Thinking Like a Chemist About Kinetics I

How fast reactions happen

UNIT 7 DAY 4

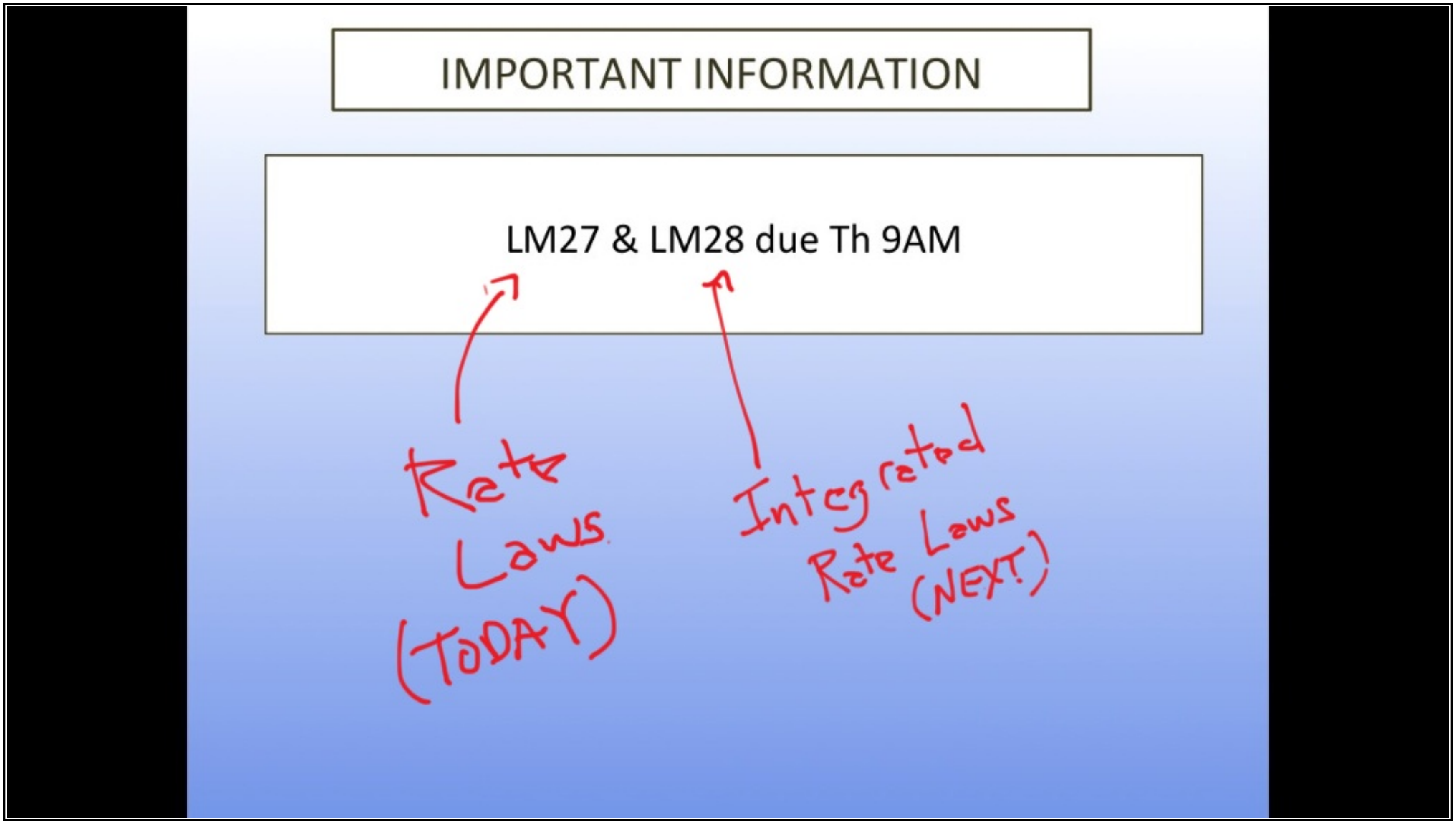
CAN TELL US HOW CHEMISTRY TAKES PLACE

What are we going to learn today?

Reaction Rates and the Rate Law

Method of Initial Rates

Must be measured!!


IMPORTANT INFORMATION
LM27 & LM28 due Th 9AM
Rate Laws (TODAY)
Integrated Rate Laws (NEXT)

Quiz: Clicker Question

Hydrogen-3 (tritium, H-3) is sometimes formed in the primary coolant water of a nuclear reactor. Tritium is a beta emitter with a $t_{1/2}$ = 12. 3 years. For a given sample containing tritium, after how many years will only about 12% of the sample remain?

A) 12.3 years
B) 24.6 years
C) 36.9 years ✓
D) 49.2 years
E) 61.5 years

$1 \times t_{1/2} = 50\%$

$2 \times t_{1/2} = 25\%$

$3 \times t_{1/2} = 12.5\%$

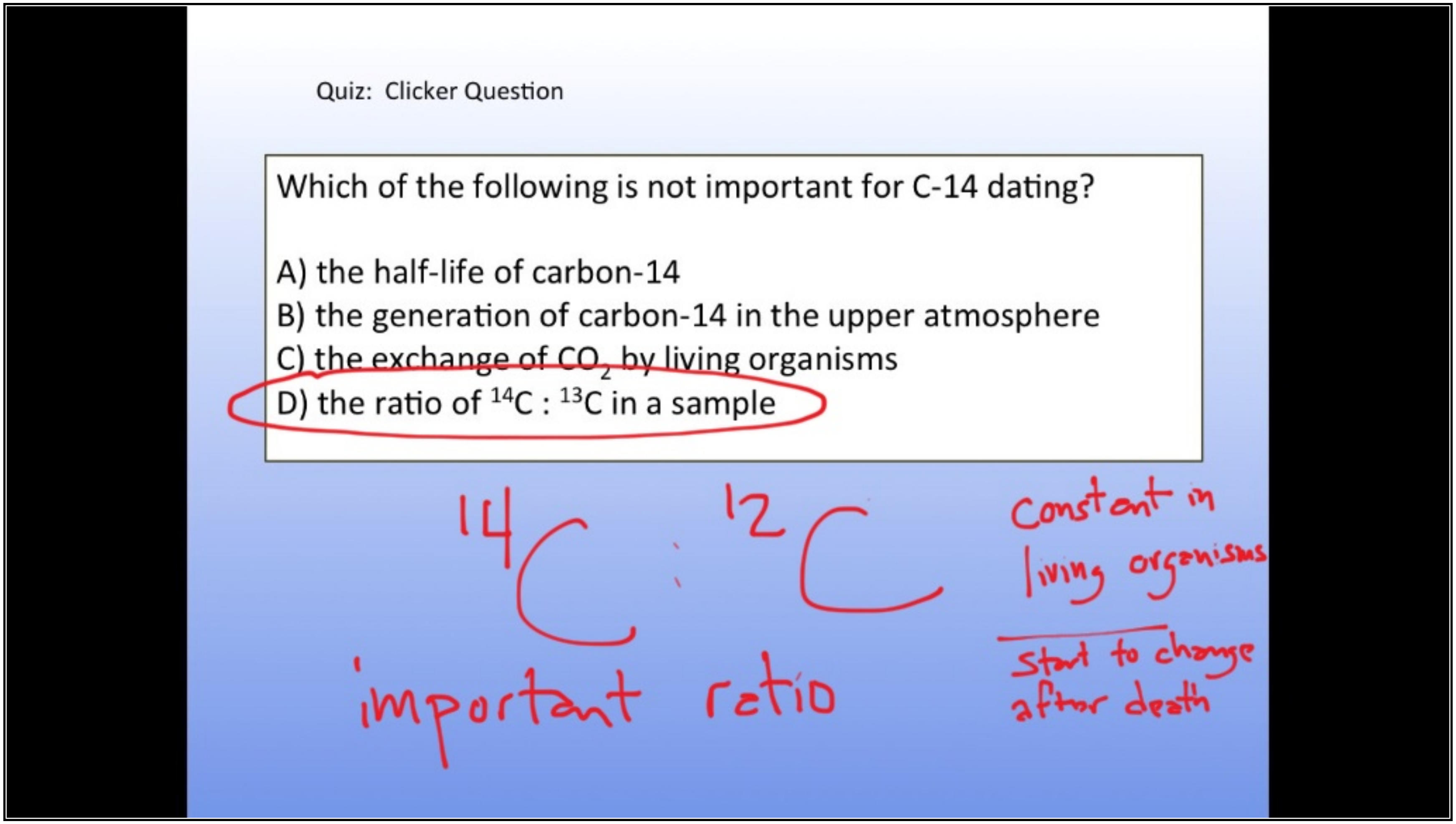
$3 \times 12 \sim 36$

Quiz: Clicker Question

Positron Emission Tomography (PET Scans) are generally used?

A) make 3-D images with radio-labeled molecules
B) to provide radiation therapy for cancer patients
C) collect 3-D x-ray images
D) to track radio-labeled metabolites in urine
E) to measure half-lives of rare radioactive nuclei

Radio-label
= molecule isotopically
labelled w/ radioactive isotope

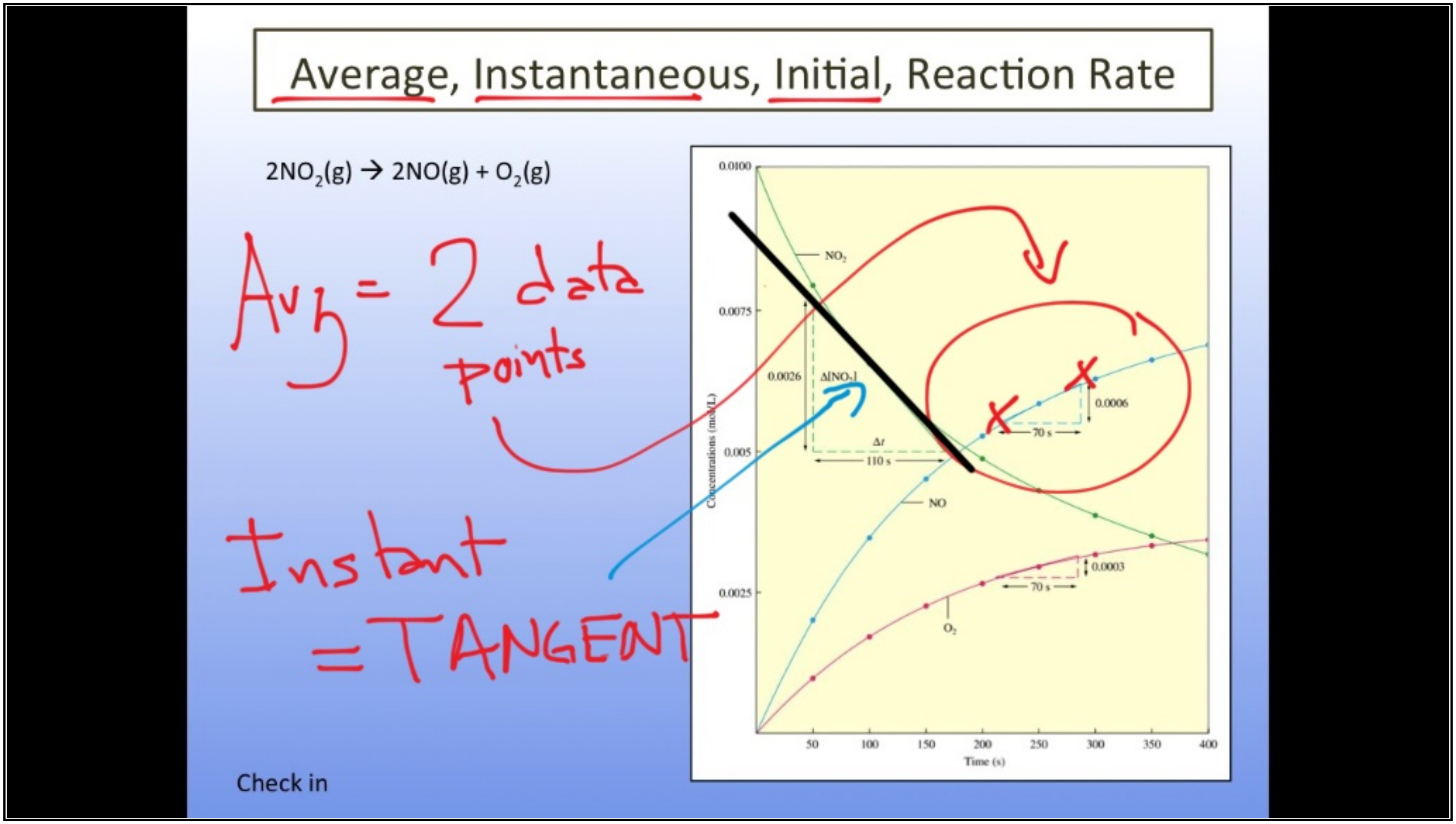

Quiz: Clicker Question
Which of the following is not important for C-14 dating?
A) the half-life of carbon-14
B) the generation of carbon-14 in the upper atmosphere
C) the exchange of CO_2 by living organisms
D) the ratio of $^{14}C : ^{13}C$ in a sample
$^{14}C : ^{12}C$
important ratio
constant in living organisms
start to change after death

Kinetics

Kinetics is about how fast chemical reactions occur.

Measuring the rates of reactions (macroscopic) gives us insight into the way reactions are actually happening (microscopic)

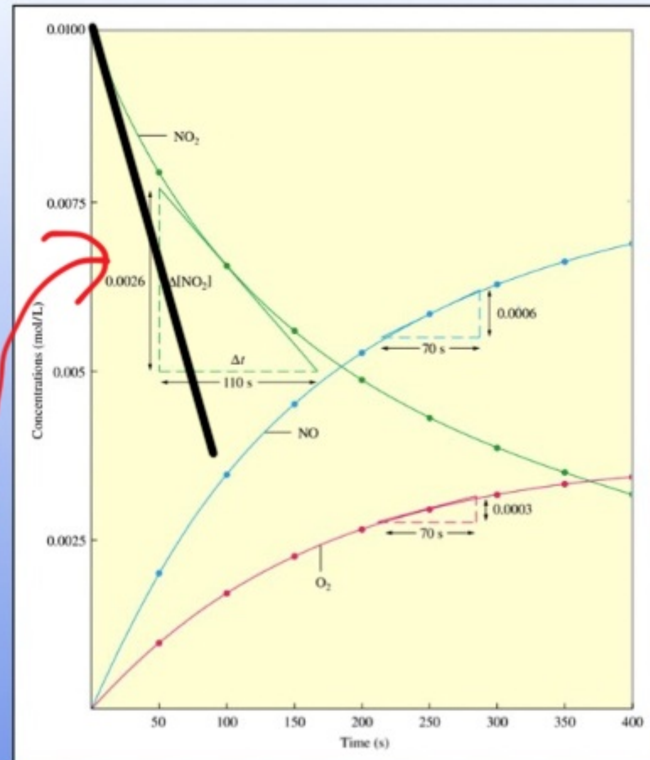
START ACTIVITY!


Average, Instantaneous, Initial, Reaction Rate
$2NO_2(g) \rightarrow 2NO(g) + O_2(g)$
Avg = 2 data points
Instant = TANGENT
0.0100
0.0075
0.005
0.0025
Concentrations (mol/L)
NO_2
NO
O_2
0.0026
$\Delta[NO_2]$
Δt
110 s
0.0006
70 s
0.0003
70 s
50
100
150
200
250
300
350
400
Time (s)
Check in

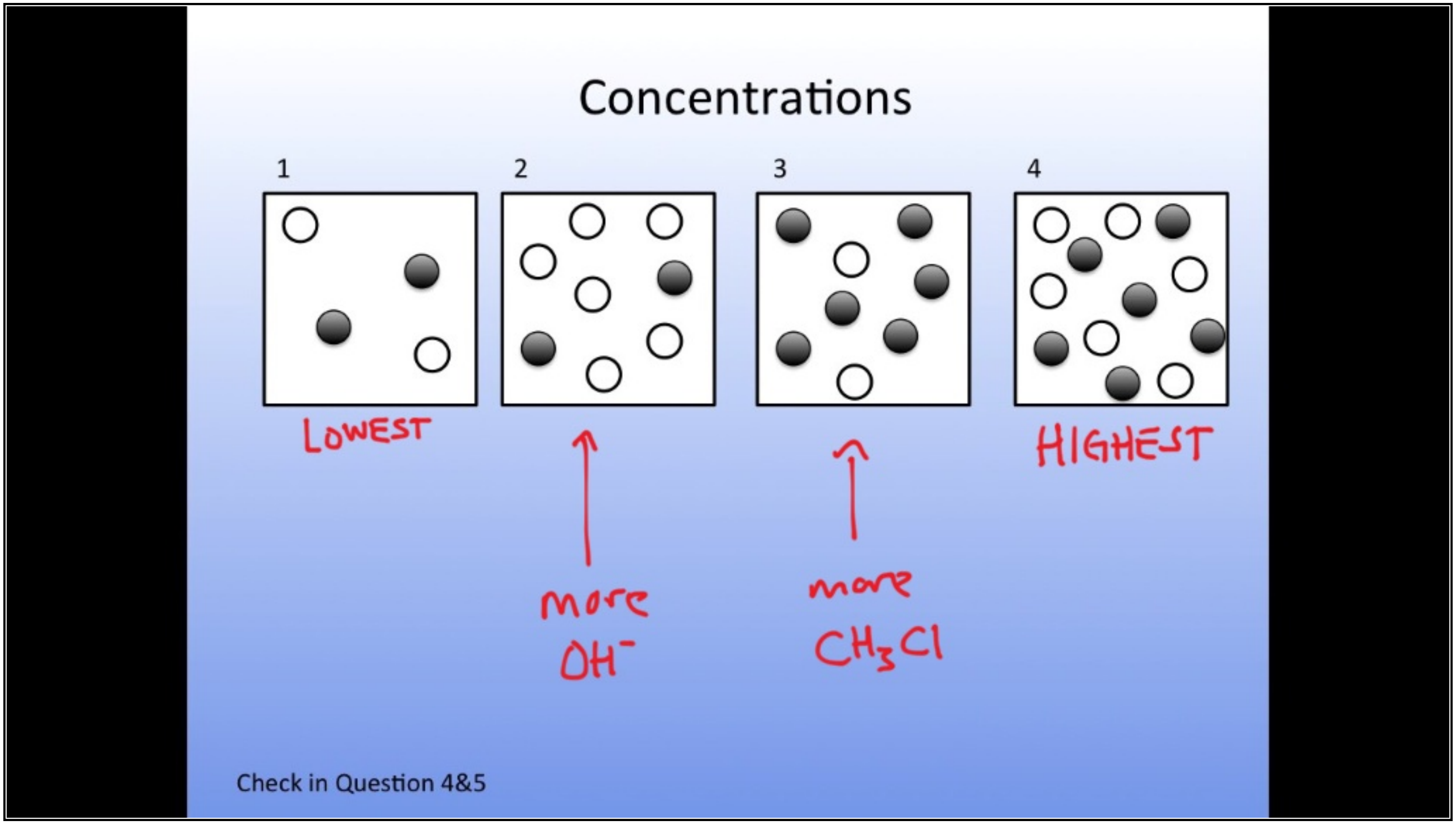
Average, Instantaneous, Initial, Reaction Rate

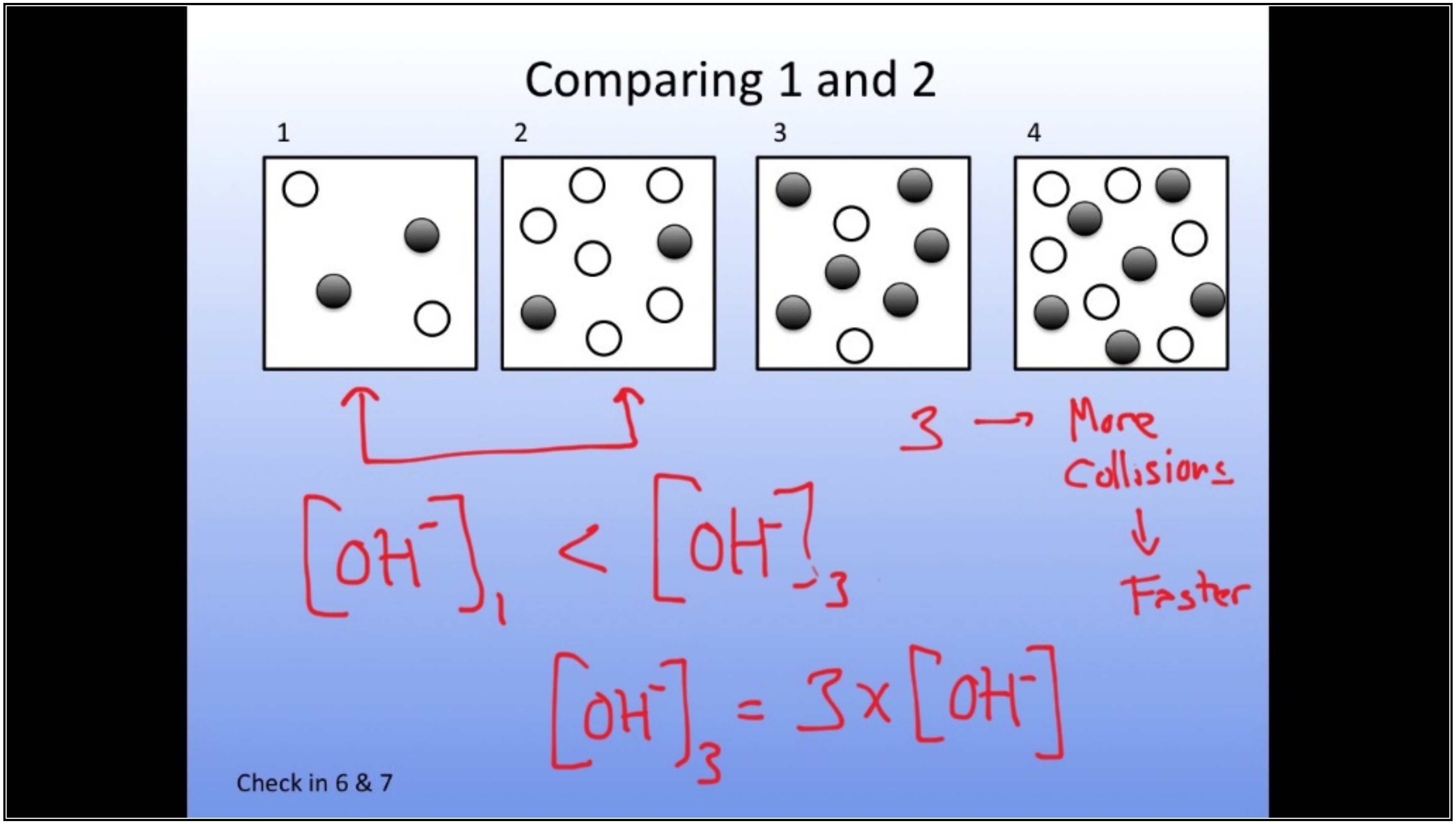
$2NO_2(g) \rightarrow 2NO(g) + O_2(g)$

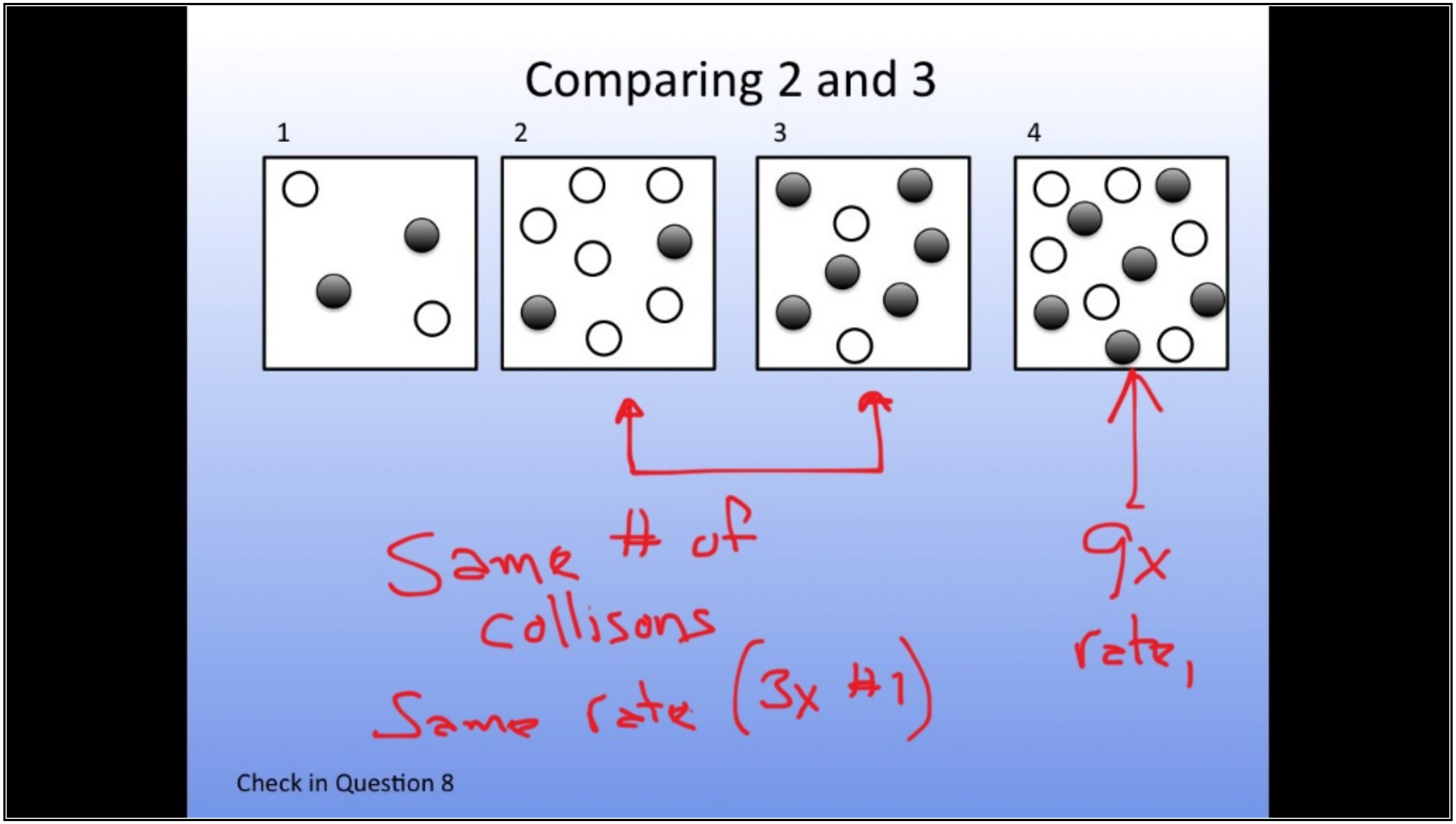
Initial
= tangent
@ t = 0



Check in


Concentrations
1
2
3
4
LOWEST
HIGHEST
more
OH⁻
more
CH3Cl
Check in Question 4&5


Comparing 1 and 2
1
2
3
4
[OH-]1 < [OH-]3
3 → More Collisions ↓ Faster
[OH-]3 = 3x[OH-]
Check in 6 & 7


Comparing 2 and 3
1
2
3
4
Same # of collisons
Same rate (3x #1)
9x rate,
Check in Question 8

Kinetics

Imagine the following reaction

$$CH_3Cl + OH^- \longrightarrow CH_3OH + Cl^-$$

Macroscopic

IN THE LAB

Microscopic

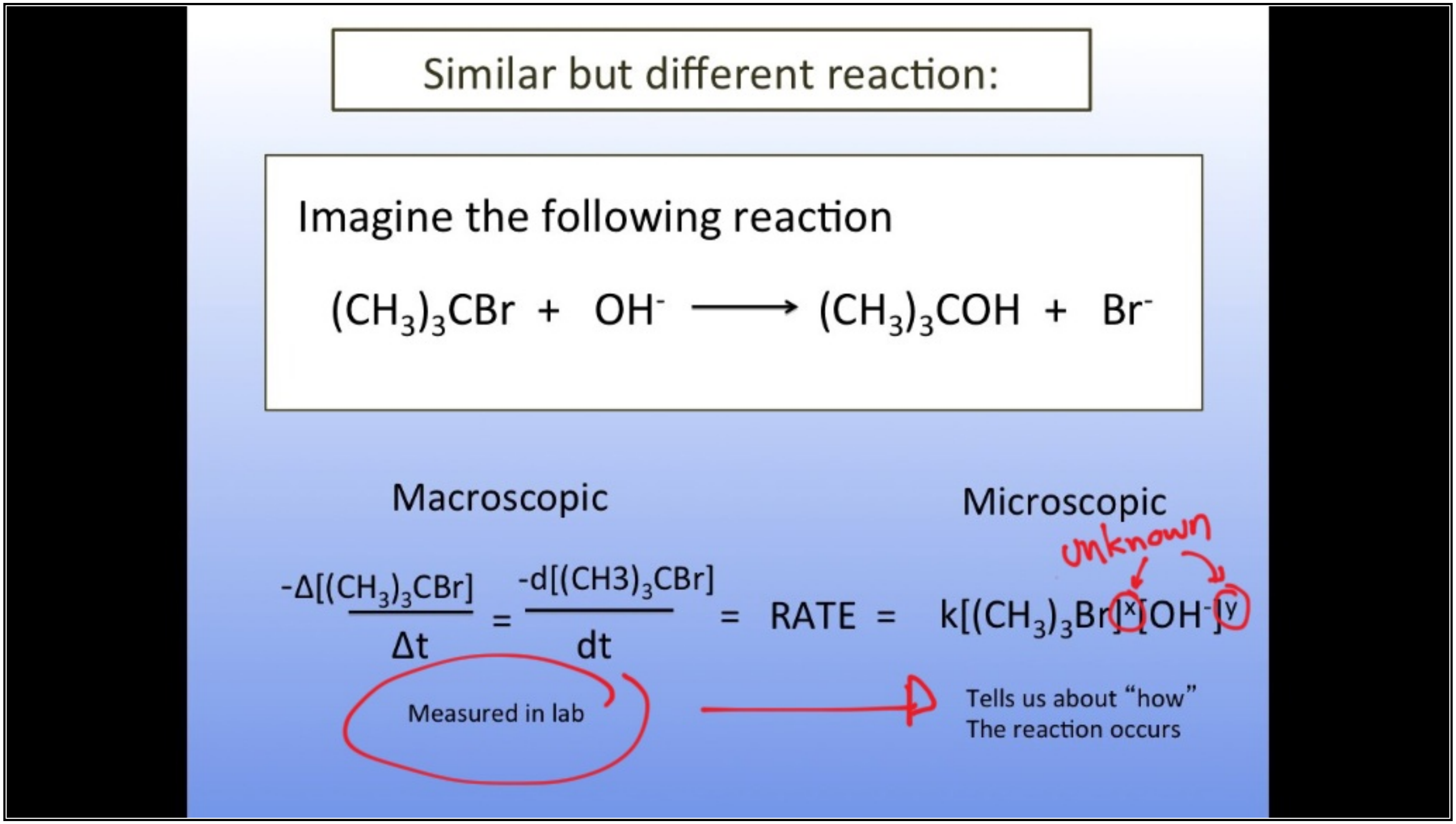
what is happening with the molecules

$$\frac{-\Delta[CH_3Cl]}{\Delta t} = \frac{-d[CH_3Cl]}{dt} = RATE = k[CH_3Cl][OH^-]$$

Measured in lab

Tells us about "how"
The reaction occurs

Check at end of activity


Similar but different reaction:
Imagine the following reaction
$(CH_3)_3CBr + OH^- \longrightarrow (CH_3)_3COH + Br^-$
Macroscopic
Microscopic
unknown
$\frac{-\Delta[(CH_3)_3CBr]}{\Delta t} = \frac{-d[(CH3)_3CBr]}{dt}$ = RATE = $k[(CH_3)_3Br]^x[OH^-]^y$
Measured in lab
Tells us about "how"
The reaction occurs

Poll: Clicker Question

Method of Initial Rates-Empirically Determine Rate Law

$$(CH_3)_3CBr + OH^- \longrightarrow (CH_3)_3COH + Br^-$$

What is the rate law for this reaction?

Experiment	$[(CH)_3CBr]_o$	$[OH\text{-}]_o$	initial rate ($M\ s^{-1}$)
1	0.1M	0.1M	2.5×10^{-3}
2	0.2M	0.1M	5.0×10^{-3}
3	0.1M	0.2M	2.5×10^{-3}

A. Rate = $k[(CH_3)_3CBr][OH^-]$
B. Rate = $k[(CH_3)_3CBr][OH^-]^2$
C. Rate = $k[(CH_3)_3CBr]^2[OH^-]$
D. Rate = $k[(CH_3)_3CBr]$
E. Rate = $k[OH^-]$

Poll: Clicker Question

Method of Initial Rates-Empirically Determine Rate Law

$$A + 2B \longrightarrow C$$

The reaction is what order in B?

Experiment	$[A]_o$	$[B]_o$	initial rate ($M\ s^{-1}$)
1	0.1M	0.1M	2.73
2	0.15M	0.1M	6.14
3	0.1M	0.2M	2.74

A. 0
B. 1
C. 1.5
D. 2
E. 3

Keep [A] = const
change [B]
rate = const

A + 2B C

The reaction is what order in B?

Experiment	$[A]_o$	$[B]_o$	initial rate ($M\ s^{-1}$)
1	0.1M	0.1M	2.73
2	0.15M	0.1M	6.14
3	0.1M	0.2M	2.74

$$\frac{\text{rate 3}}{\text{rate 1}} = \frac{k[A]_3^x[B]_3^y}{k[A]_1^x[B]_1^y} = \frac{k(.1)^x(.2)^y}{k(.1)^x(.1)^y} = \left(\frac{.2}{.1}\right)^y = 2^y = 1 \quad \left(\frac{2.74}{2.73}\right)$$

$$= \frac{2.74}{2.73} = 1$$

$$Y = 0\ !$$

Poll: Clicker Question

Method of Initial Rates-Empirically Determine Rate Law

$$A + 2B \longrightarrow C$$

The reaction is what order in A?

Experiment	$[A]_o$	$[B]_o$	initial rate ($M\ s^{-1}$)
1	0.1M	0.1M	2.73
2	0.15M	0.1M	6.14
3	0.1M	0.2M	2.74

A. 0
B. 1
C. 1.5
D. 2
E. 3

Method of Initial Rates-Empirically Determine Rate Law

$A + 2B \qquad C$

The reaction is what order in A?

Experiment	$[A]_o$	$[B]_o$	initial rate ($M\ s^{-1}$)
1	0.1M	0.1M	2.73
2	0.15M	0.1M	6.14
3	0.1M	0.2M	2.74

$$\frac{\text{rate }2}{\text{rate }1} = \frac{6.14}{2.73} = \frac{k(.15)^x(.1)^y}{k(.1)^x(.1)^0} = (1.5)^x$$

$x = 2$

What is k?

$A + 2B \qquad C$

Experiment	$[A]_o$	$[B]_o$	initial rate ($M\ s^{-1}$)
1	0.1M	0.1M	2.73
2	0.15M	0.1M	6.14
3	0.1M	0.2M	2.74

$$\text{rate} = k[A]^2[B]^0$$

$$2.73\ M s^{-1} = k(.1M)^2$$

$$k = 273\ M^{-1} s^{-1}$$

What is k?

A + 2B C

Experiment	$[A]_o$	$[B]_o$	initial rate ($M\ s^{-1}$)
1	0.1M	0.1M	2.73
2	0.15M	0.1M	6.14
3	0.1M	0.2M	2.74

Poll: Clicker Question

The empirical rate law for the reaction

$$CO + H_2O \quad CO_2 + H_2$$

Is $rate = k[CO][H_2O]$

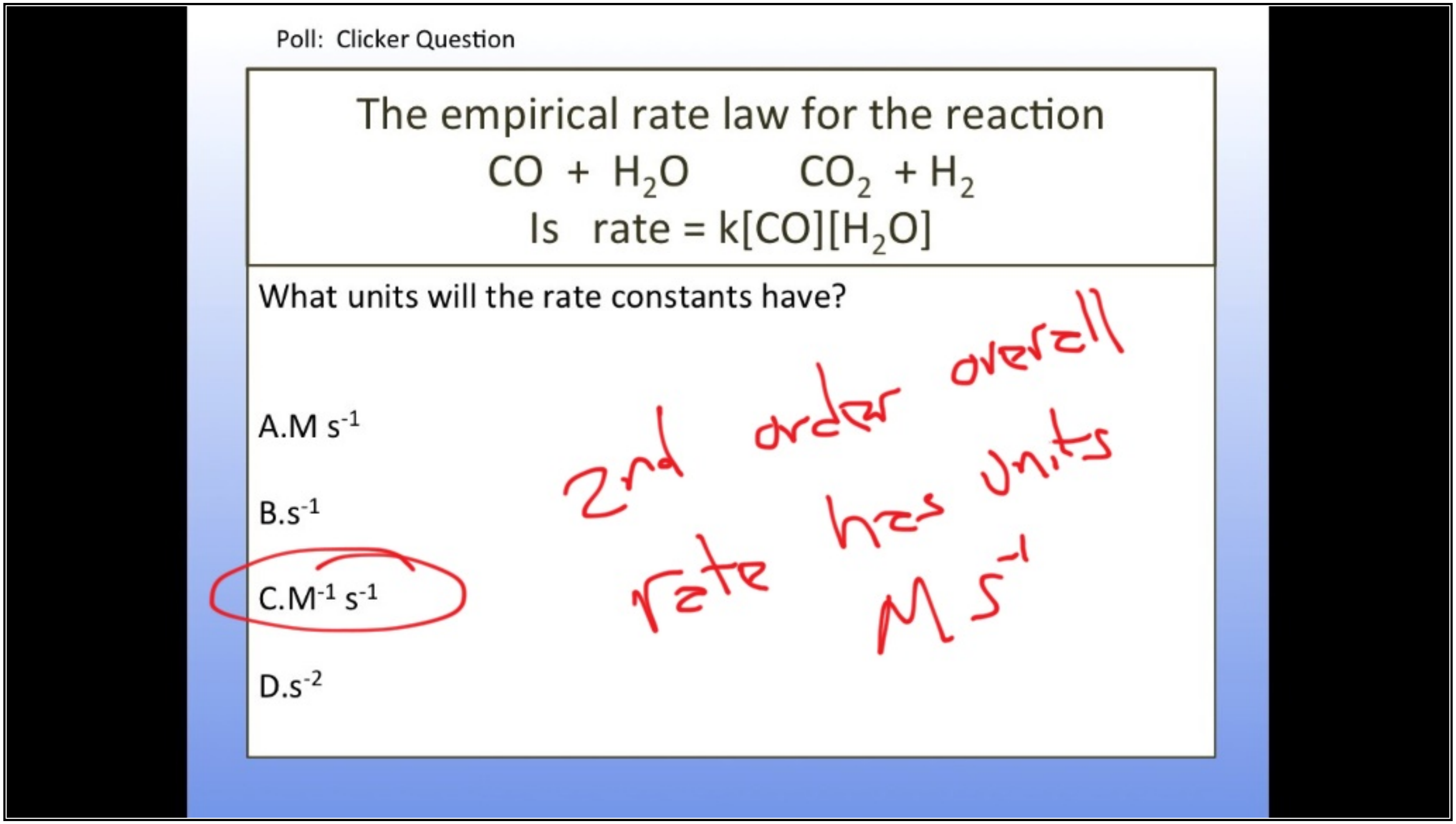
This reaction is best described as

A. First order in CO and first order in H_2O

B. First order in CO only

C. Second order in CO

D. Second order in CO and second order in H_2O


Poll: Clicker Question
The empirical rate law for the reaction
$CO + H_2O \quad CO_2 + H_2$
Is rate = $k[CO][H_2O]$
What units will the rate constants have?
A. $M\ s^{-1}$
B. s^{-1}
C. $M^{-1}\ s^{-1}$
D. s^{-2}
2nd order overall
rate has units
$M\ s^{-1}$

Learning Outcomes

Understand the concept of rate of change associated with chemical change, recognizing that the rate of change for a chemical reaction can be determined by experimentally by monitoring the change in concentration of a reactant or product with time.

Be able to identify the reaction order for a chemical change.

Apply integrated rate equations to solve for the concentration of chemical species during a reaction of different orders