## Thinking Like a

 Chemist About Kinetics II
## UNIT7 DAY5

What are we going to learn today?
$\square$
Investigating Integrated Rate Law

HW9 due Tue 9 AM
LM 29 .. Question was Killed

Quiz: Clicker Question 1

The rate constant for a mystery reaction is $4.5 \times 10^{-2} \mathrm{M} \mathrm{s}^{-1}$ By what order does this reaction proceed?
(a) 0 order
b) $1^{\text {st }}$ order
c) $2^{\text {nd }}$ order
d) $3^{\text {rd }}$ order

Kinetics - Review from Last time

Imagine the following reaction occurring in one elementary step:

$$
\mathrm{CH}_{3} \mathrm{Br}+\mathrm{OH}^{-} \longrightarrow \mathrm{CH}_{3} \mathrm{OH}+\mathrm{Br}^{-}
$$

$$
\begin{gathered}
\text { Macroscopic } \\
\frac{-\Delta\left[\mathrm{CH}_{3} \mathrm{Br}\right]}{\Delta \mathrm{t}}=\frac{-\mathrm{d}\left[\mathrm{CH}_{3} \mathrm{Br}\right]}{\mathrm{dt}}=\text { RATE }=\mathrm{k}\left[\mathrm{CH}_{3} \mathrm{Br}\right]^{x}\left[\mathrm{OH}^{-}\right]^{y}
\end{gathered}
$$

Measured in lab

Integrated rate laws
(the concentration as a function of time)
We need a situation in which either

1. The rate law depends on only one reactant
2)平. Only one reactant is changing much in

 so effectively only one concentration is changing

## Principles of Chemistry II

First order.
Integrated Rate Law $\square$

The rate of the reaction is directly proportional to the concentration of one of reactant

For a generic reaction let's call that reactant " $A$ "

$$
\frac{-\mathrm{d}[\mathrm{~A}]}{\mathrm{dt}}=\mathrm{RATE}=\mathrm{k}[\mathrm{~A}]
$$

## Integrated Rate Law

First order.

$$
\begin{aligned}
y & =m x+b \\
\ln [A] & =-k t+\ln [A]_{0}
\end{aligned}
$$

Integrated Rate Law


Half
Life: $\mathrm{t}_{1 / 2}=\frac{\ln (2)}{k} \quad \ln \frac{[A]_{t}}{[A]_{0}}=-k t$
Rearrange
CH302 Vanden Bout/LaBrake Spring 2013


TABLE 15．6 Summary of the Kinetics for Reactions of the Type $a \mathrm{~A} \longrightarrow$ Products That Are Zero，First，or Second Order in［A］


Principles of Chemistry II

Poll：Clicker Question 2

Refer to Activity Q1．What is the concentration of $\mathrm{N}_{2} \mathrm{O}$ after 100 ms ？
a） 0.34 M
b） 0.24 M
c） 0.14 M
d）I have not mastered this skill and cannot get the answer without help．

Poll：Clicker Question 3

Refer to Activity Q2：The value of the k could be determined：
a）By using this data in the rate law equation applying the method of initial rates and solving for $k$
b）By taking the natural log of all the values and then taking the difference between natural log and concentration at time， t
c）By determining the slope of the line from a plot of $\ln \left[\mathrm{N}_{2} \mathrm{O}_{5}\right]$ versus time．
d）By determining the slope of the line from a plot of $\ln \left[\mathrm{N}_{2} \mathrm{O}_{5}\right]$ versus time．The value of $k$ unputd be the quppositite oft
a) By using this data in the rate law equation applying the method of initial rates and solving for $k$
b) By taking the natural log of all the values and then taking the difference between natural log and concentration at time, t
c) By determining the slope of the line from a plot of $\ln \left[\mathrm{N}_{2} \mathrm{O}_{5}\right]$ versus time.
d) By determining the slope of the line from a plot of $\ln \left[\mathrm{N}_{2} \mathrm{O}_{5}\right]$ versus time. The value of $k$ would be the opposite of the slope.

Poll: Clicker Question 4

Refer to Activity Q3: How long will it take A to decrease to 1\% of starting amount?
a) 0 seconds
bi) 5 seconds
c) 100 seconds
d) I have not mastered this skill enough to figure out how to work this problem.

Poll: Clicker Question 5

Refer to Activity Q4: How many years will it take the isotope to drop to $30 \%$ of original amounts?
a) $24,000 \mathrm{yrs}$
b) $36,200 \mathrm{yrs}$
c) $41,660 \mathrm{yrs}$
d) $43,580 \mathrm{yrs}$
e) $48,000 \mathrm{yrs}$

Poll: Clicker Question 6

Refer to Activity Q5: How much time passes to reduce starting concentration to $20 \%$ of original amount?
a)41 seconds
b) 82 seconds
c) 160 seconds
d) 202 seconds

Refer to Activity Q5: How much time passes to reduce starting concentration to $20 \%$ of original amount?
a) 41 seconds
b) 82 seconds
c) 160 seconds

d) 202 seconds
e) I have not mastered this skill enough to solve this problem.

$$
\mathrm{CO}(\mathrm{~g})+\mathrm{H}_{2} \mathrm{O}(\mathrm{~g}) \longleftrightarrow \mathrm{CO}_{2}(\mathrm{~g})+\mathrm{H}_{2}(\mathrm{~g})
$$

The rate law for this reaction is

$$
\begin{aligned}
& \text { rate }=\mathrm{k}\left[\mathrm{H}_{2} \mathrm{O}\right][\mathrm{CO}] \\
& \\
& \\
& \text { Overall : } 2^{\text {rd }} \\
& \text { order first order in } \mathrm{H}_{2} \mathrm{O} \text { and } \\
& \text { first order in } \mathrm{CO}
\end{aligned}
$$

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Poll: Clicker Question 7

$$
\begin{aligned}
& \mathrm{CO}(\mathrm{~g})+\mathrm{H}_{2} \mathrm{O}(\mathrm{~g}) \rightarrow \mathrm{CO}_{2}(\mathrm{~g})+\mathrm{H}_{2}(\mathrm{~g}) \\
& \text { rate }=\mathrm{k}\left[\mathrm{H}_{2} \mathrm{O}\right][\mathrm{CO}] \\
& {[\mathrm{CO}]_{\mathrm{o}}=0.01 \mathrm{M}} \\
& {\left[\mathrm{H}_{2} \mathrm{O}_{\mathrm{o}}=0.01 \mathrm{M}\right.} \\
& -\frac{d[\mathrm{CO}]}{d t}=-\frac{d\left[\mathrm{H}_{2} \mathrm{O}\right]}{d t}
\end{aligned}
$$



Why is the plot of $\ln [C O]$ not a straight line?
A. It is not $1^{\text {st }}$ order in [CO]
8. Both [CO] and $\left[\mathrm{H}_{2} \mathrm{O}\right]$ are changing
C. It is $2^{\text {nd }}$ order in [CO]
D. The [CO] is changing at a different rate than $\mathrm{H}_{2} \mathrm{O}$

$\mathrm{CO}(\mathrm{g})+\mathrm{H}_{2} \mathrm{O}(\mathrm{g}) \rightarrow \mathrm{CO}_{2}(\mathrm{~g})+\mathrm{H}_{2}(\mathrm{~g})$
rate $=k\left[\mathrm{H}_{2} \mathrm{O}\right][\mathrm{CO}]$
$[\mathrm{CO}]_{0}=0.01 \mathrm{M}$
$\left[\mathrm{H}_{2} \mathrm{O}\right]_{0}=2.00 \mathrm{M}$


Why is the plot of $\ln [\mathrm{CO}]$ now a steep straight line?
A. $\left[\mathrm{H}_{2} \mathrm{O}\right]$ is nearly constant B. $\left[\mathrm{H}_{2} \mathrm{O}\right]$ is changing faster than [CO] C. The reaction is $2^{\text {nd }}$ order in [CO] Rate is the same
D. The reaction is 0 order in [CO]

Poll: Clicker Question 8

$$
\mathrm{CO}(\mathrm{~g})+\mathrm{H}_{2} \mathrm{O}(\mathrm{~g}) \rightarrow \mathrm{CO}_{2}(\mathrm{~g})+\mathrm{H}_{2}(\mathrm{~g})
$$

For the initial conditions of
$[\mathrm{CO}]_{\mathrm{o}}=0.01 \mathrm{M}$
$\left[\mathrm{H}_{2} \mathrm{O}\right]_{0}=2.00 \mathrm{M}$


What is the concentration of $\left[\mathrm{H}_{2} \mathrm{O}\right]$ at very long times (when the reaction has "gone to completion")
A. 0.01 M
B. 2.00 M
C. 1.99 M

Small
D. $\ln (.01) \mathrm{M}$

$$
\mathrm{CO}(\mathrm{~g})+\mathrm{H}_{2} \mathrm{O}(\mathrm{~g}) \longleftrightarrow \mathrm{CO}_{2}(\mathrm{~g})+\mathrm{H}_{2}(\mathrm{~g})
$$

What if we started with a whole lot of $\mathrm{H}_{2} \mathrm{O}$ compared to CO ?
(The $\left[\mathrm{H}_{2} \mathrm{O}\right]$ ~ constant (since there is so much of it)
Now we can combine the $\left[\mathrm{H}_{2} \mathrm{O}\right]$ with $k$ (since both are constant)

we now say the reaction is pseudo-first order in CO
Principles of Chemistry II

$$
\mathrm{CO}(\mathrm{~g})+\mathrm{H}_{2} \mathrm{O}(\mathrm{~g}) \longleftrightarrow \mathrm{CO}_{2}(\mathrm{~g})+\mathrm{H}_{2}(\mathrm{~g})
$$

rate $=k\left[\mathrm{H}_{2} \mathrm{O}\right][\mathrm{CO}]=\mathrm{k}^{\prime}[\mathrm{CO}]$
we now say the reaction is pseudo-first order in CO

Determine $k$ ' from a plot of $\ln [\mathrm{CO}]$ vs time

Determine k from k' since we
 know the $\left[\mathrm{H}_{2} \mathrm{O}\right]$

## Learning Outcomes

| Apply integrated rate equations to solve for the concentration of chemical |
| :--- |
| species during reaction of different orders. |
| Apply the concept of half life to kinetics problems |
| Understand and interpret pseudo first order kinetics data |

