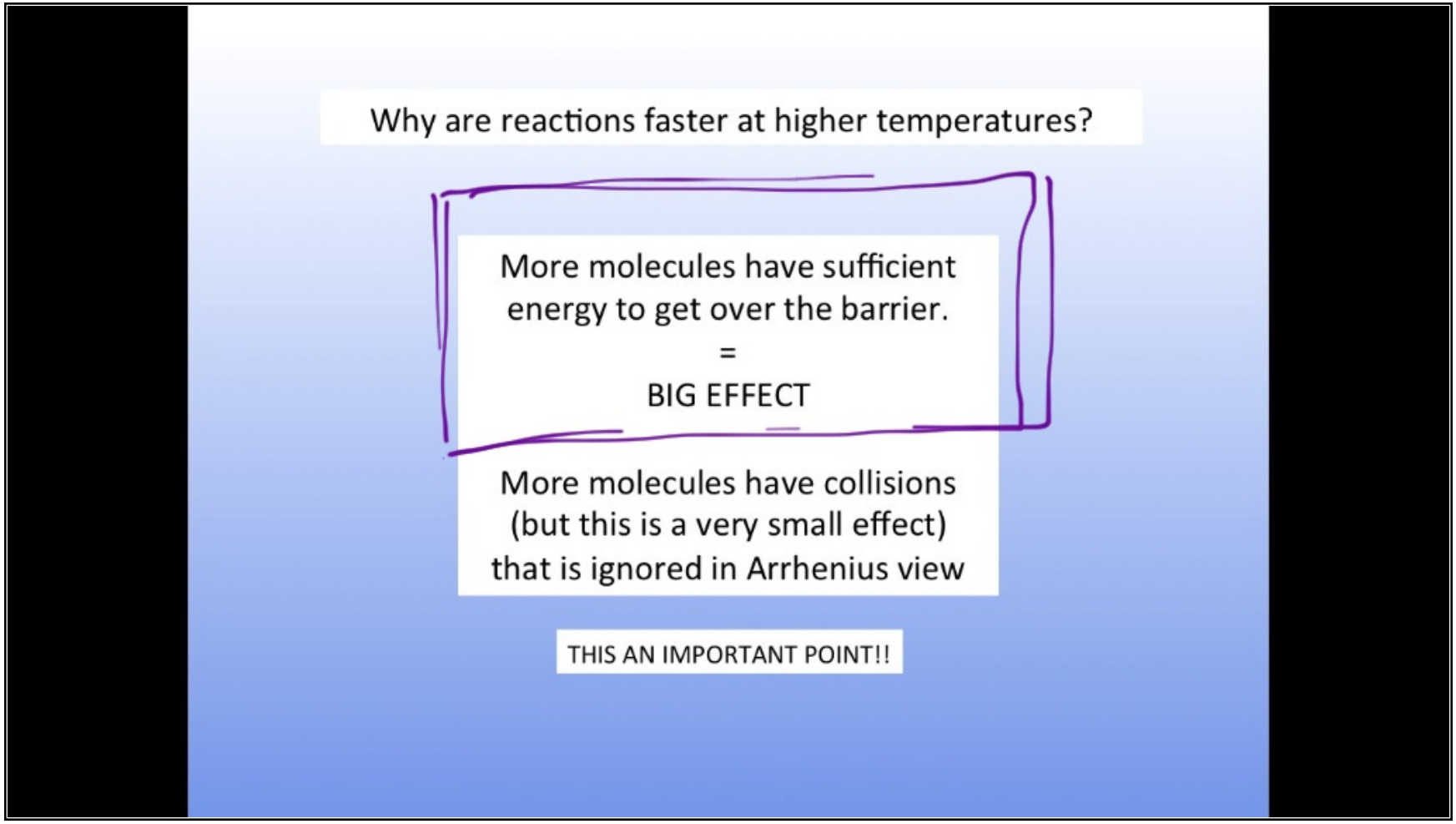
A. -1.2×10^4 K

B. 1×10^5 J mol^{-1}

C. 1.2×10^4 J mol^{-1}

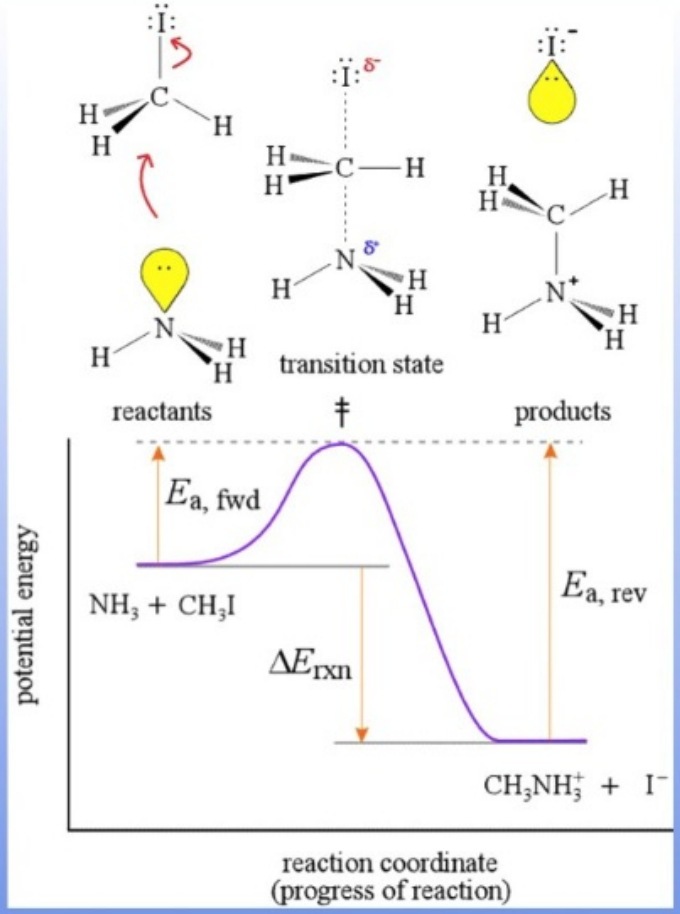
D. 1×10^5 K

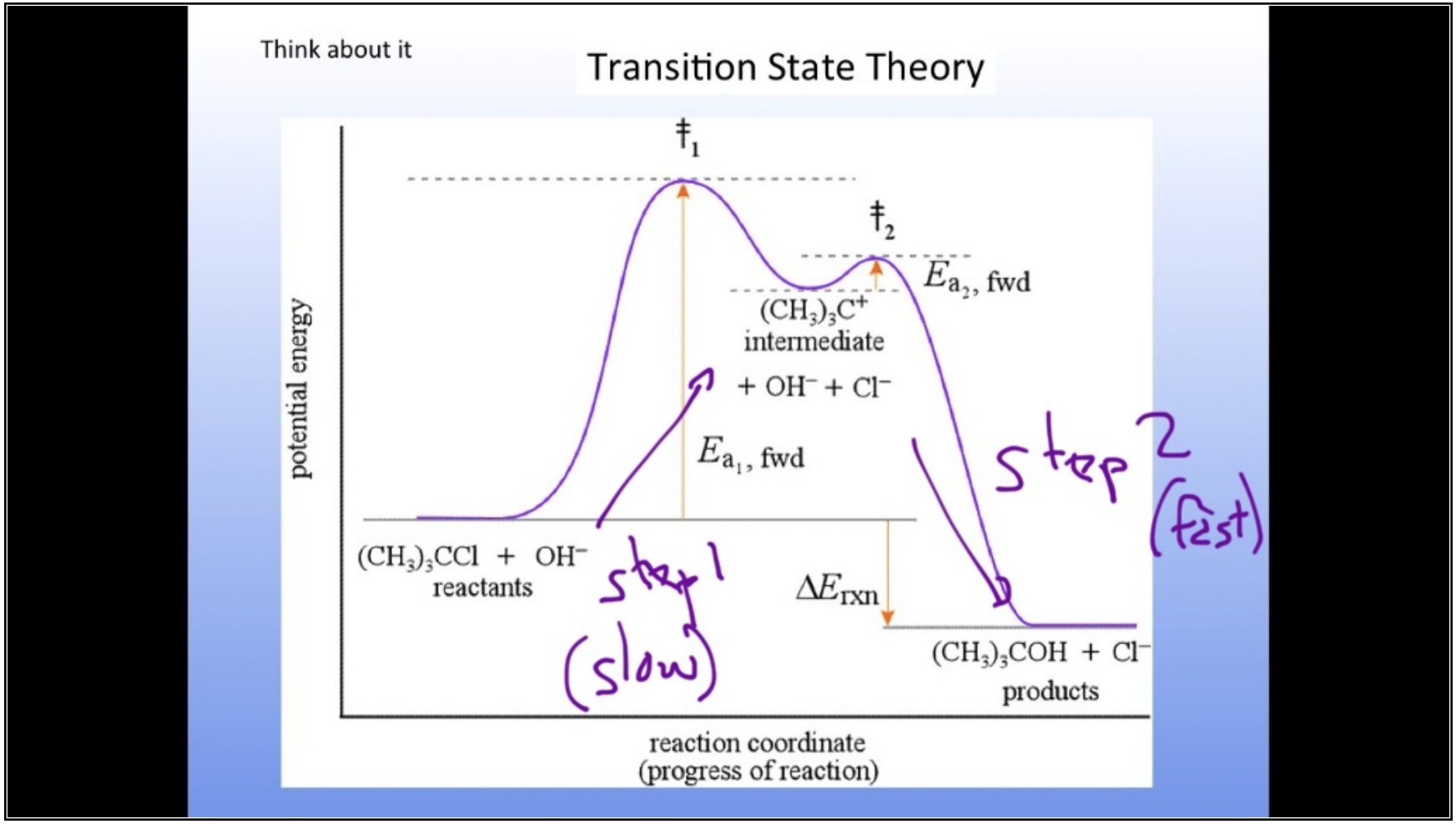
E. -1×10^2 kJ mol^{-1}


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

1 step
1 barrier
1 transition state



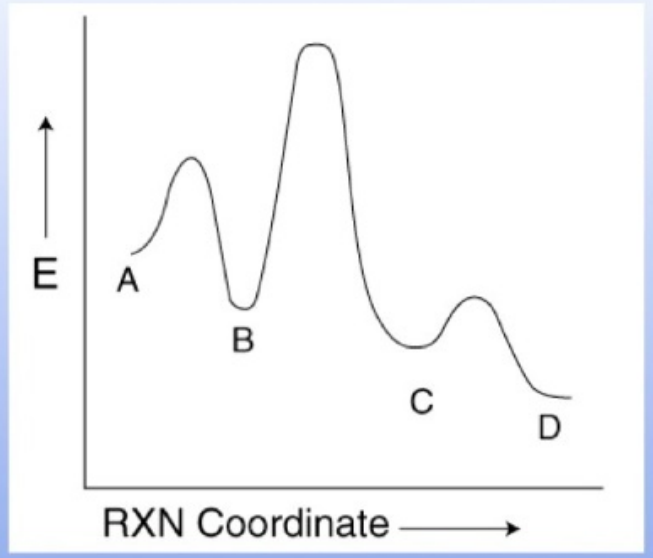

Think about it
Transition State Theory
‡1
‡2
Ea2, fwd
(CH3)3C+
intermediate
+ OH− + Cl−
Ea1, fwd
potential energy
(CH3)3CCl + OH−
reactants
ΔErxn
(CH3)3COH + Cl−
products
reaction coordinate
(progress of reaction)
step 1
(slow)
step 2
(fast)

Poll: Clicker Question

Transition State Theory

According to the graph, the mechanism for this reaction will have ___ steps.

A. 1
B. 2
C. 3
D. 4



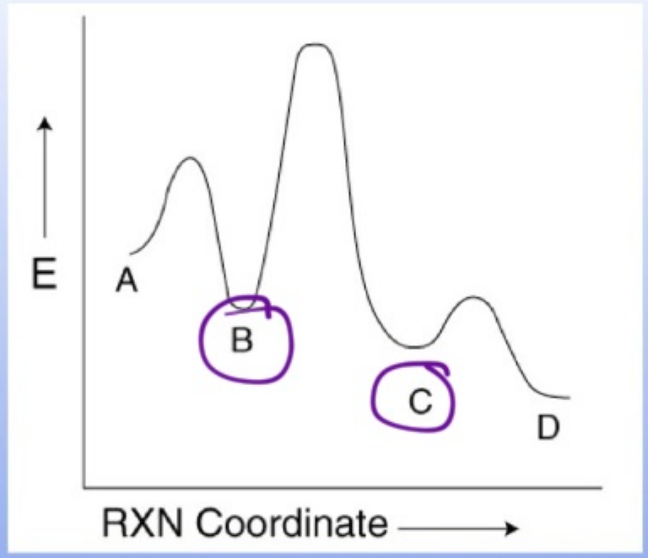
A → B B → C C → D

Poll: Clicker Question

Transition State Theory

According to the graph, the reaction will have ___ intermediates.

A. 1
B. 2
C. 3
D. 4

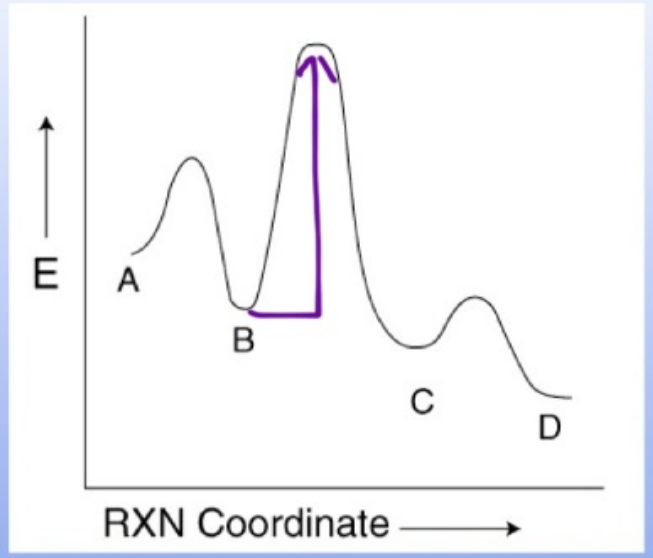


Poll: Clicker Question

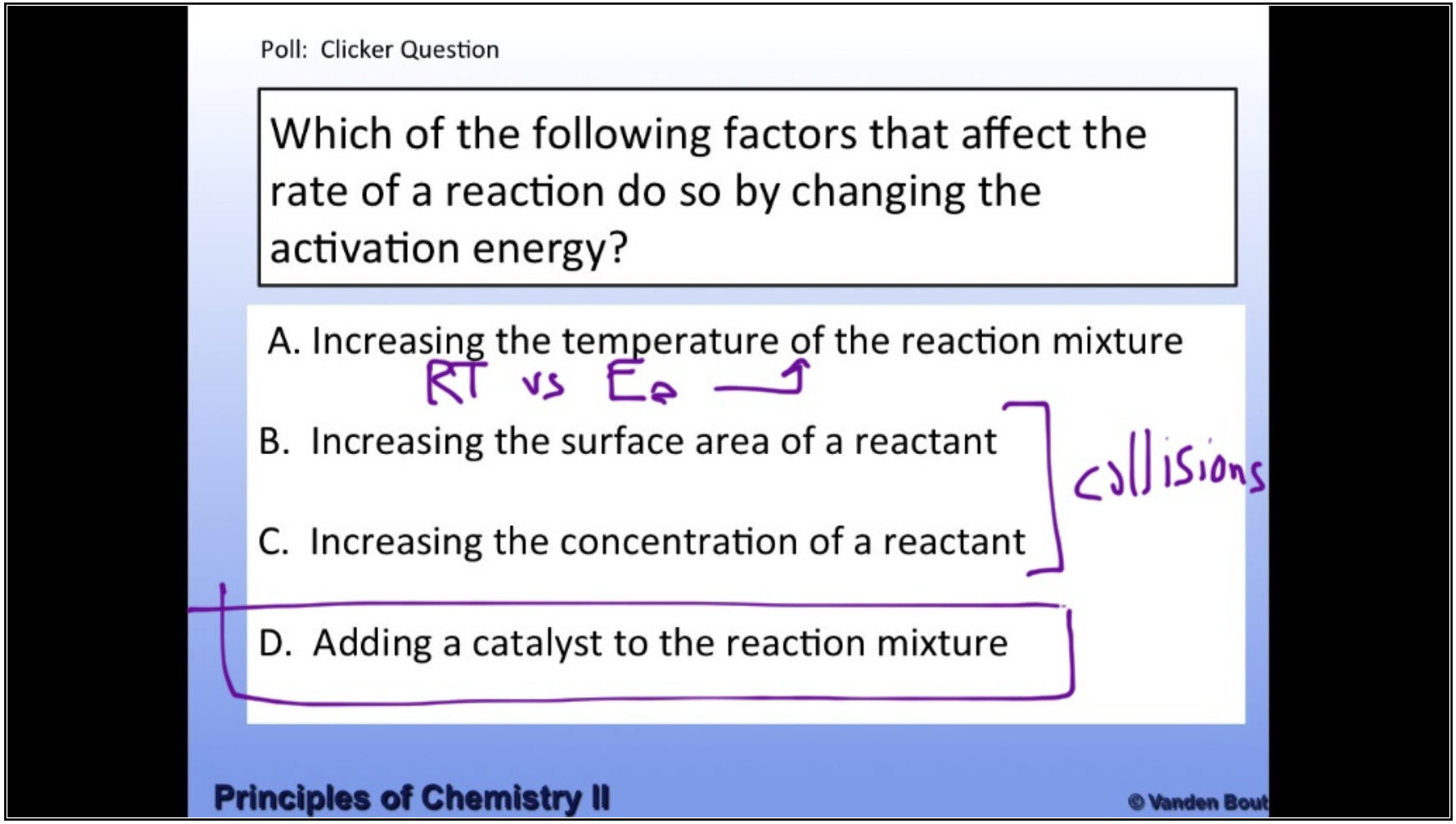
Transition State Theory

According to the graph, the slow step will be.

A. step 1, A → B
B. step 2, B → C
C. step 3, C → D



Biggest Barrier


Poll: Clicker Question
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
RT vs Ea
B. Increasing the surface area of a reactant
C. Increasing the concentration of a reactant
collisions
D. Adding a catalyst to the reaction mixture
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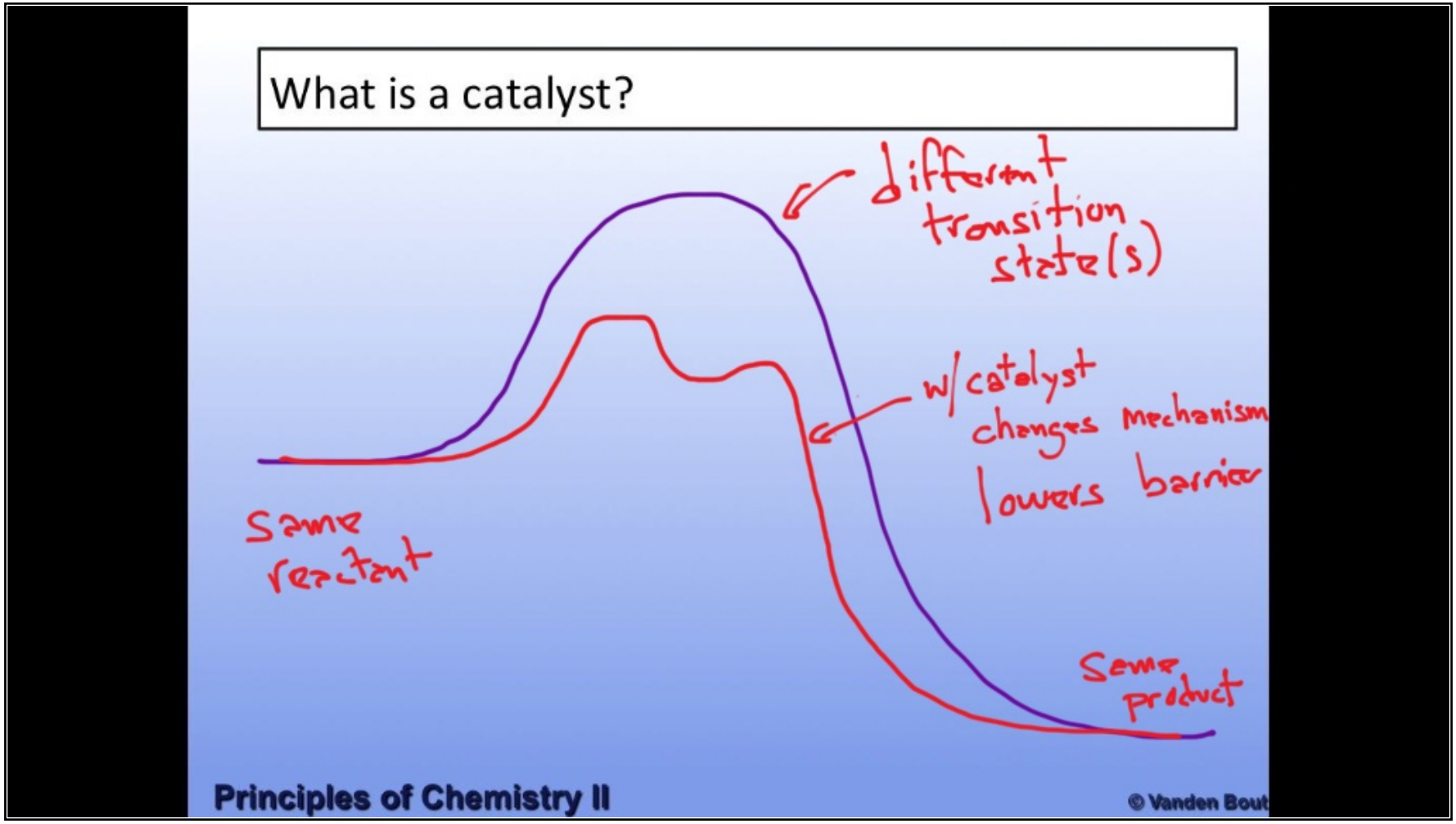
What is a catalyst?
different transition state(s)
w/ catalyst changes mechanism lowers barrier
Same reactant
Same product
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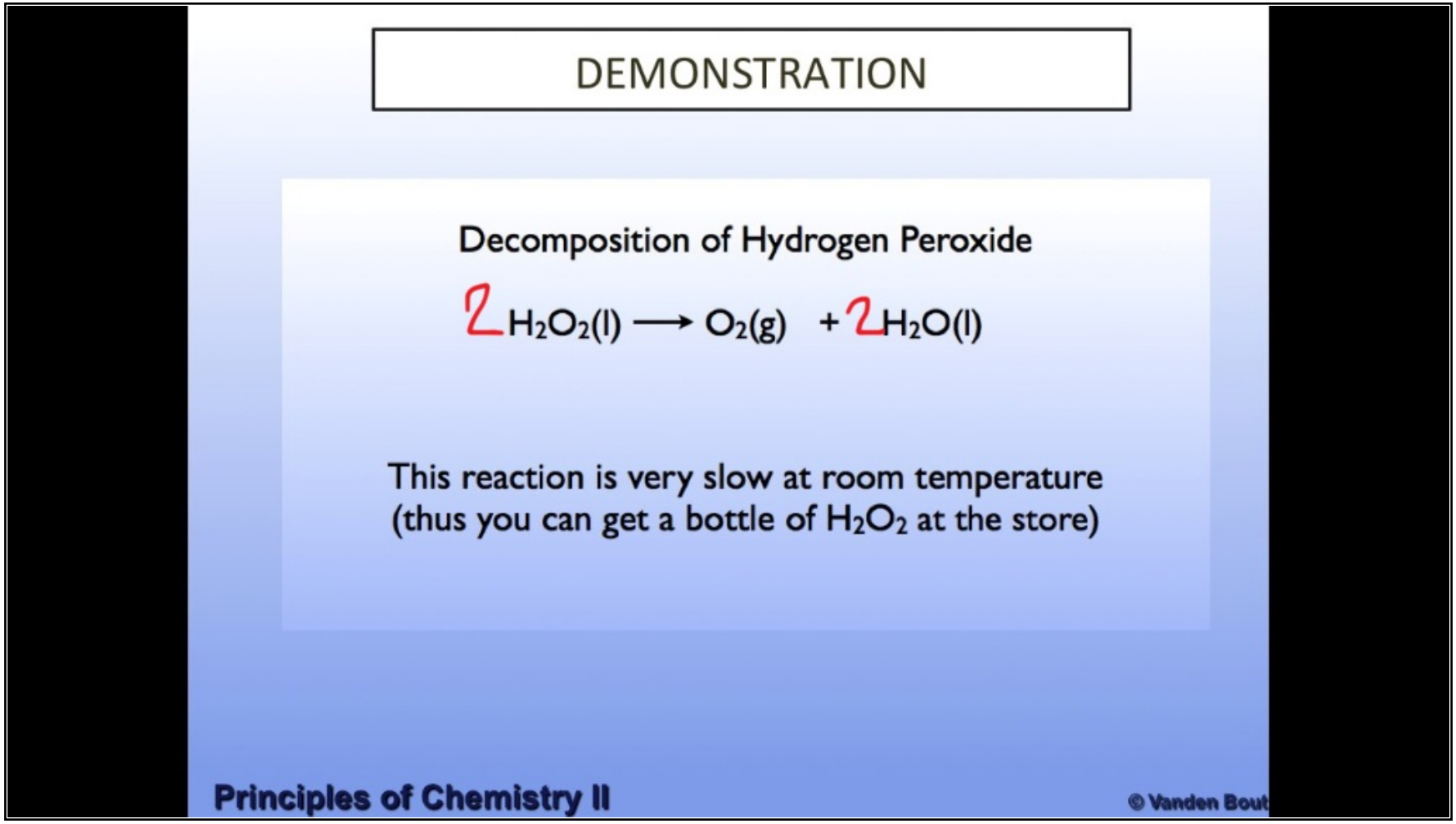
DEMONSTRATION
Decomposition of Hydrogen Peroxide
2 H2O2(l) → O2(g) + 2 H2O(l)
This reaction is very slow at room temperature
(thus you can get a bottle of H2O2 at the store)
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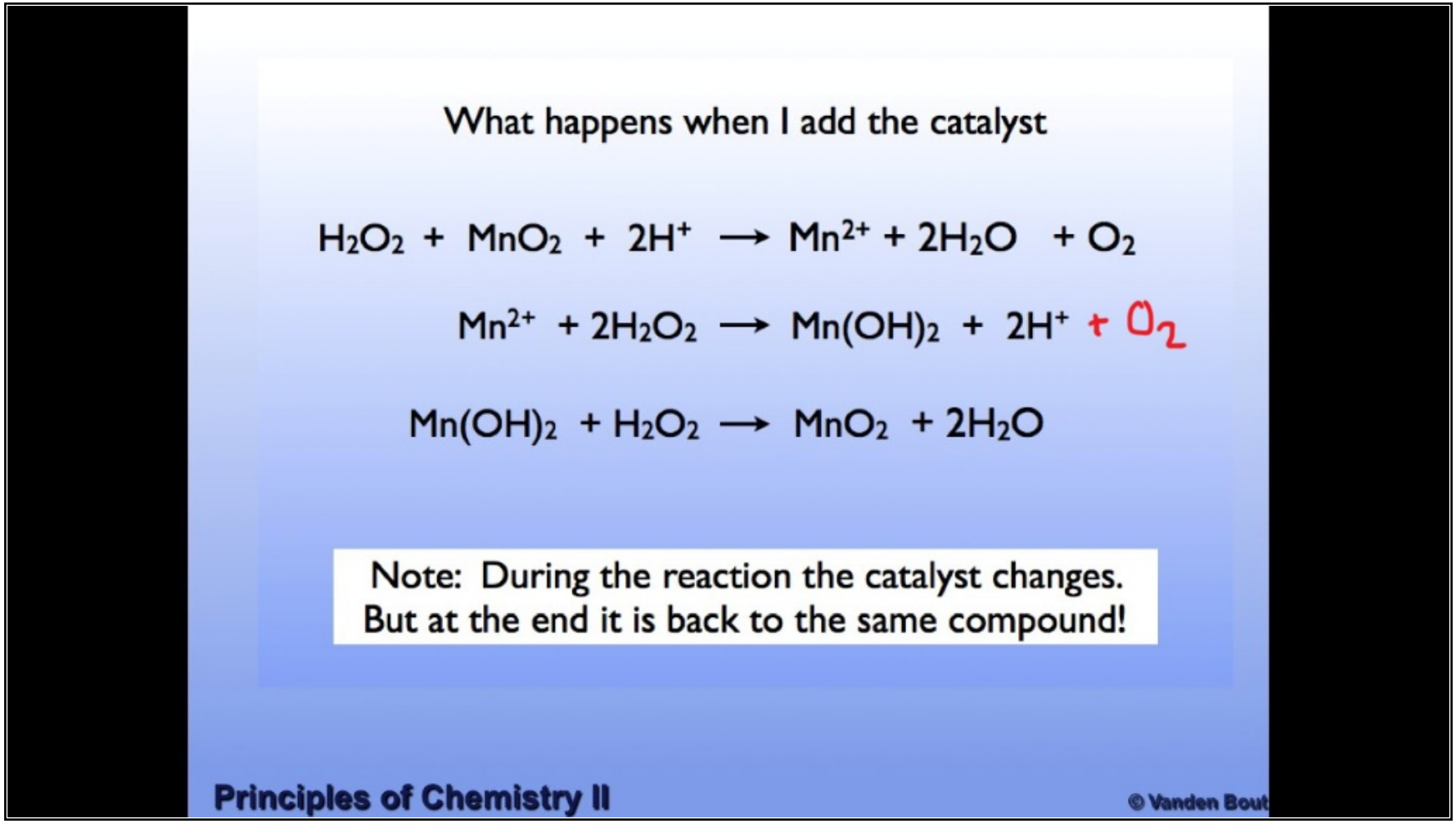
What happens when I add the catalyst
$H_2O_2 + MnO_2 + 2H^+ \rightarrow Mn^{2+} + 2H_2O + O_2$
$Mn^{2+} + 2H_2O_2 \rightarrow Mn(OH)_2 + 2H^+ + O_2$
$Mn(OH)_2 + H_2O_2 \rightarrow MnO_2 + 2H_2O$
Note: During the reaction the catalyst changes.
But at the end it is back to the same compound!
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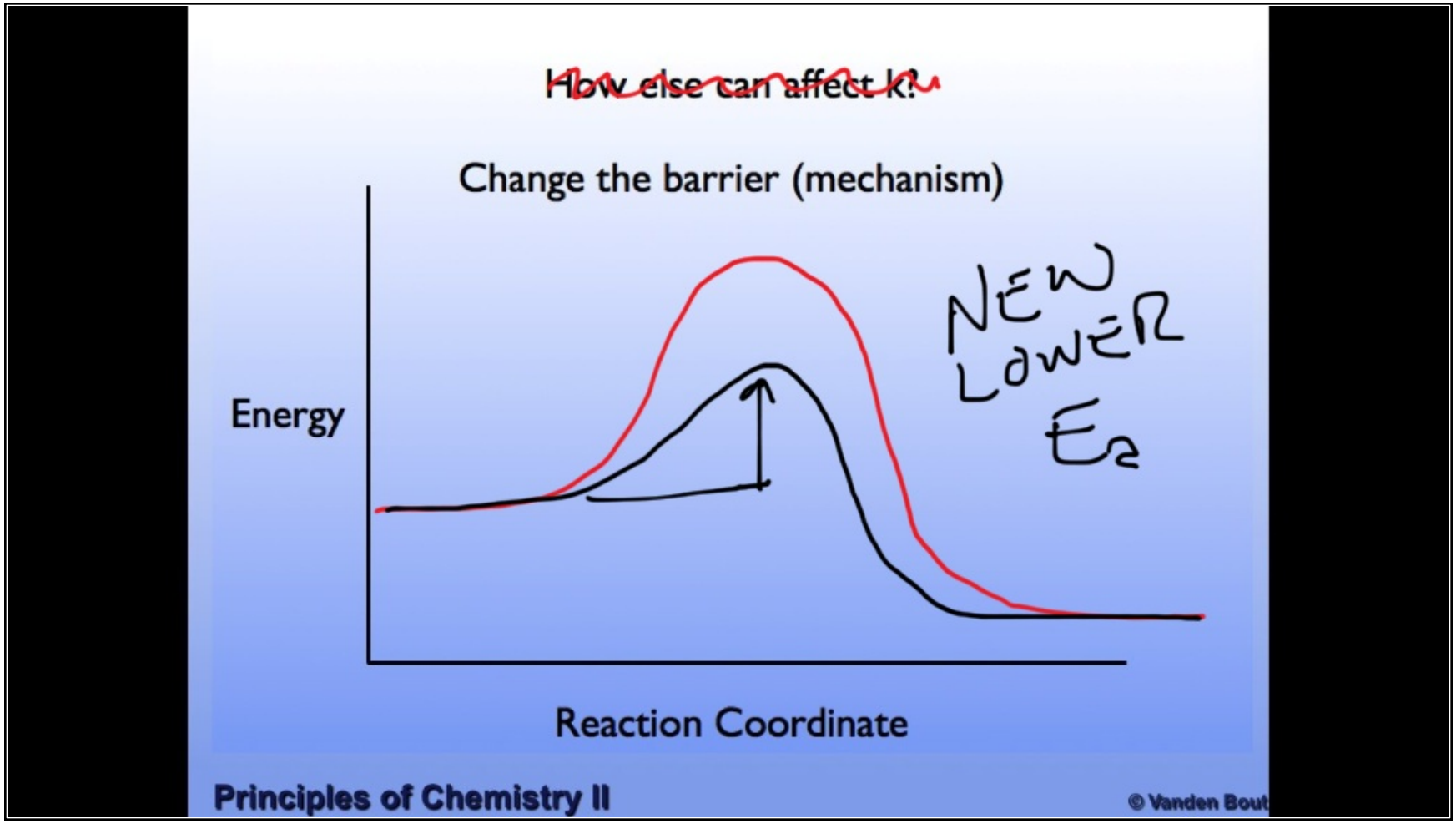
How else can affect k?
Change the barrier (mechanism)
NEW
LOWER
E_a
Energy
Reaction Coordinate
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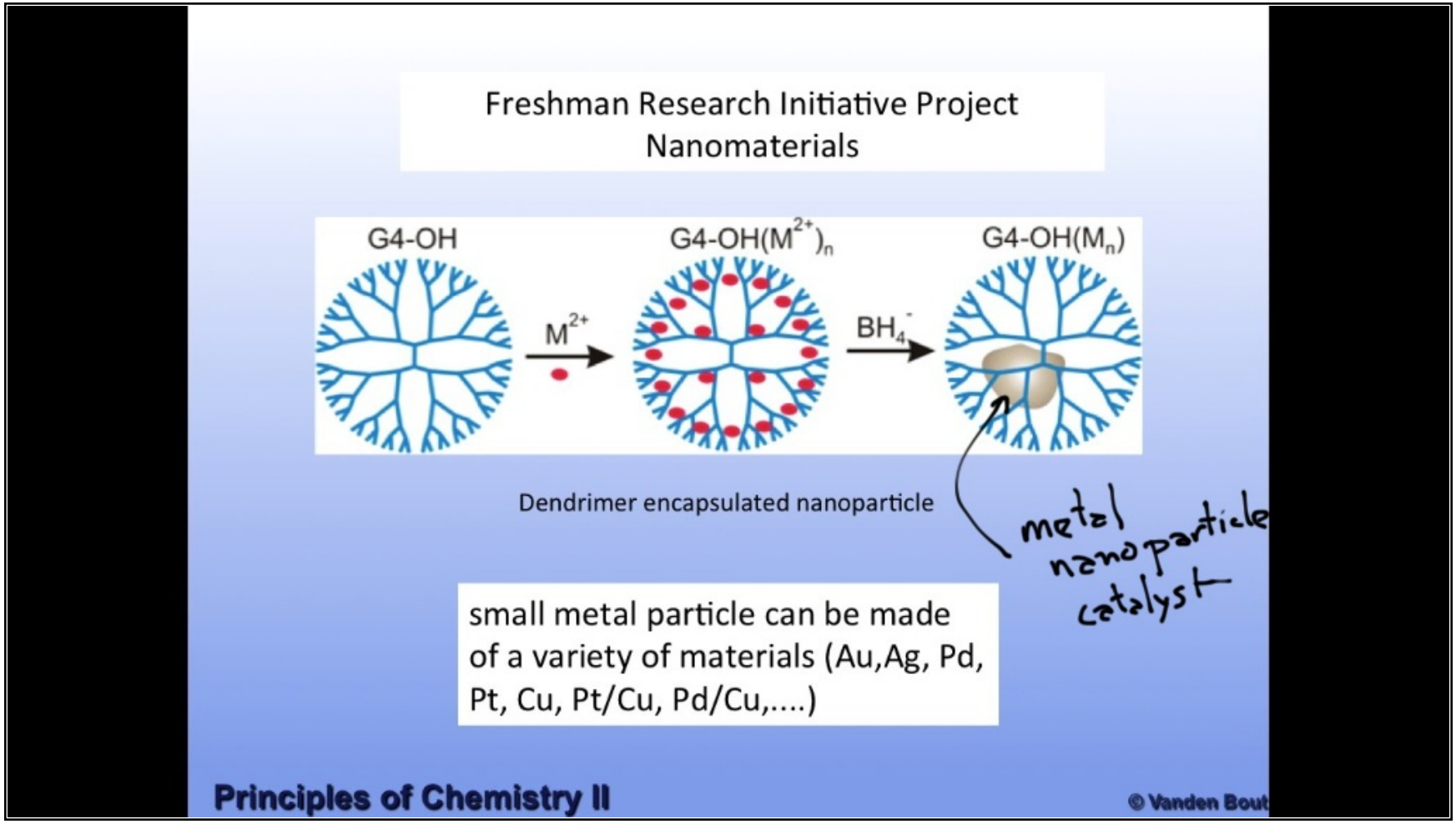
Freshman Research Initiative Project
Nanomaterials
G4-OH
G4-OH(M^{2+})$_n$
G4-OH(M_n)
M^{2+}
BH_4^-
Dendrimer encapsulated nanoparticle
metal nanoparticle catalyst
small metal particle can be made of a variety of materials (Au,Ag, Pd, Pt, Cu, Pt/Cu, Pd/Cu,....)
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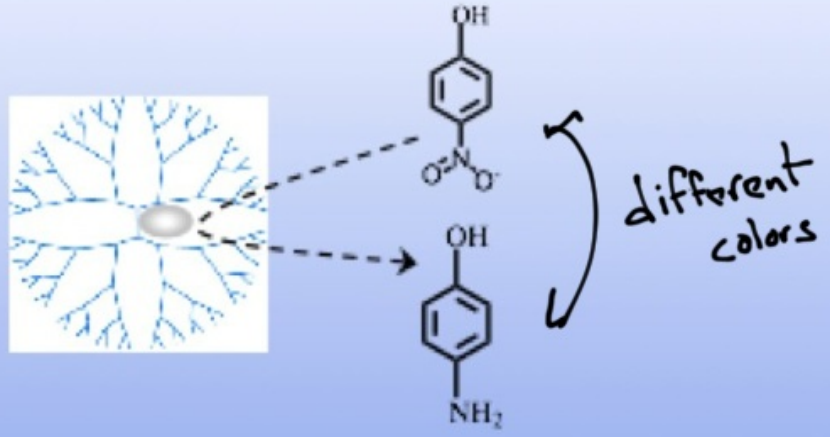
How good is the catalyst? Measure the kinetics.
Do the worksheet……



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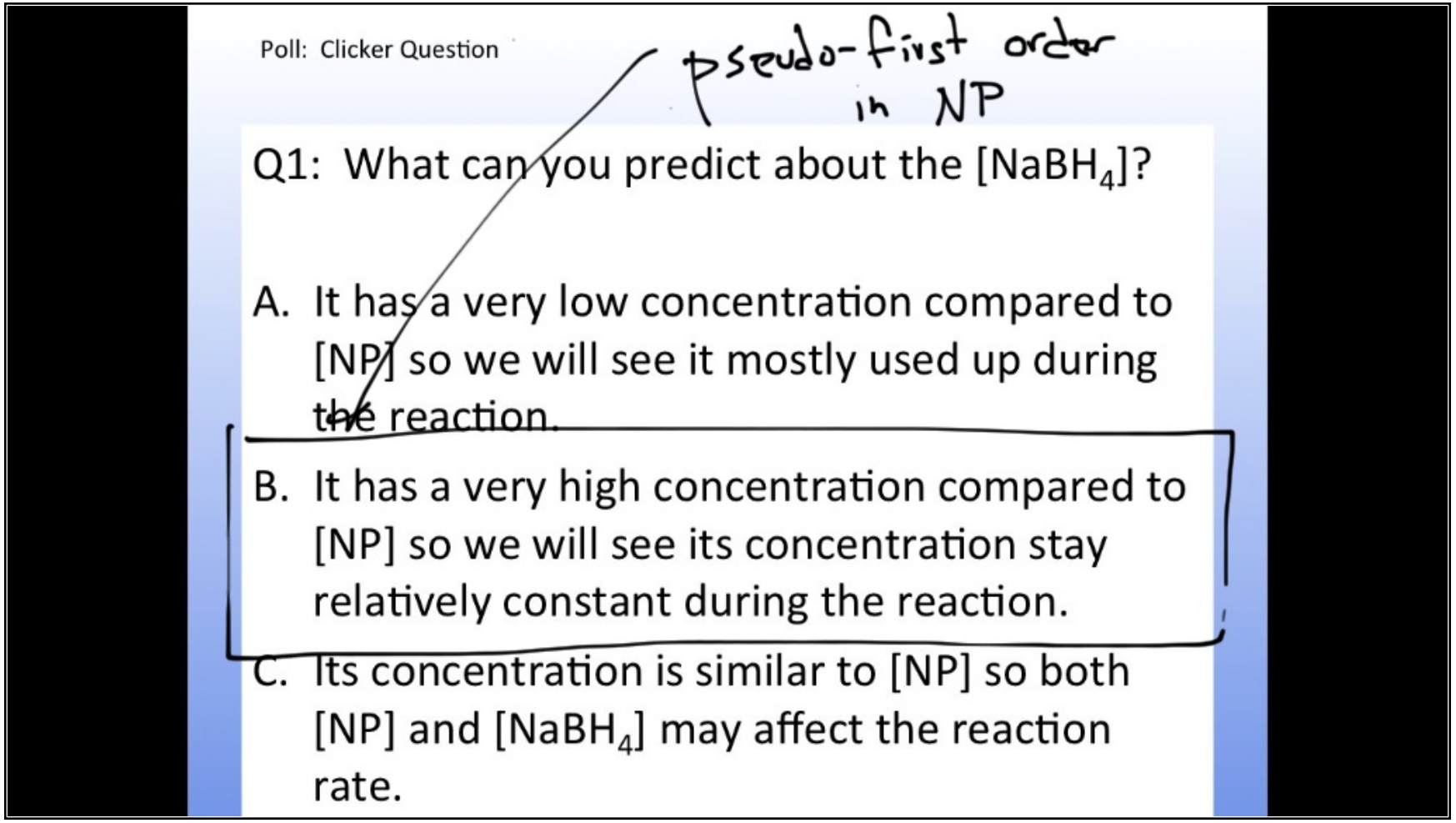
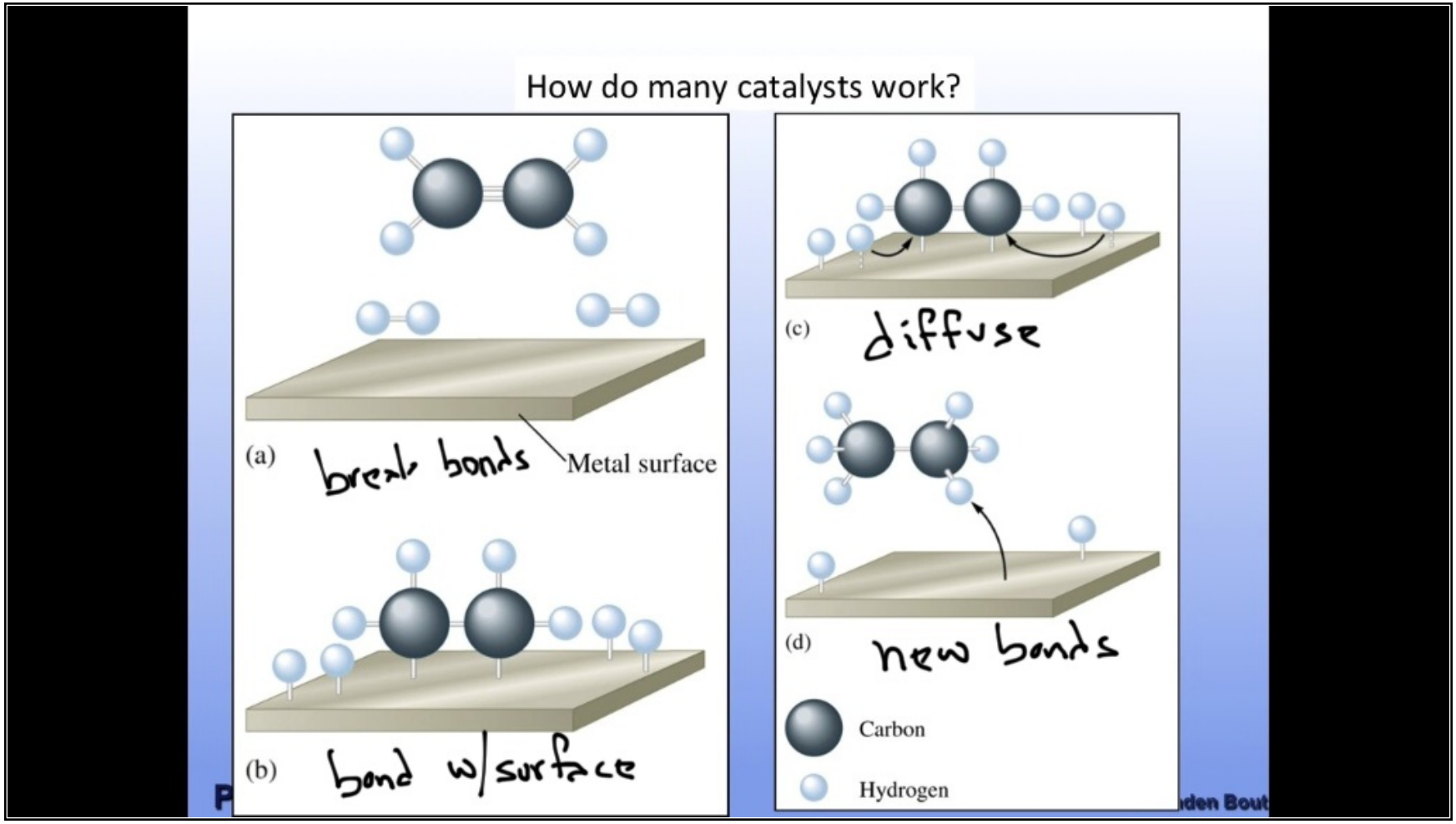
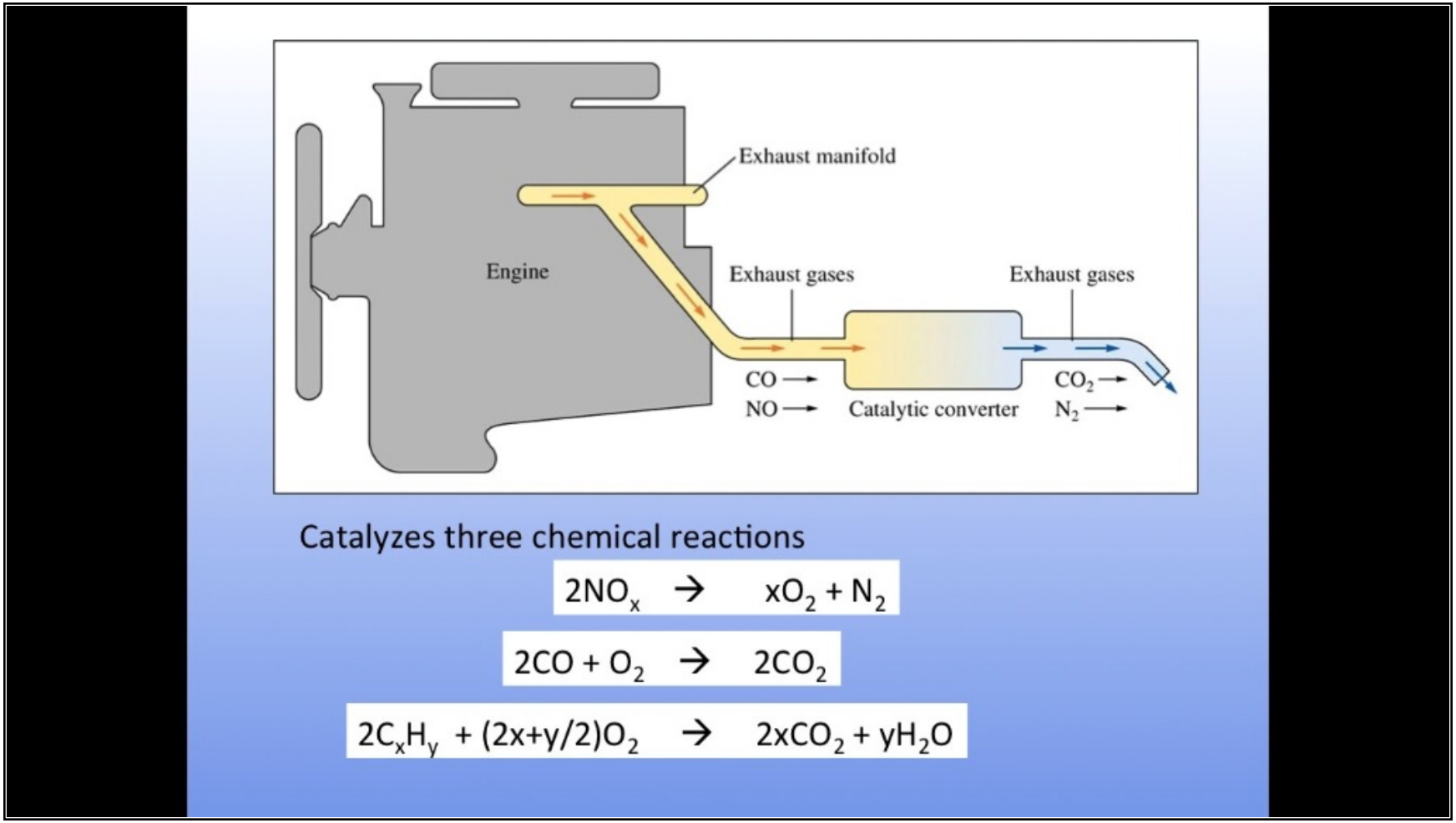

Poll: Clicker Question
pseudo-first order in NP
Q1: What can you predict about the [$NaBH_4$]?
A. It has a very low concentration compared to [NP] so we will see it mostly used up during the reaction.
B. It has a very high concentration compared to [NP] so we will see its concentration stay relatively constant during the reaction.
C. Its concentration is similar to [NP] so both [NP] and [$NaBH_4$] may affect the reaction rate.


How do many catalysts work?
(a)
break bonds
Metal surface
(b)
bond w/surface
(c)
diffuse
(d)
new bonds
Carbon
Hydrogen



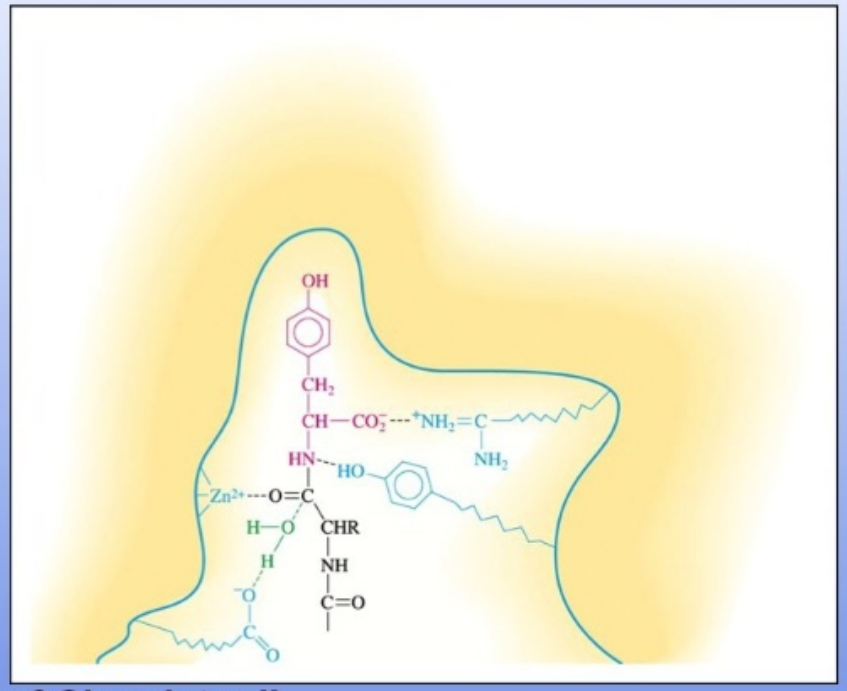
Catalyzes three chemical reactions

$$2NO_x \rightarrow xO_2 + N_2$$

$$2CO + O_2 \rightarrow 2CO_2$$

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

Enzymes
Biological Catalysts



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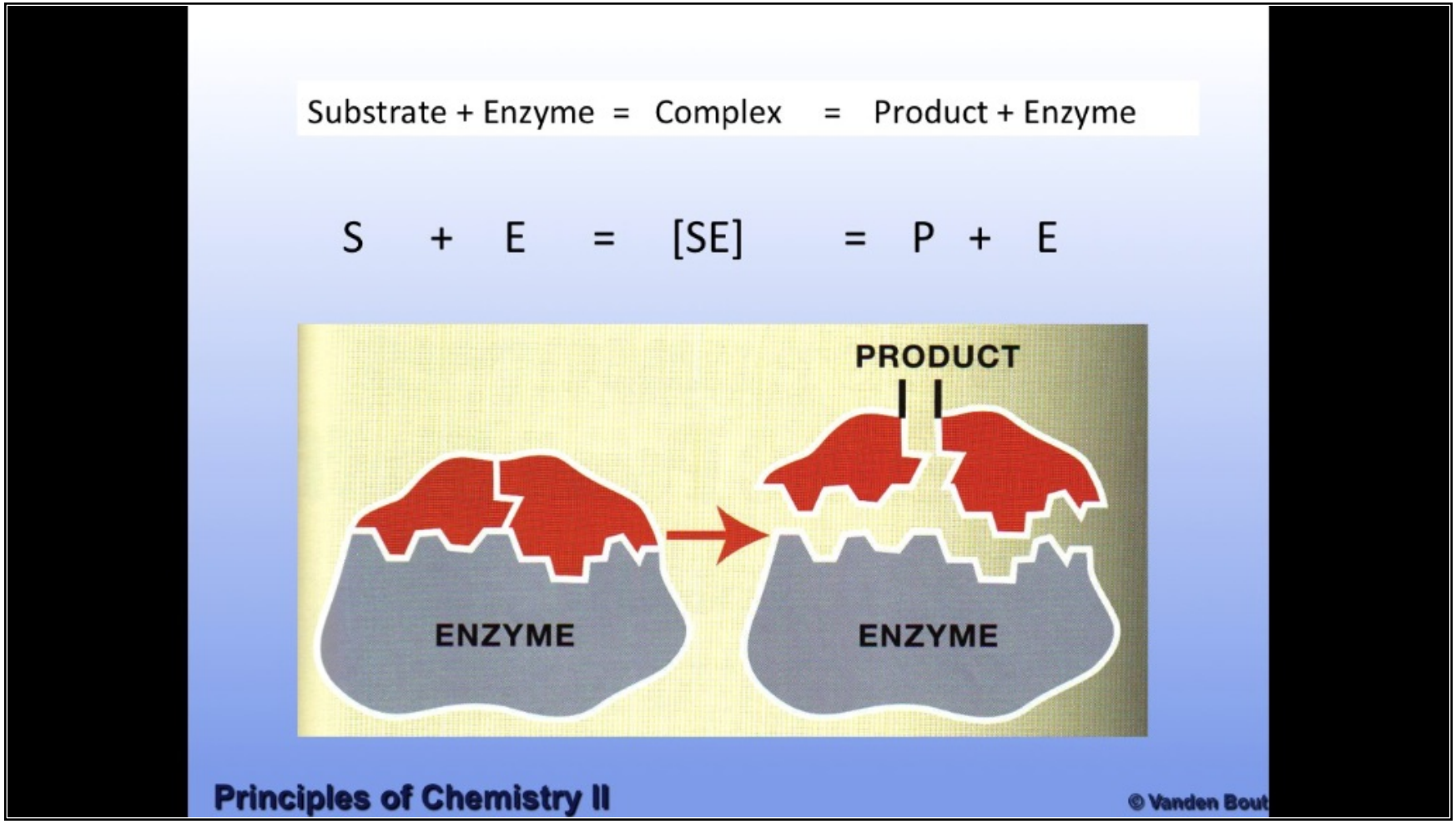
Substrate + Enzyme = Complex = Product + Enzyme
S + E = [SE] = P + E
PRODUCT
ENZYME
ENZYME
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