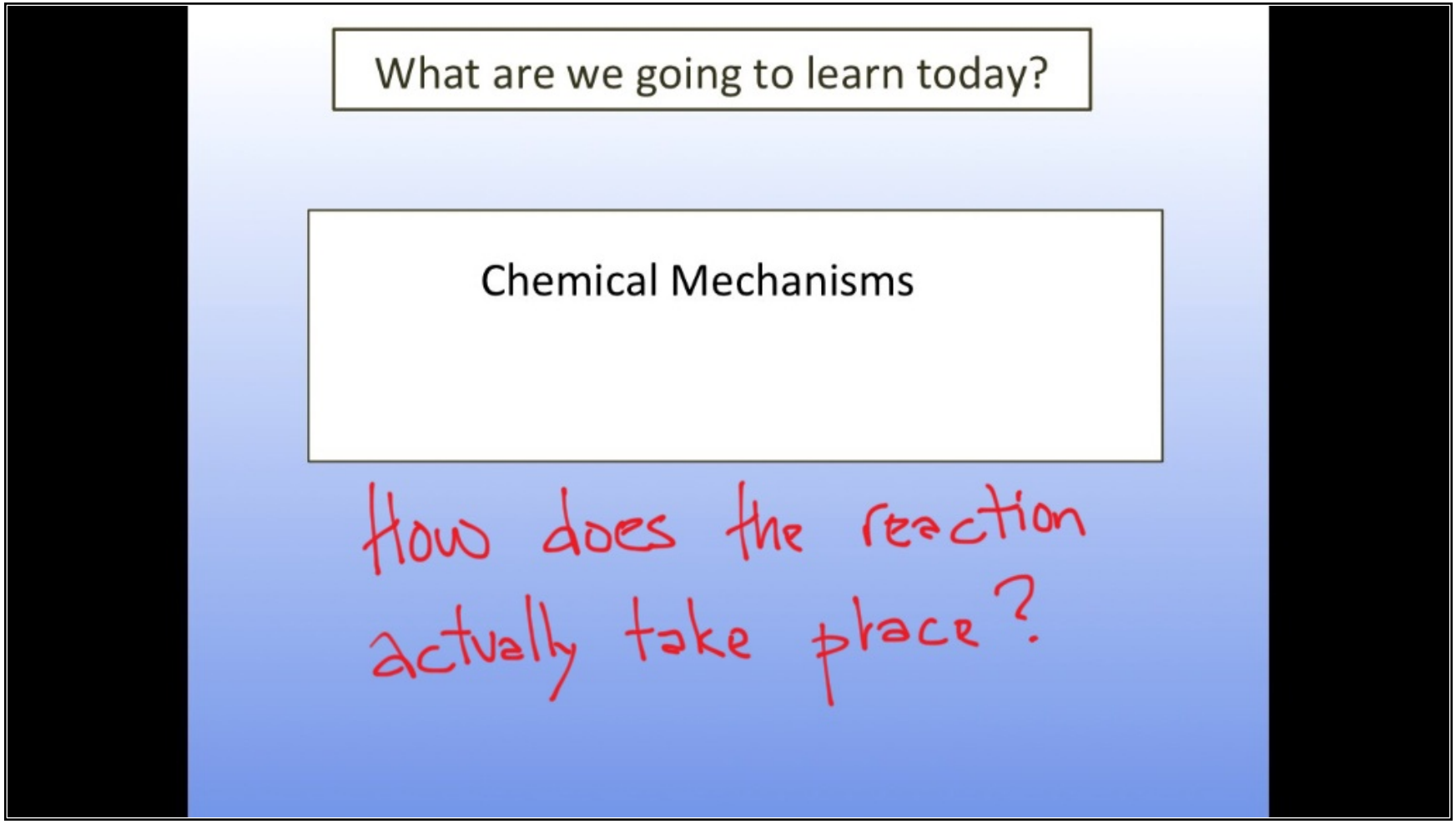
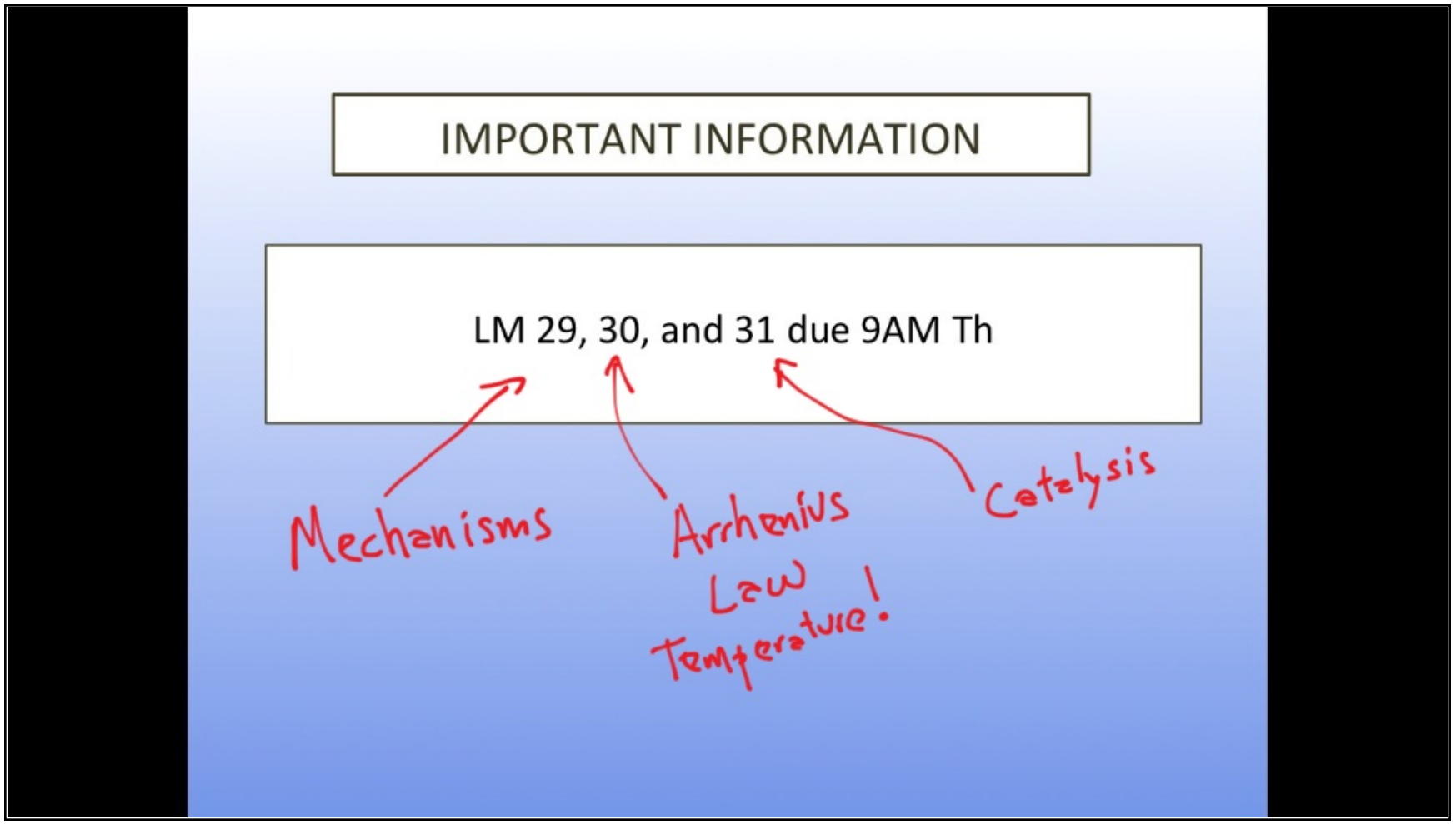
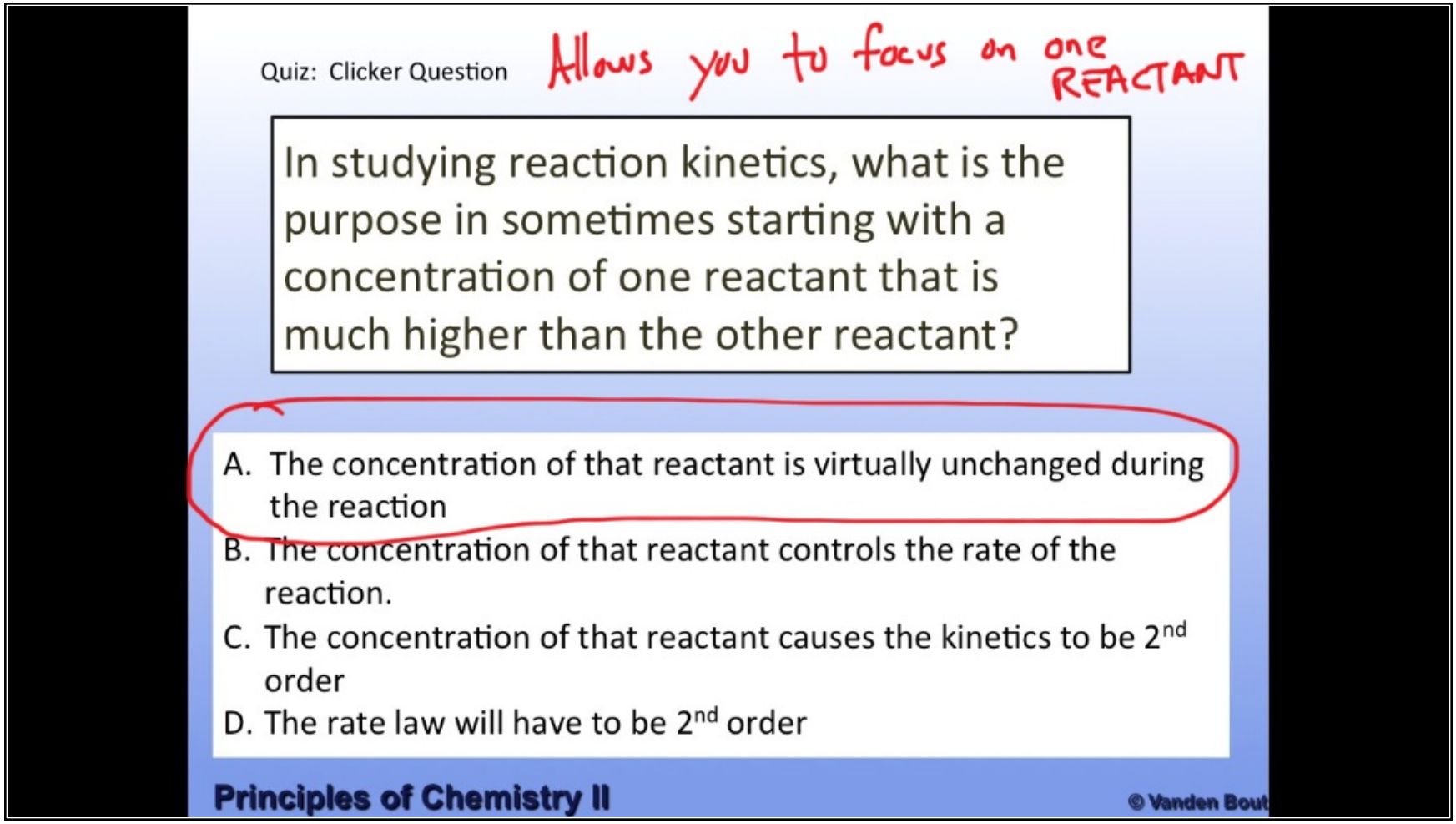

Thinking Like a
Chemist About
Kinetics III
MECHANISMS !
UNIT 7 DAY 6


What are we going to learn today?
Chemical Mechanisms
How does the reaction actually take place?


IMPORTANT INFORMATION
LM 29, 30, and 31 due 9AM Th
Mechanisms
Arrhenius Law Temperature!
Catalysis


Quiz: Clicker Question
Allows you to focus on one REACTANT
In studying reaction kinetics, what is the purpose in sometimes starting with a concentration of one reactant that is much higher than the other reactant?
A. The concentration of that reactant is virtually unchanged during the reaction
B. The concentration of that reactant controls the rate of the reaction.
C. The concentration of that reactant causes the kinetics to be 2nd order
D. The rate law will have to be 2nd order
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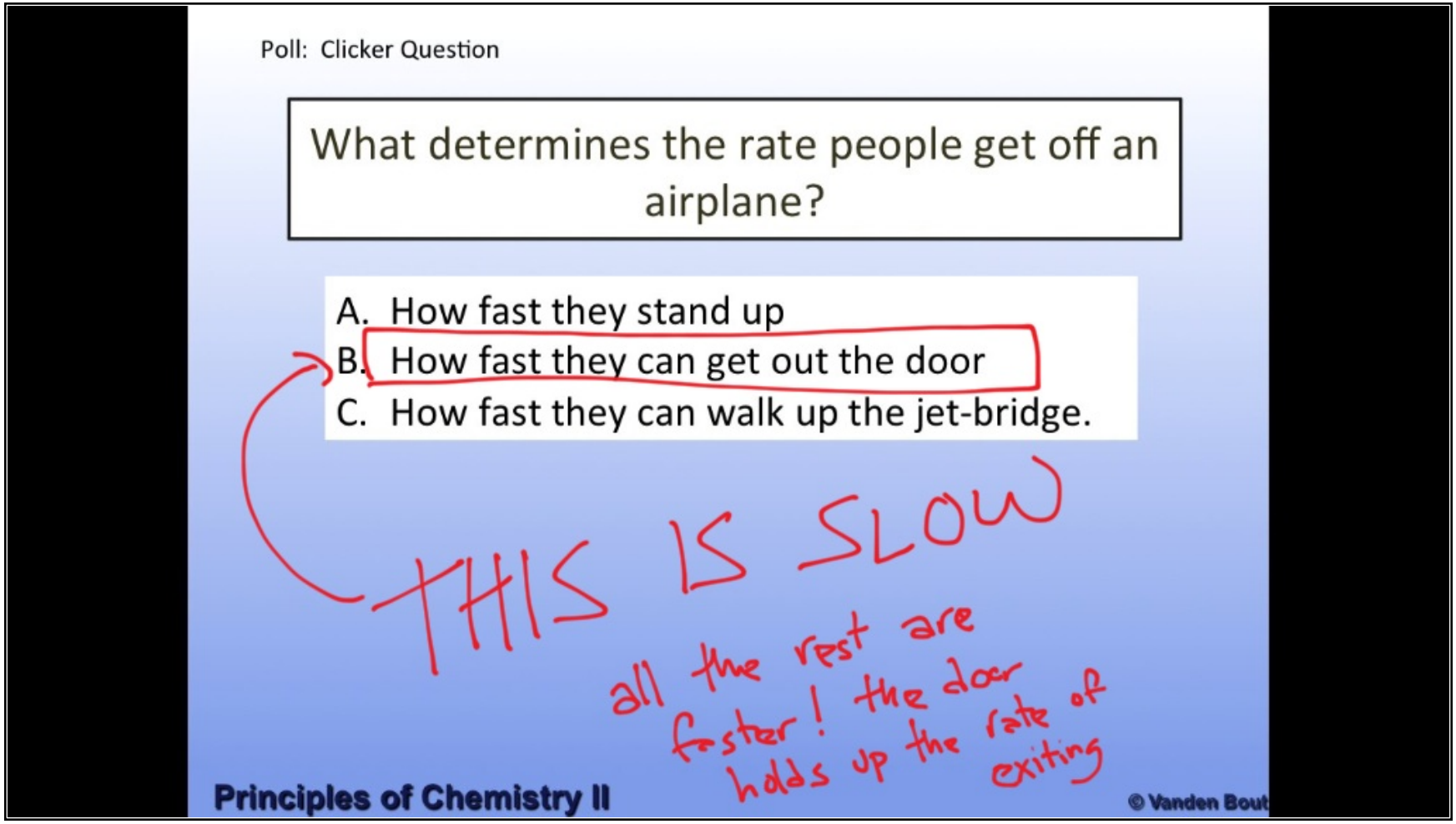
Poll: Clicker Question
What determines the rate people get off an airplane?
A. How fast they stand up
B. How fast they can get out the door
C. How fast they can walk up the jet-bridge.
THIS IS SLOW
all the rest are faster! the door holds up the rate of exiting
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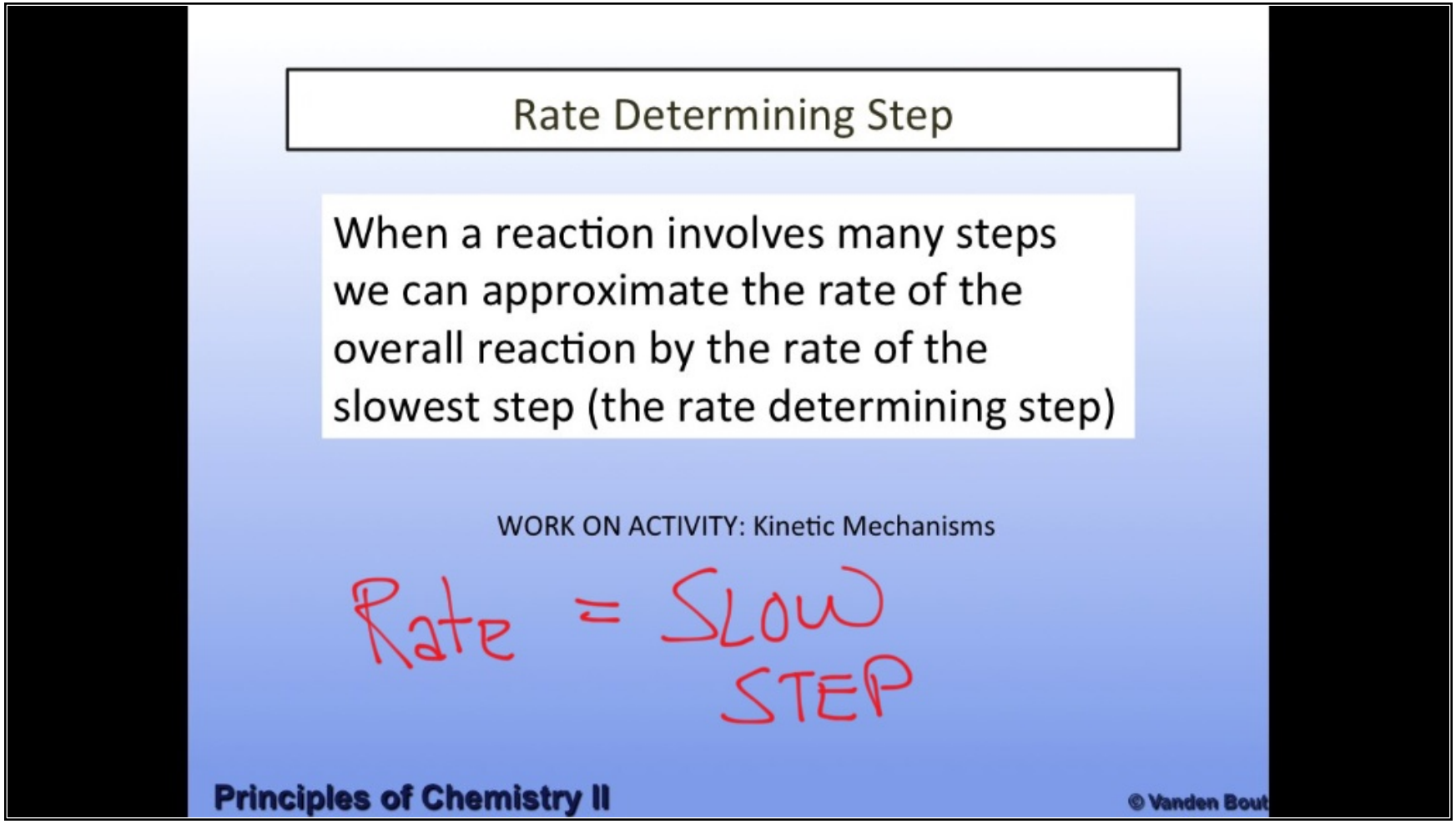
Rate Determining Step
When a reaction involves many steps we can approximate the rate of the overall reaction by the rate of the slowest step (the rate determining step)
WORK ON ACTIVITY: Kinetic Mechanisms
Rate = SLOW STEP
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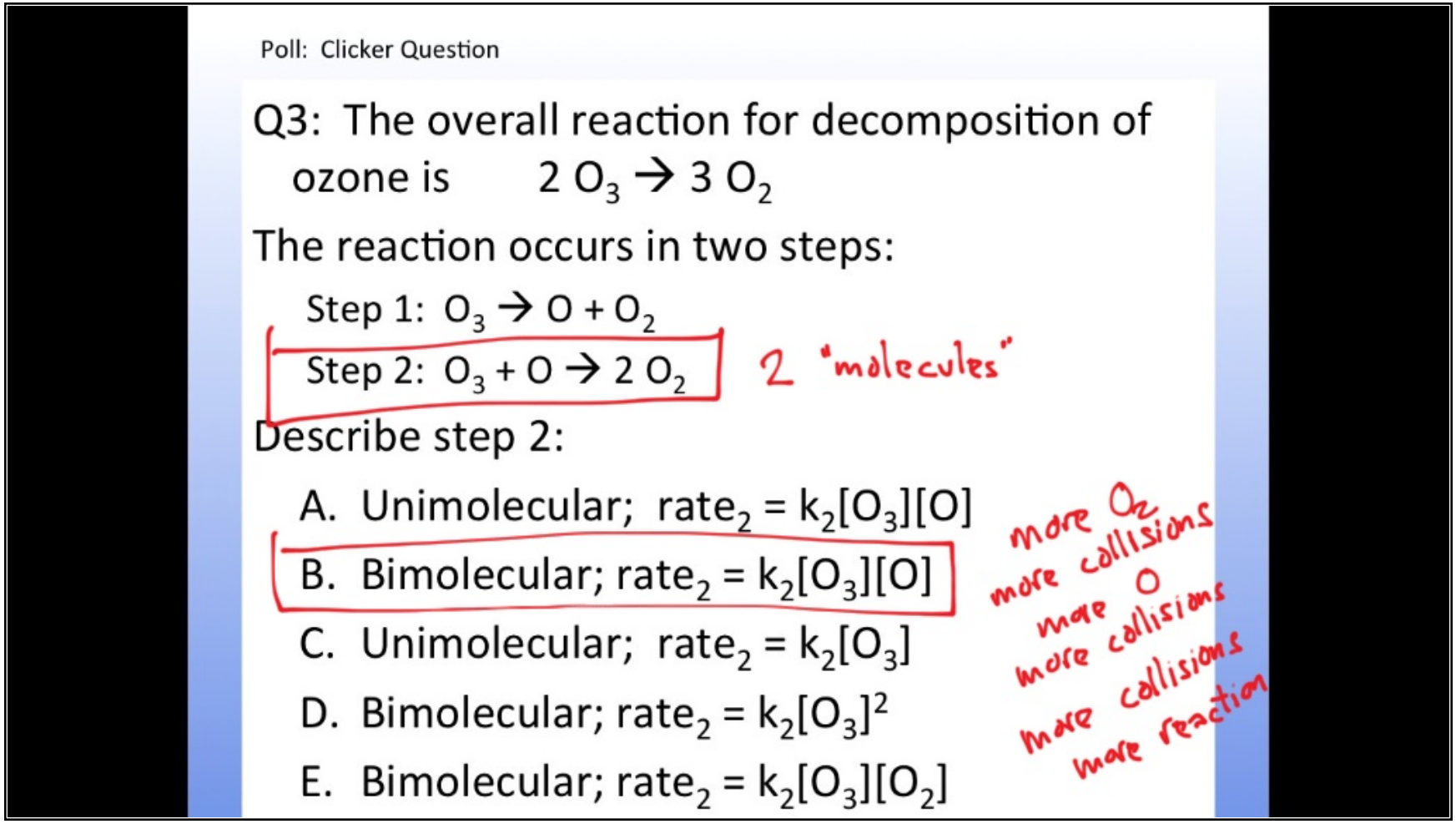
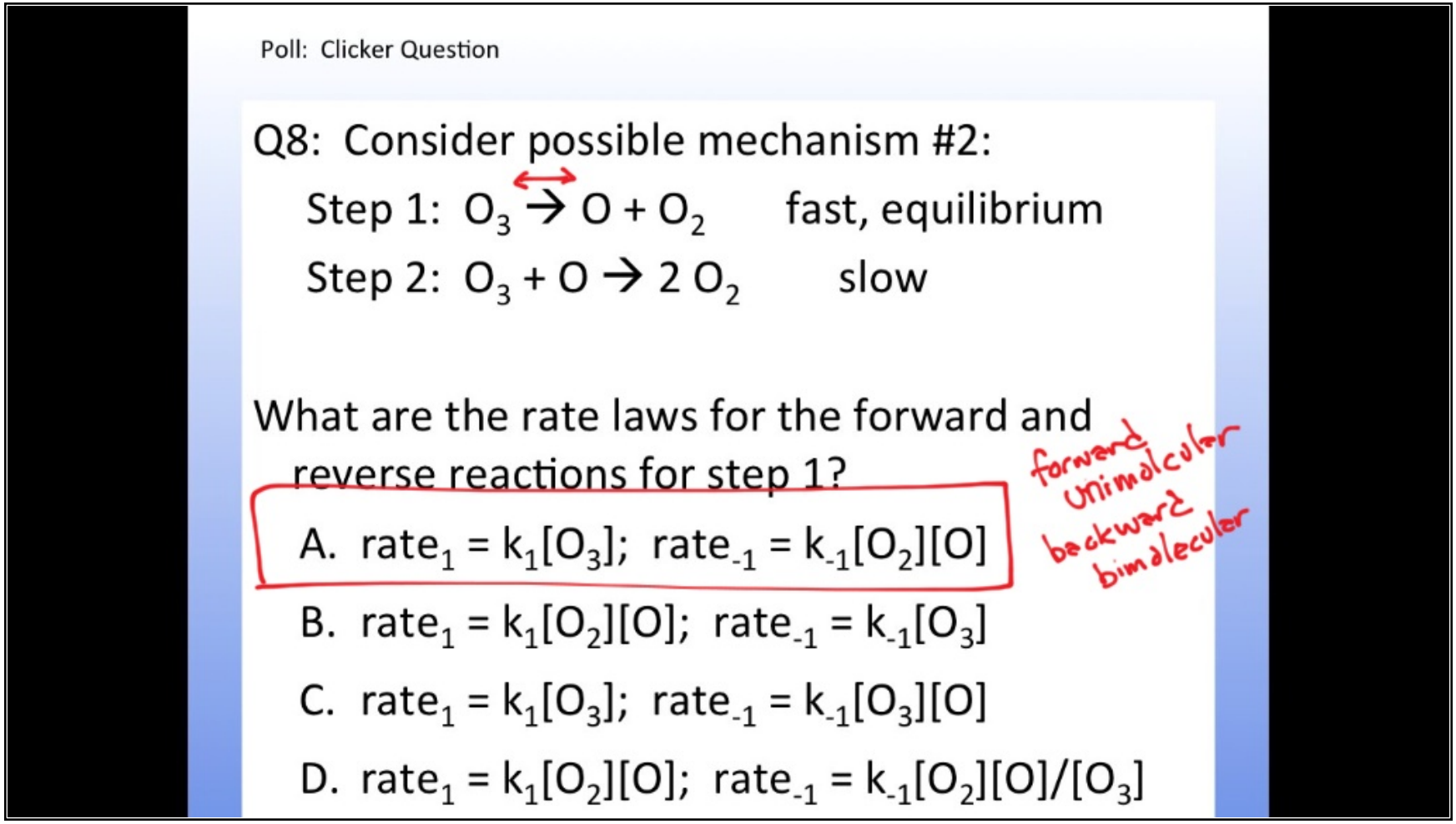
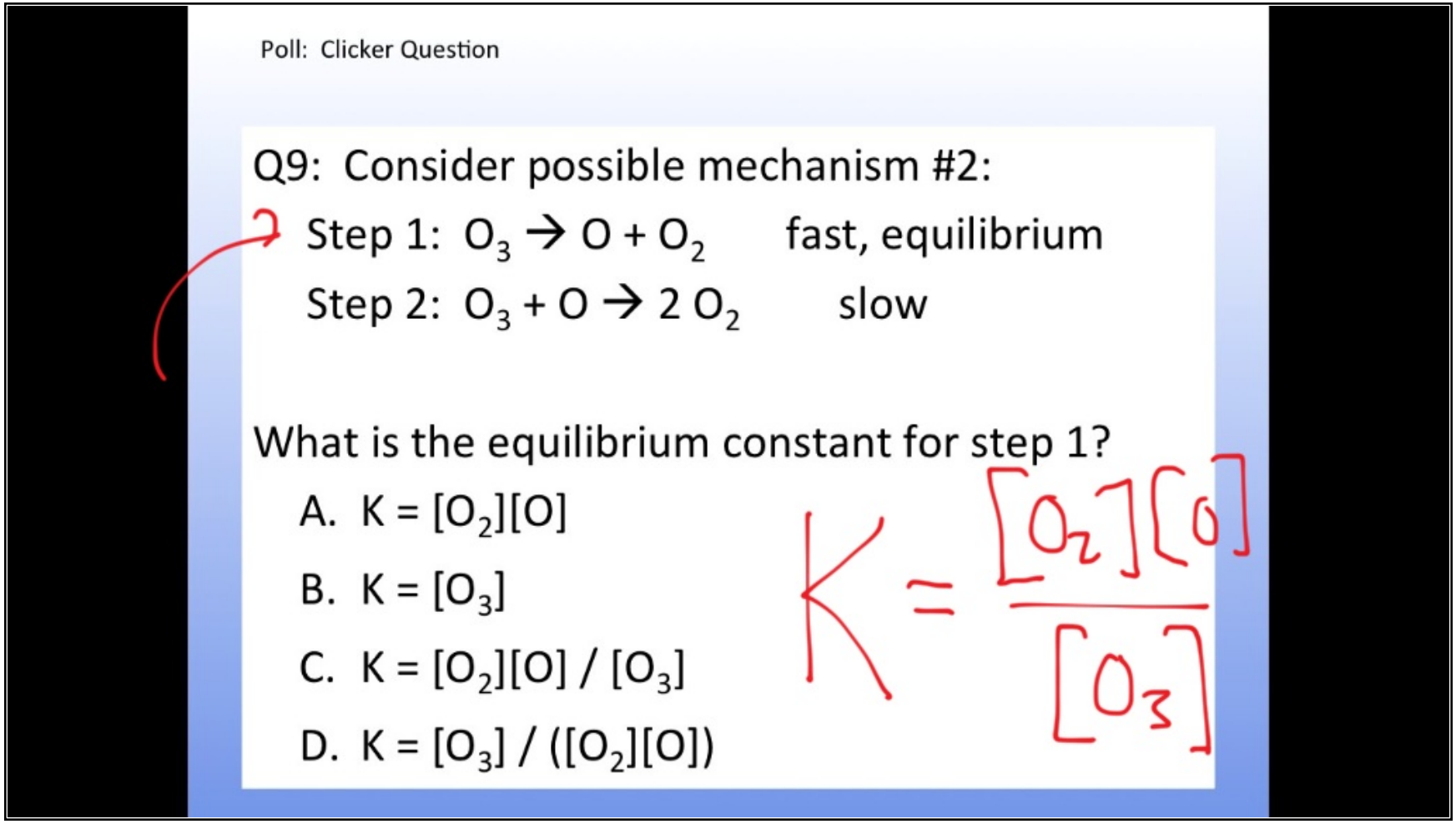
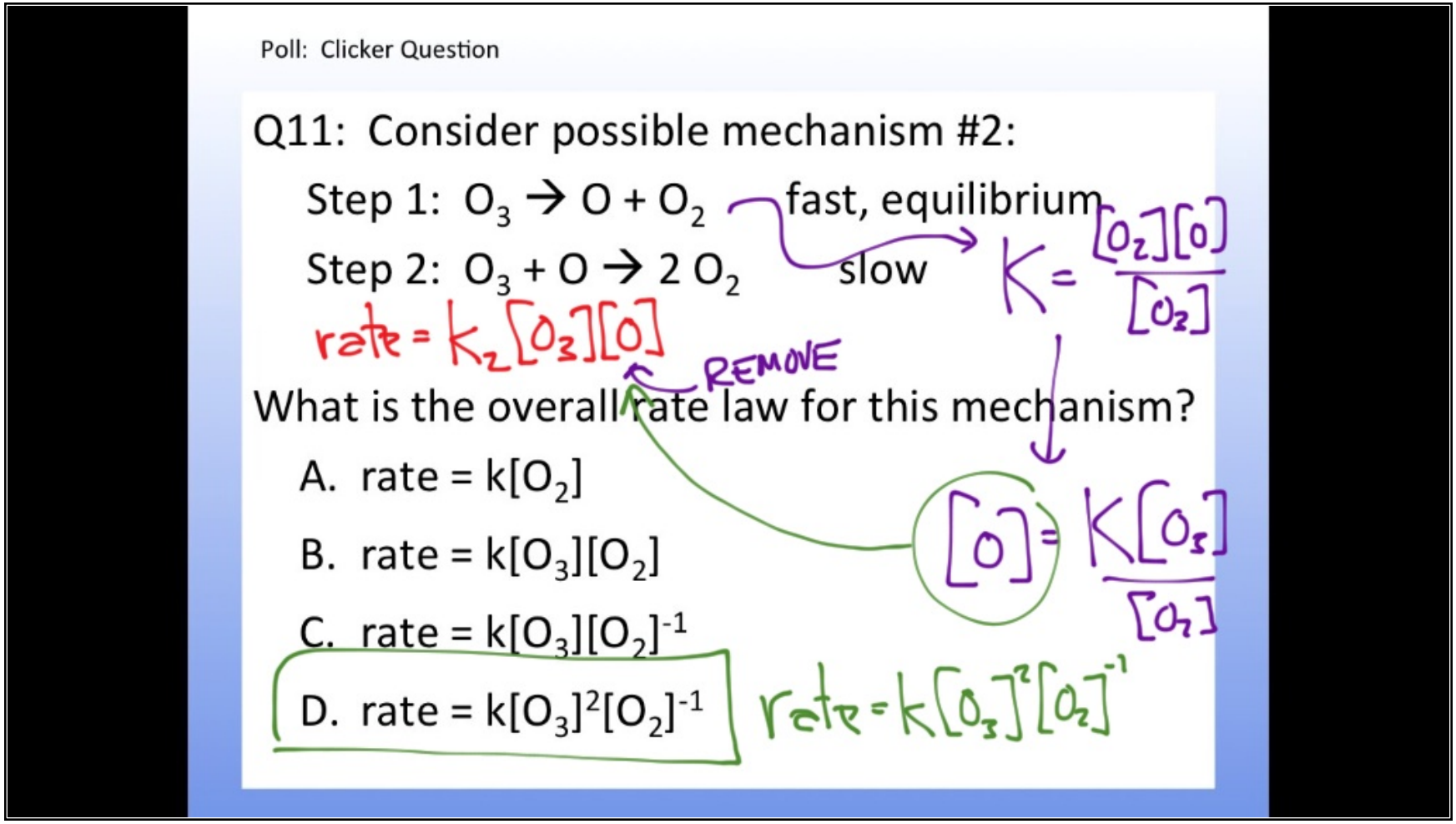
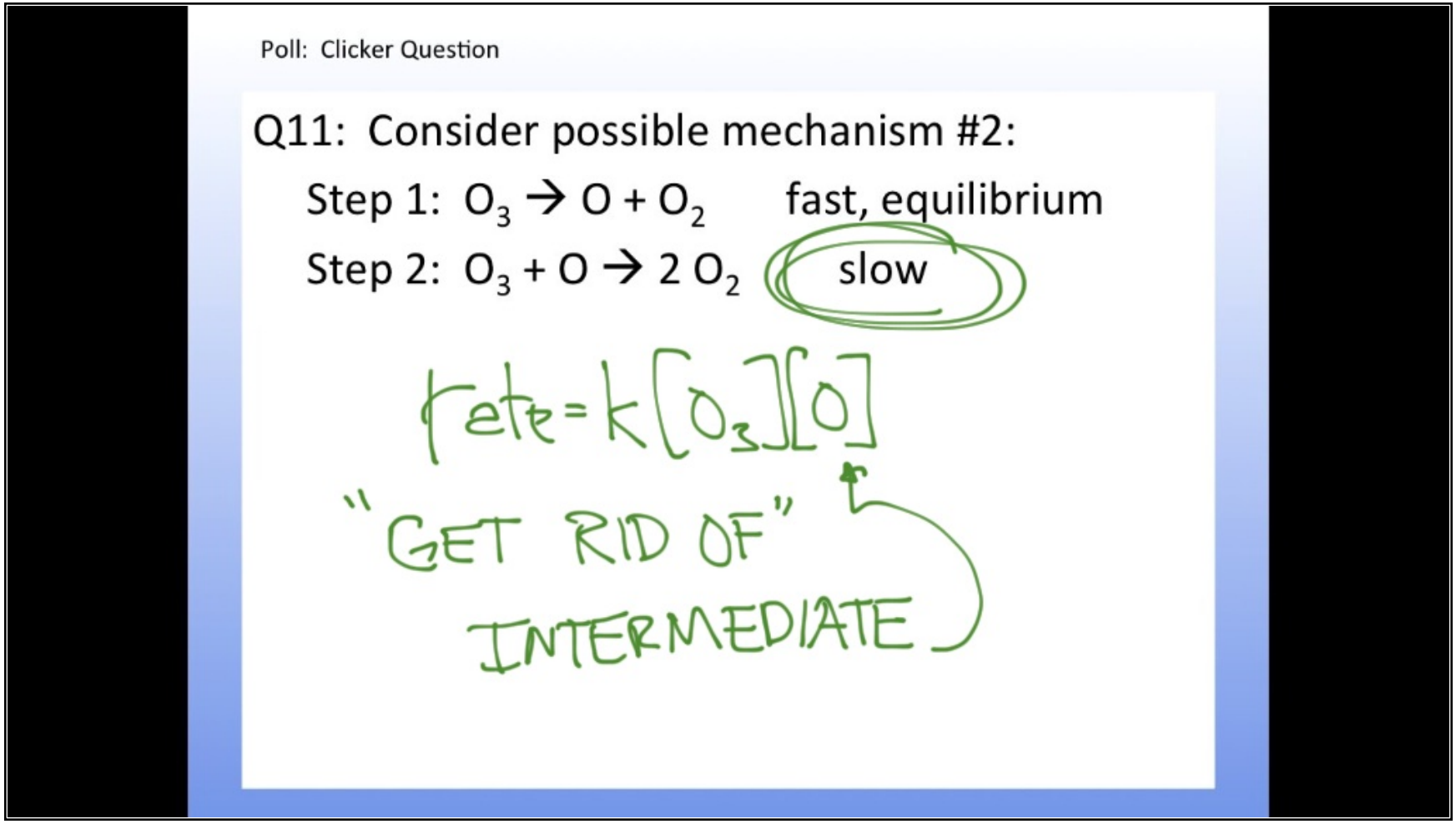
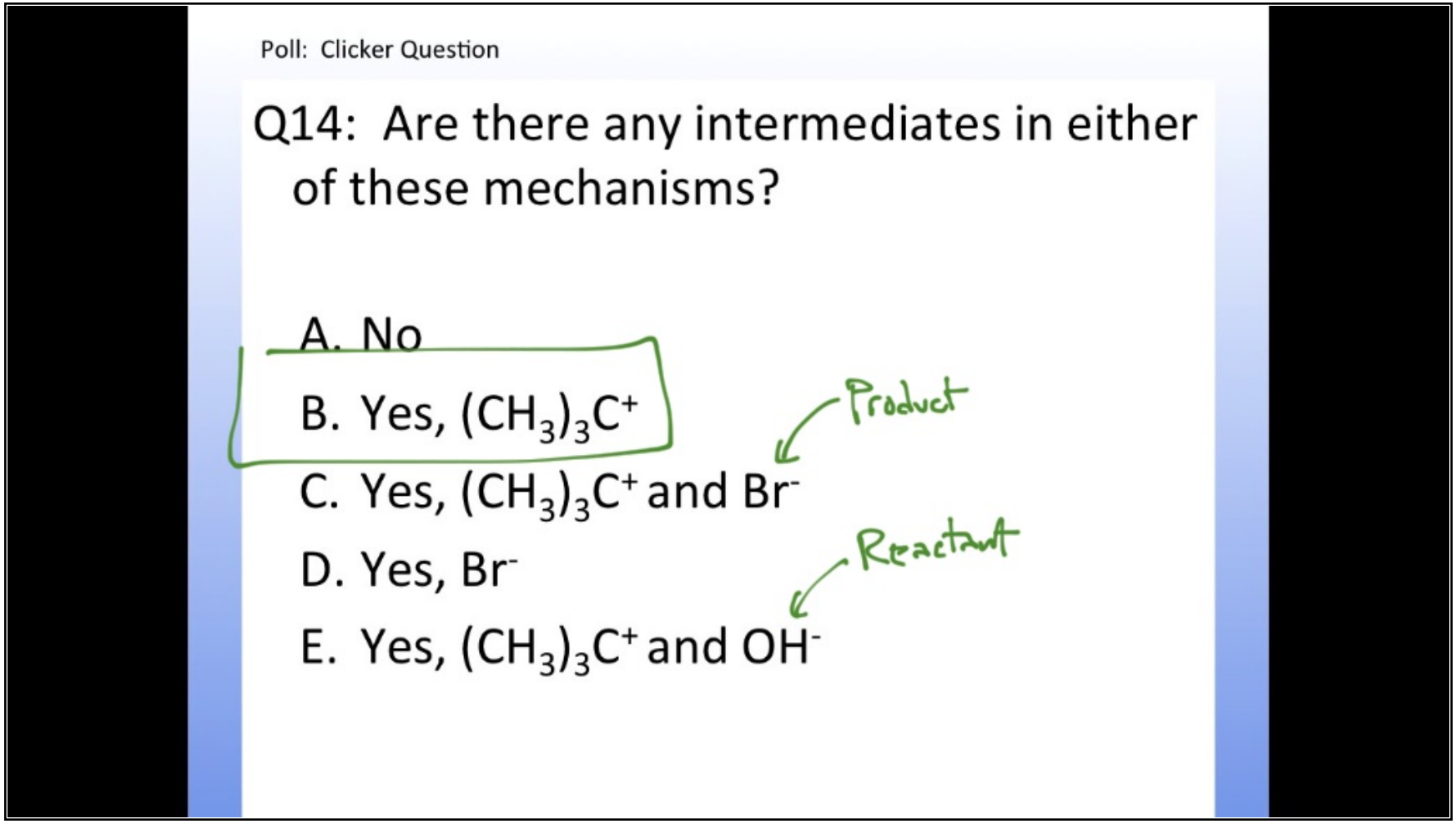

Poll: Clicker Question
Q3: The overall reaction for decomposition of ozone is 2 O_3 → 3 O_2
The reaction occurs in two steps:
Step 1: O_3 → O + O_2
Step 2: O_3 + O → 2 O_2
2 "molecules"
Describe step 2:
A. Unimolecular; $rate_2 = k_2[O_3][O]$
B. Bimolecular; $rate_2 = k_2[O_3][O]$
C. Unimolecular; $rate_2 = k_2[O_3]$
D. Bimolecular; $rate_2 = k_2[O_3]^2$
E. Bimolecular; $rate_2 = k_2[O_3][O_2]$
more O_3 more collisions
more O more collisions
more collisions more reaction

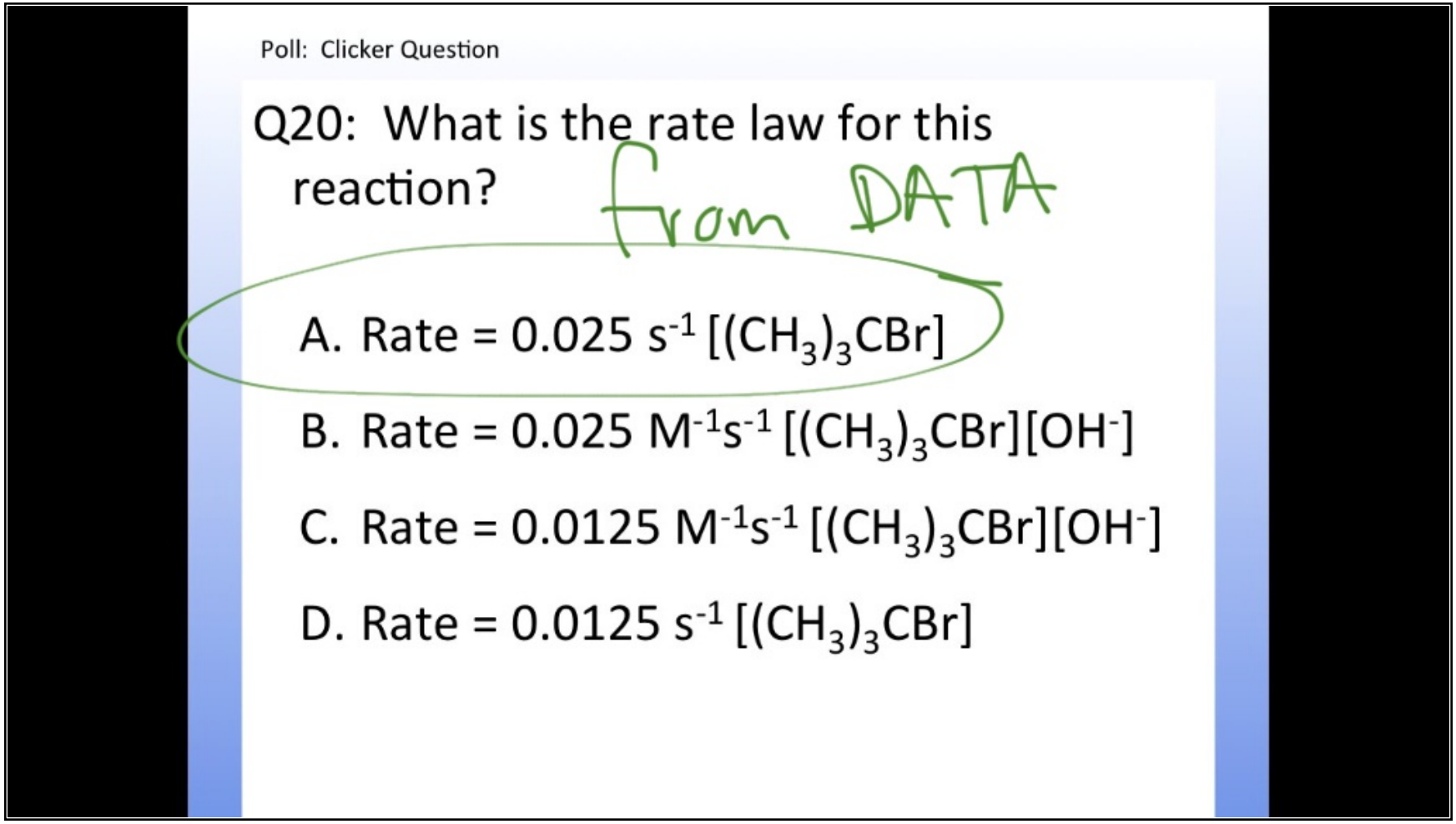

Poll: Clicker Question
Q8: Consider possible mechanism #2:
Step 1: $O_3 \rightleftarrows O + O_2$ fast, equilibrium
Step 2: $O_3 + O \rightarrow 2\ O_2$ slow
What are the rate laws for the forward and reverse reactions for step 1?
A. $rate_1 = k_1[O_3]$; $rate_{-1} = k_{-1}[O_2][O]$
B. $rate_1 = k_1[O_2][O]$; $rate_{-1} = k_{-1}[O_3]$
C. $rate_1 = k_1[O_3]$; $rate_{-1} = k_{-1}[O_3][O]$
D. $rate_1 = k_1[O_2][O]$; $rate_{-1} = k_{-1}[O_2][O]/[O_3]$
forward unimolecular
backward bimolecular

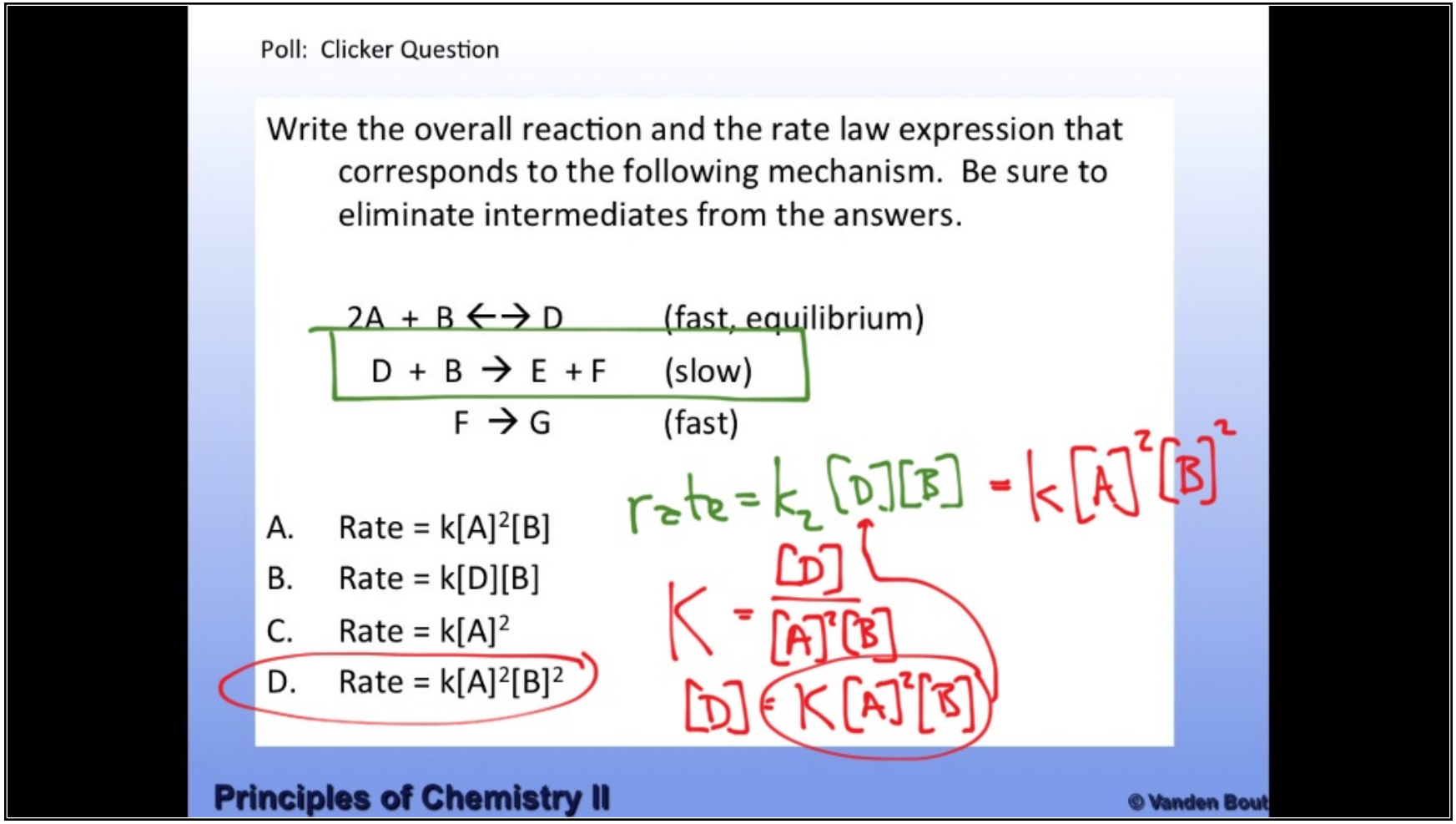

Poll: Clicker Question
Q9: Consider possible mechanism #2:
Step 1: $O_3 \rightarrow O + O_2$ fast, equilibrium
Step 2: $O_3 + O \rightarrow 2\ O_2$ slow
What is the equilibrium constant for step 1?
A. $K = [O_2][O]$
B. $K = [O_3]$
C. $K = [O_2][O] / [O_3]$
D. $K = [O_3] / ([O_2][O])$
$K = \frac{[O_2][O]}{[O_3]}$


Poll: Clicker Question
Q11: Consider possible mechanism #2:
Step 1: $O_3 \rightarrow O + O_2$ fast, equilibrium
Step 2: $O_3 + O \rightarrow 2\ O_2$ slow
$K = \frac{[O_2][O]}{[O_3]}$
rate = $k_2[O_3][O]$
REMOVE
What is the overall rate law for this mechanism?
A. rate = $k[O_2]$
B. rate = $k[O_3][O_2]$
C. rate = $k[O_3][O_2]^{-1}$
D. rate = $k[O_3]^2[O_2]^{-1}$
$[O] = \frac{K[O_3]}{[O_2]}$
rate = $k[O_3]^2[O_2]^{-1}$


Poll: Clicker Question
Q11: Consider possible mechanism #2:
Step 1: $O_3 \rightarrow O + O_2$ fast, equilibrium
Step 2: $O_3 + O \rightarrow 2\ O_2$ slow
rate = k[O3][O]
"GET RID OF" INTERMEDIATE


Poll: Clicker Question
Q14: Are there any intermediates in either of these mechanisms?
A. No
B. Yes, $(CH_3)_3C^+$
C. Yes, $(CH_3)_3C^+$ and Br^-
D. Yes, Br^-
E. Yes, $(CH_3)_3C^+$ and OH^-
Product
Reactant


Poll: Clicker Question
Q20: What is the rate law for this reaction?
From DATA
A. Rate = 0.025 s^{-1} $[(CH_3)_3CBr]$
B. Rate = 0.025 $M^{-1}s^{-1}$ $[(CH_3)_3CBr][OH^-]$
C. Rate = 0.0125 $M^{-1}s^{-1}$ $[(CH_3)_3CBr][OH^-]$
D. Rate = 0.0125 s^{-1} $[(CH_3)_3CBr]$


Poll: Clicker Question
Write the overall reaction and the rate law expression that corresponds to the following mechanism. Be sure to eliminate intermediates from the answers.
2A + B ⟷ D (fast, equilibrium)
D + B → E + F (slow)
F → G (fast)
A. Rate = k[A]²[B]
B. Rate = k[D][B]
C. Rate = k[A]²
D. Rate = k[A]²[B]²
rate = k₂[D][B] = k[A]²[B]²
K = [D] / [A]²[B]
[D] = K[A]²[B]
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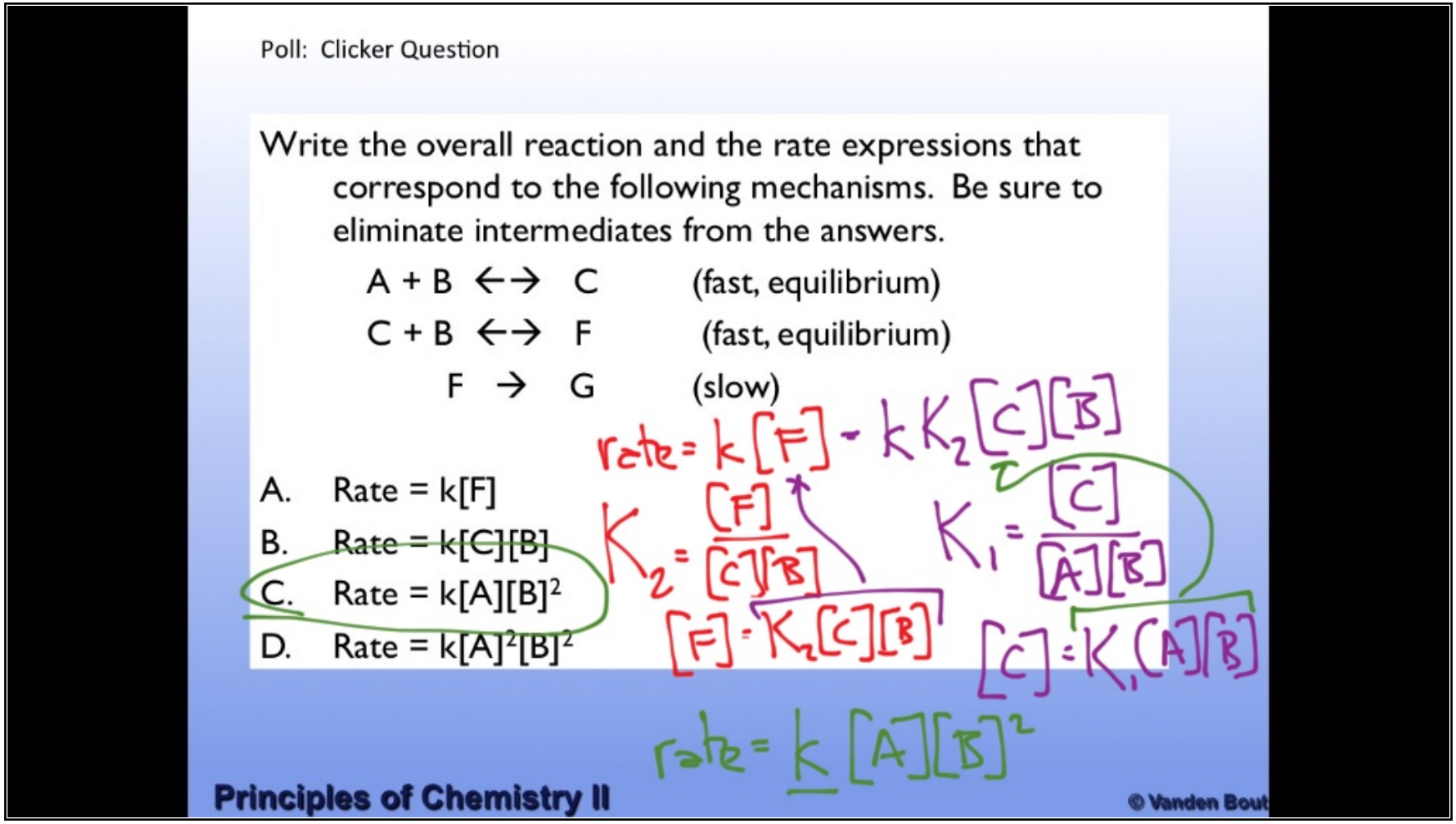
Poll: Clicker Question
Write the overall reaction and the rate expressions that correspond to the following mechanisms. Be sure to eliminate intermediates from the answers.
A + B ←→ C (fast, equilibrium)
C + B ←→ F (fast, equilibrium)
F → G (slow)
A. Rate = k[F]
B. Rate = k[C][B]
C. Rate = k[A][B]²
D. Rate = k[A]²[B]²
rate = k[F] = kK₂[C][B]
K₂ = [F]/[C][B]
K₁ = [C]/[A][B]
[F] = K₂[C][B]
[C] = K₁[A][B]
rate = k[A][B]²
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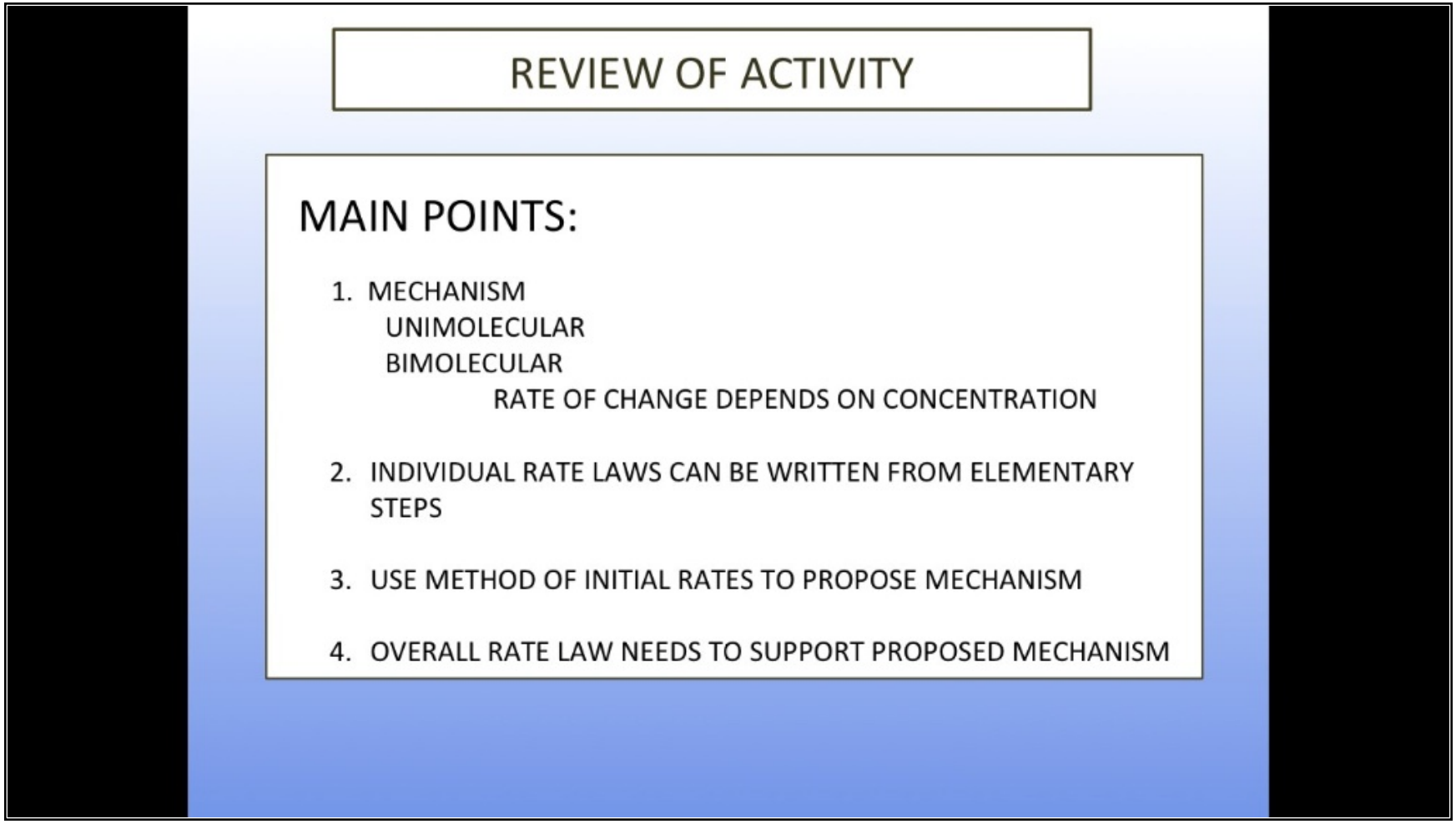
REVIEW OF ACTIVITY
MAIN POINTS:
1. MECHANISM
UNIMOLECULAR
BIMOLECULAR
RATE OF CHANGE DEPENDS ON CONCENTRATION
2. INDIVIDUAL RATE LAWS CAN BE WRITTEN FROM ELEMENTARY STEPS
3. USE METHOD OF INITIAL RATES TO PROPOSE MECHANISM
4. OVERALL RATE LAW NEEDS TO SUPPORT PROPOSED MECHANISM