

Thinking Like a  
Chemist About  
Kinetics II

*Integrated Rate Laws*

UNIT 7 DAY 5

What are we going to learn today?

Investigating Integrated Rate Law

Concentration as a  
function of time

IMPORTANT INFORMATION

HW 9 due Tue 9 AM

---

NO LM.  
JUST HW

## Quiz: Clicker Question

The rate constant for a mystery reaction is  $4.5 \times 10^{-3} \text{ M s}^{-1}$ . By what order does this reaction proceed?

a) 0 order

b) 1<sup>st</sup> order

c) 2<sup>nd</sup> order

d) 3<sup>rd</sup> order

$\text{s}^{-1}$   
 $\text{M}^{-1} \text{s}^{-1}$   
 $\text{M}^{-2} \text{s}^{-1}$

$$\text{rate} = k[A]^x$$
$$\text{M s}^{-1} = ? \times \text{M}^x$$

$$k \text{ M s}^{-1}$$
$$x=0$$

## Kinetics – Review from Last time

Imagine the following reaction occurring in one elementary step:



Macroscopic

$$\frac{-\Delta[\text{CH}_3\text{Br}]}{\Delta t} = \frac{-d[\text{CH}_3\text{Br}]}{dt}$$

Measured in lab

Microscopic

$$= \text{RATE} = k[\text{CH}_3\text{Br}]^x[\text{OH}^-]^y$$

Tells us about "how"  
The reaction occurs

connect

by integration

## Integrated rate laws (the concentration as a function of time)

- We need a situation in which either
  - The rate law depends on only one reactant.

OR

- Only one reactant is changing much in concentrations, so effectively only one concentration is changing.

TYPICALLY "A"

# Get out Activity Chemical Kinetics

## Rate Law First order

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"

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

$$\frac{d[A]}{[A]} = -k dt \quad \text{SOLVE}$$



## Integrated Rate Law First order

From this:  $\frac{-d[A]}{dt} = \text{RATE} = k[A]$

$$\int_{[A]_0}^{[A]} \frac{d[A]}{[A]} = \int_0^t -k dt$$

We can get the **Integrated Rate Law**:

$$\ln \frac{[A]}{[A]_0} = -kt$$

$$[A]_t = [A]_0 e^{-kt}$$

$$\frac{[A]}{[A]_0} = e^{-kt}$$

$$t_{1/2} = \frac{\ln(2)}{k}$$

Work on Activity

**TABLE 15.6** Summary of the Kinetics for Reactions of the Type  $aA \longrightarrow$  Products That Are Zero, First, or Second Order in  $[A]$

	Order		
	Zero	First	Second
Rate law	Rate = $k$	Rate = $k[A]$	Rate = $k[A]^2$
Integrated rate law	$[A] = -kt + [A]_0$	$\ln[A] = -kt + \ln[A]_0$	$\frac{1}{[A]} = kt + \frac{1}{[A]_0}$
Plot needed to give a straight line	$[A]$ versus $t$	$\ln[A]$ versus $t$	$\frac{1}{[A]}$ versus $t$
Relationship of rate constant to the slope of straight line	Slope = $-k$	Slope = $-k$	Slope = $k$
Half-life	$t_{1/2} = \frac{[A]_0}{2k}$	$t_{1/2} = \frac{0.693}{k}$	$t_{1/2} = \frac{1}{k[A]_0}$

Doesn't depend on initial conc!

## Poll: Clicker Question

Refer to Activity Q1. What is the concentration of  $N_2O$  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.

It MUST be "C" as that is the only value lower than 0.2 M

$$\begin{aligned} [N_2O] &= [N_2O]_0 e^{-kt} \\ &= (0.2 \text{ M}) e^{-(3.4)(0.1)} = 0.14 \text{ M} \end{aligned}$$

Poll: Clicker Question

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  $\ln[\text{N}_2\text{O}_5]$  versus time.
- d) By determining the slope of the line from a plot of  $\ln[\text{N}_2\text{O}_5]$  versus time. The value of  $k$  would be the opposite of the slope.

$$\text{slope} = -k$$

Poll: Clicker Question

Refer to Activity Q3: How long will it take A to decrease to 1% of starting amount?

- a) 0 seconds
- b) 5 seconds
- c) 100 seconds
- d) I have not mastered this skill enough to figure out how to work this problem.

4.6 s

$$x = ? \quad [A] = 0.01[A]_0$$

$$\frac{.01 [A]_0}{[A]_0} = 0.01 = e^{-kt}$$

Poll: Clicker Question

Refer to Activity Q4: How many years will it take the isotope to drop to 30% of original amounts?

- a) 24,000 yrs
- b) 36,200 yrs
- c) 41,690 yrs
- d) 43,580 yrs
- e) 48,000 yrs

SEE KEY



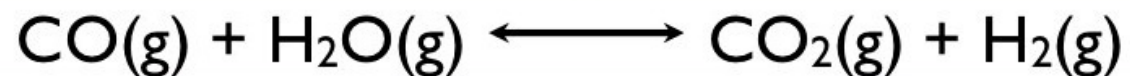
Poll: Clicker Question

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.

SEE KEY



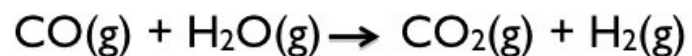


The rate law for this reaction is

$$\text{rate} = k[\text{H}_2\text{O}][\text{CO}]$$

it is first order in  $\text{H}_2\text{O}$  and  
first order in  $\text{CO}$

Poll: Clicker Question

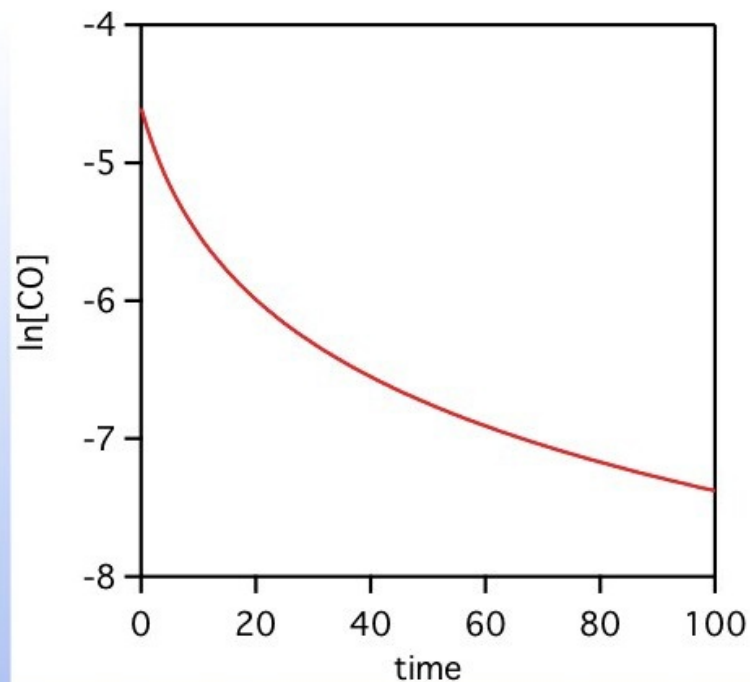


$$\text{rate} = k[\text{H}_2\text{O}][\text{CO}]$$

$$[\text{CO}]_0 = 0.01\text{M}$$

$$[\text{H}_2\text{O}]_0 = 0.01\text{M}$$

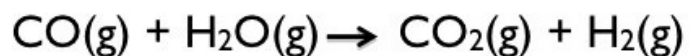
*2<sup>nd</sup> order overall*



Why is the plot of  $\ln[\text{CO}]$  not a straight line?

- A. It is not 1<sup>st</sup> order in  $[\text{CO}]$
- B. Both  $[\text{CO}]$  and  $[\text{H}_2\text{O}]$  are changing
- C. It is 2<sup>nd</sup> order in  $[\text{CO}]$
- D. The  $[\text{CO}]$  is changing at a different rate than  $\text{H}_2\text{O}$

Poll: Clicker Question

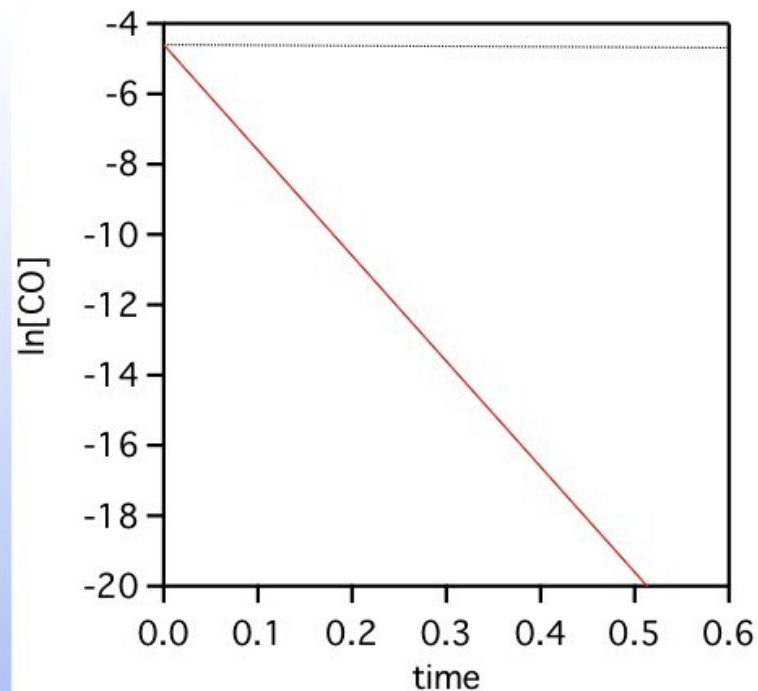


$$\text{rate} = k[\text{H}_2\text{O}][\text{CO}]$$

CONST

$$[\text{CO}]_0 = 0.01\text{M}$$

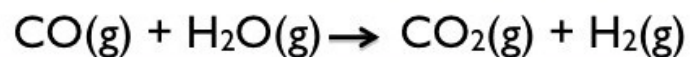
$$[\text{H}_2\text{O}]_0 = 2.00\text{M}$$



Why is the plot of  $\ln[\text{CO}]$  now a steep straight line?

- A.  $[\text{H}_2\text{O}]$  is nearly constant
- B.  $[\text{H}_2\text{O}]$  is changing faster than  $[\text{CO}]$
- C. The reaction is 2<sup>nd</sup> order in  $[\text{CO}]$
- D. The reaction is 0 order in  $[\text{CO}]$

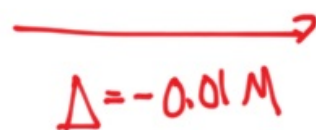
Poll: Clicker Question



For the initial conditions of

$$[\text{CO}]_0 = 0.01 \text{ M}$$

$$[\text{H}_2\text{O}]_0 = 2.00 \text{ M}$$



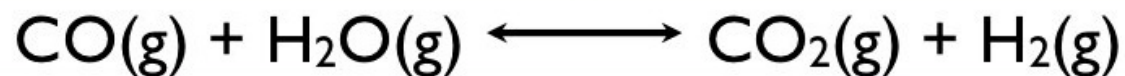
$$t = \infty$$

$$[\text{CO}] = 0 \text{ M}$$

$$[\text{H}_2\text{O}] = 1.99 \text{ M}$$

What is the concentration of  $[\text{H}_2\text{O}]$  at very long times (when the reaction has “gone to completion”)

- A. 0.01 M
- B. 2.00 M
- C. 1.99 M
- D.  $\ln(.01)$  M



What if we started with a whole lot of  $\text{H}_2\text{O}$   
compared to  $\text{CO}$ ?

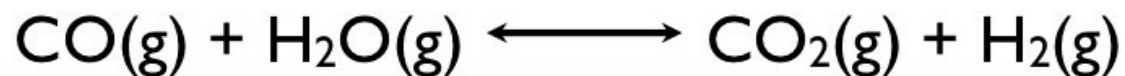
The  $[\text{H}_2\text{O}] \sim \text{constant}$  (since there is so much of it)

Now we can combine the  $[\text{H}_2\text{O}]$  with  $k$   
(since both are constant)

and write the rate law as  
 $\text{rate} = k[\text{H}_2\text{O}][\text{CO}] = k'[\text{CO}]$

we now say the reaction is **pseudo-first order** in  $\text{CO}$





$$\text{rate} = k[\text{H}_2\text{O}][\text{CO}] = k'[\text{CO}]$$

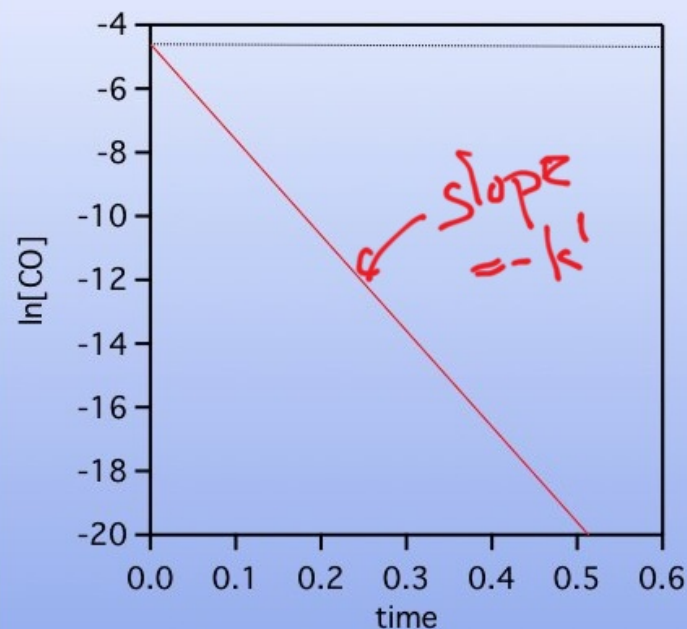
CONST

→ k'

we now say the reaction is  
pseudo-first order in CO

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

Determine  $k$  from  $k'$  since we  
know the  $[\text{H}_2\text{O}]$   $k' = k[\text{H}_2\text{O}]$



## 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

KINETIC ARE  
AWESOME