N-42 Instantaneous Rate and Rate Law

Target: I can determine the instantaneous rate of a reaction at an exact moment and can perform rate law calculations to find rate data

Link to YouTube Presentation: https://youtu.be/oMjg7QISP8k

Instantaneous Rates

Instantaneous Rate

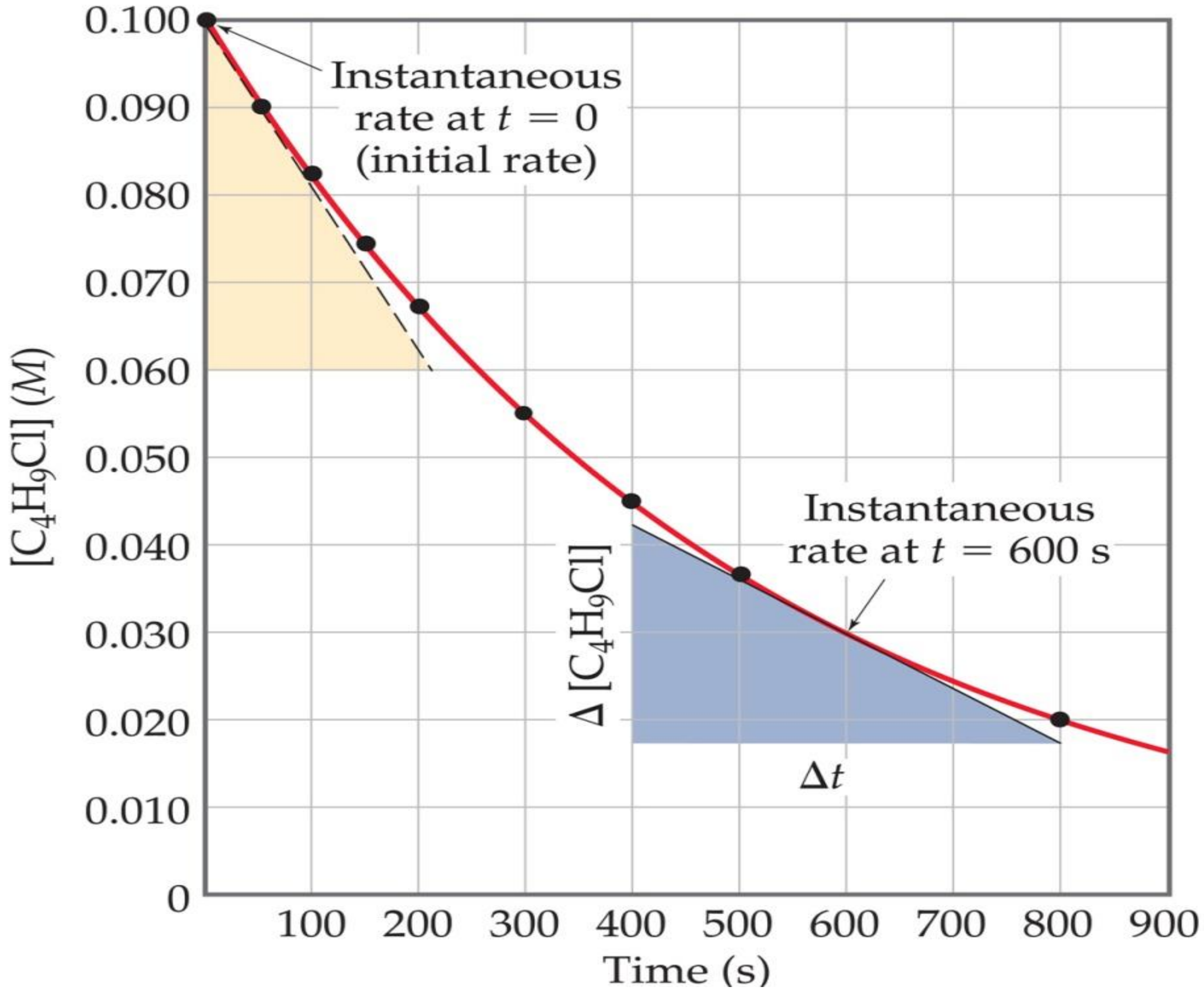
Average rate tells us the speed of a reaction over two time points, but what if we want to know the rate at an *exact* time point?

Calculate the **Instantaneous Rate!**

Instantaneous Rate

$C_4H_9Cl(aq) + H_2O(l) \longrightarrow C_4H_9OH(aq) + HCl(aq)$

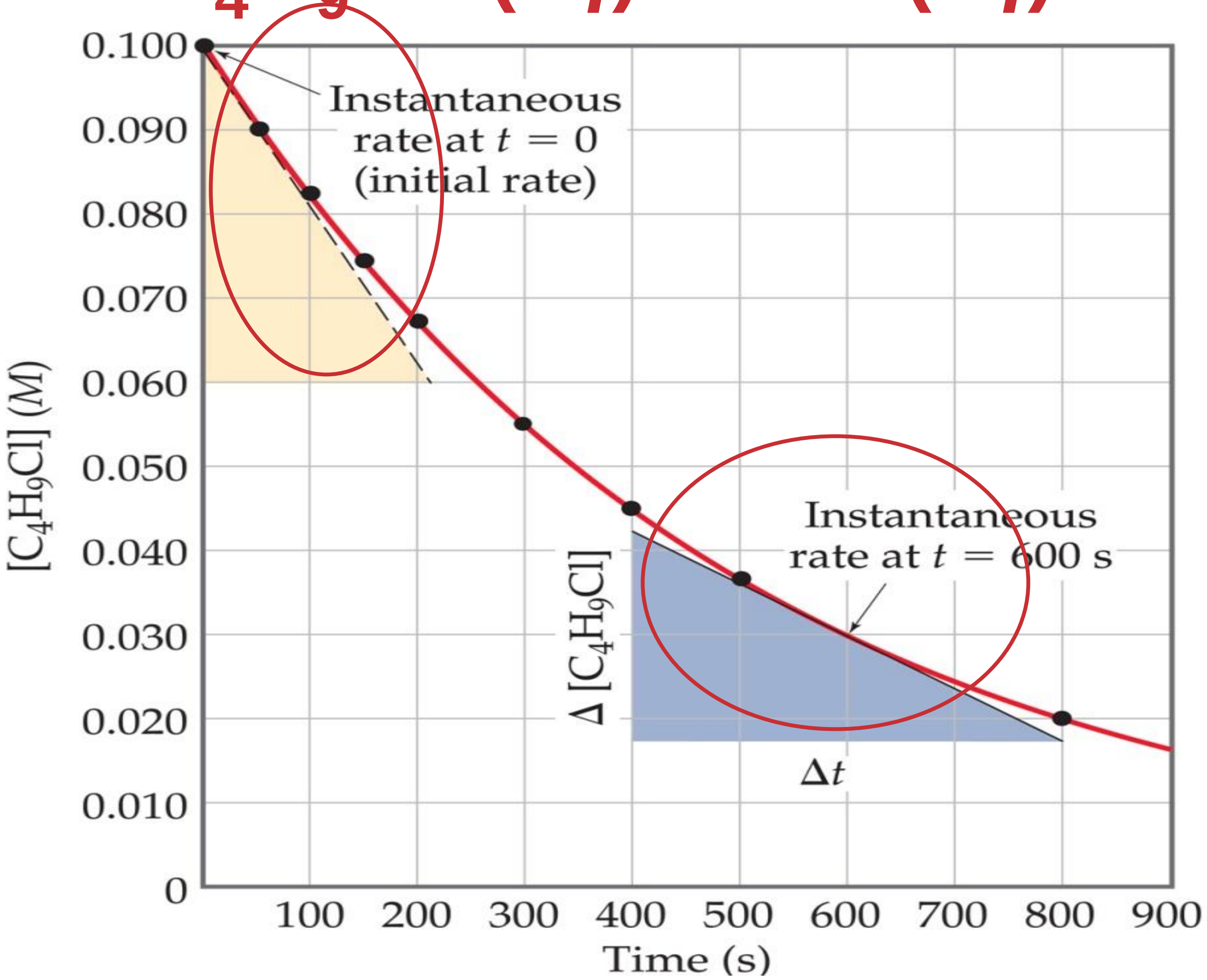
- Plot concentration vs. time
- The slope of a line tangent to the curve at any point is the instantaneous rate at that time.



Instantaneous Rate

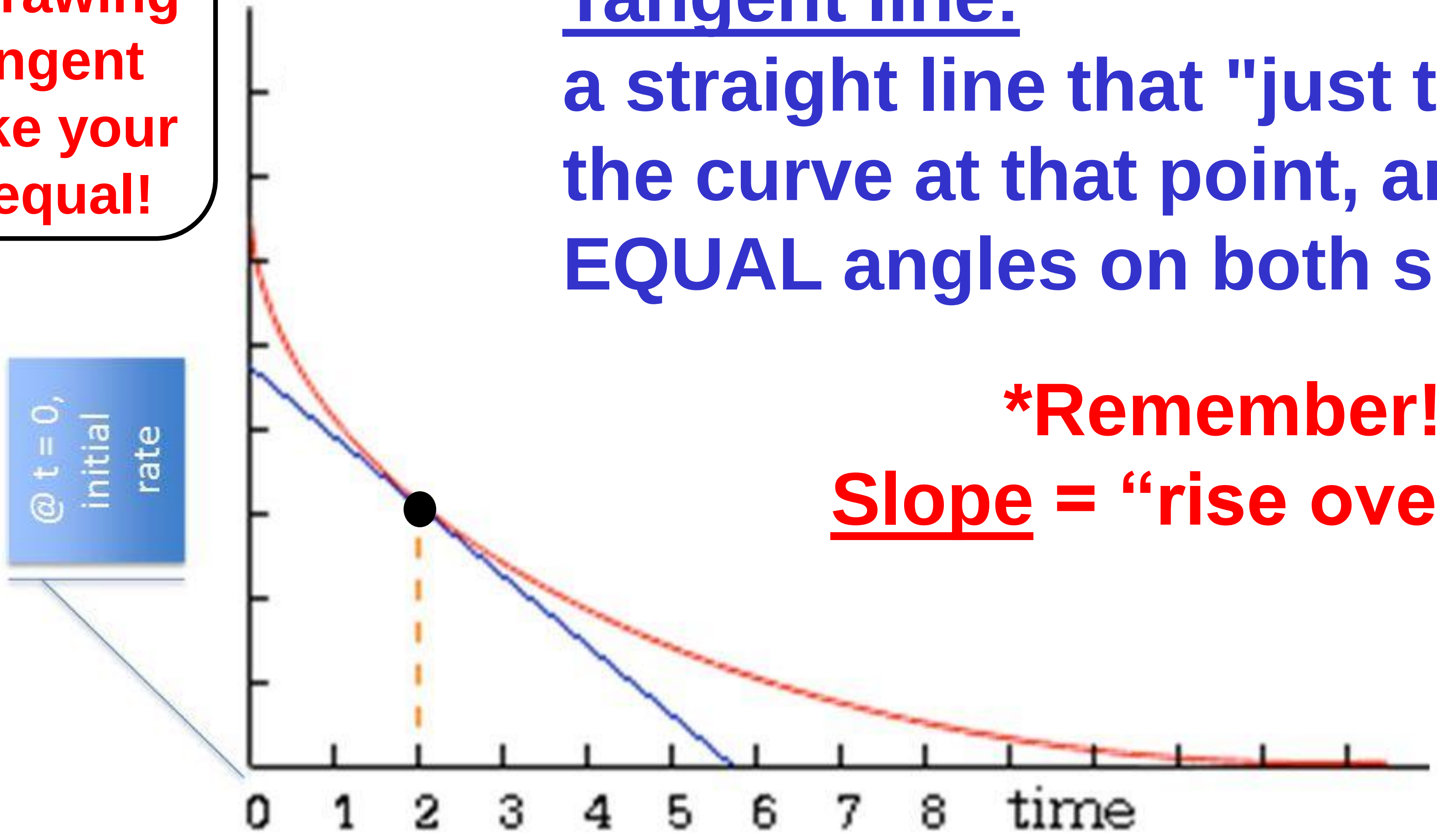
$C_4H_9Cl(aq) + H_2O(l) \longrightarrow C_4H_9OH(aq) + HCl(aq)$

- The reaction slows down as time goes on because the concentration of the reactants decreases.
- Steeper slope = faster



Instantaneous rate = slope of tangent line to curve at a specific point

Don’t be sloppy drawing your tangent line! Make your angles equal!



Tangent line:

a straight line that "just touches" the curve at that point, and has EQUAL angles on both sides.

Remember!

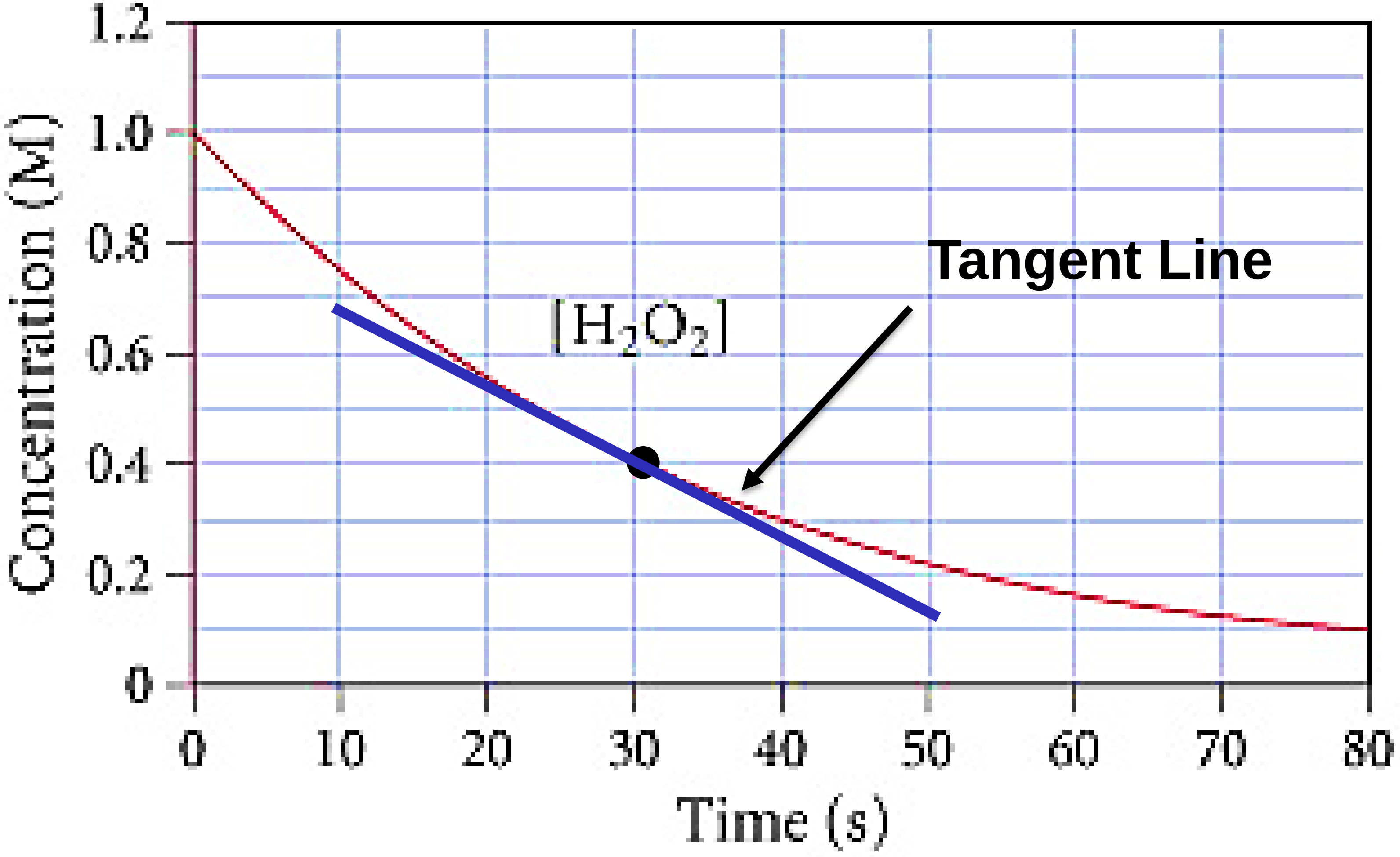
Slope = “rise over run”

Practice Problem

- Glue in the practice graph into your notebook
- Draw the tangent line to the curve and calculate the instantaneous rate.

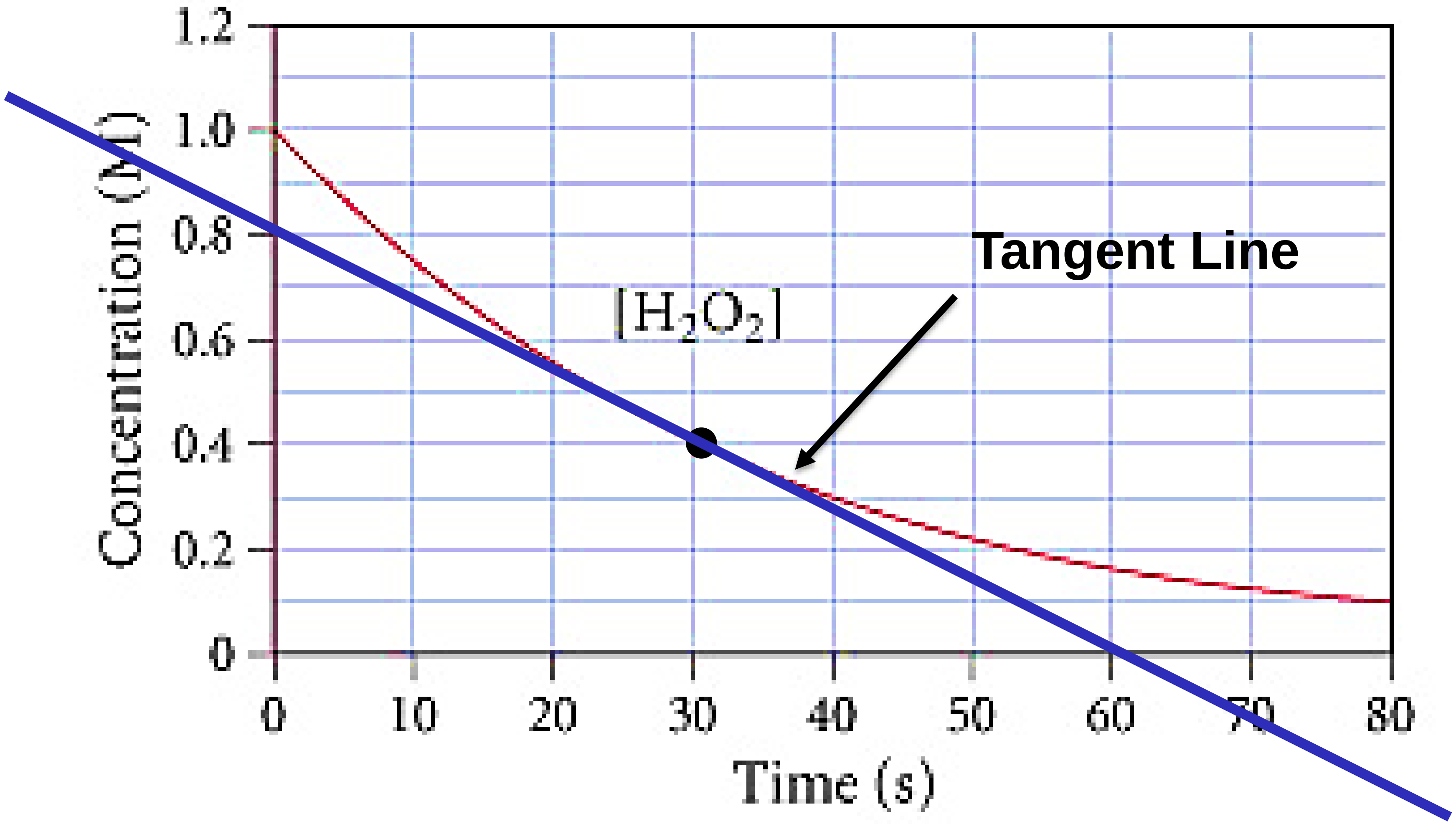
Practice Problem

What is the instantaneous rate at 30 seconds for the decomposition of hydrogen peroxide?



Practice Problem

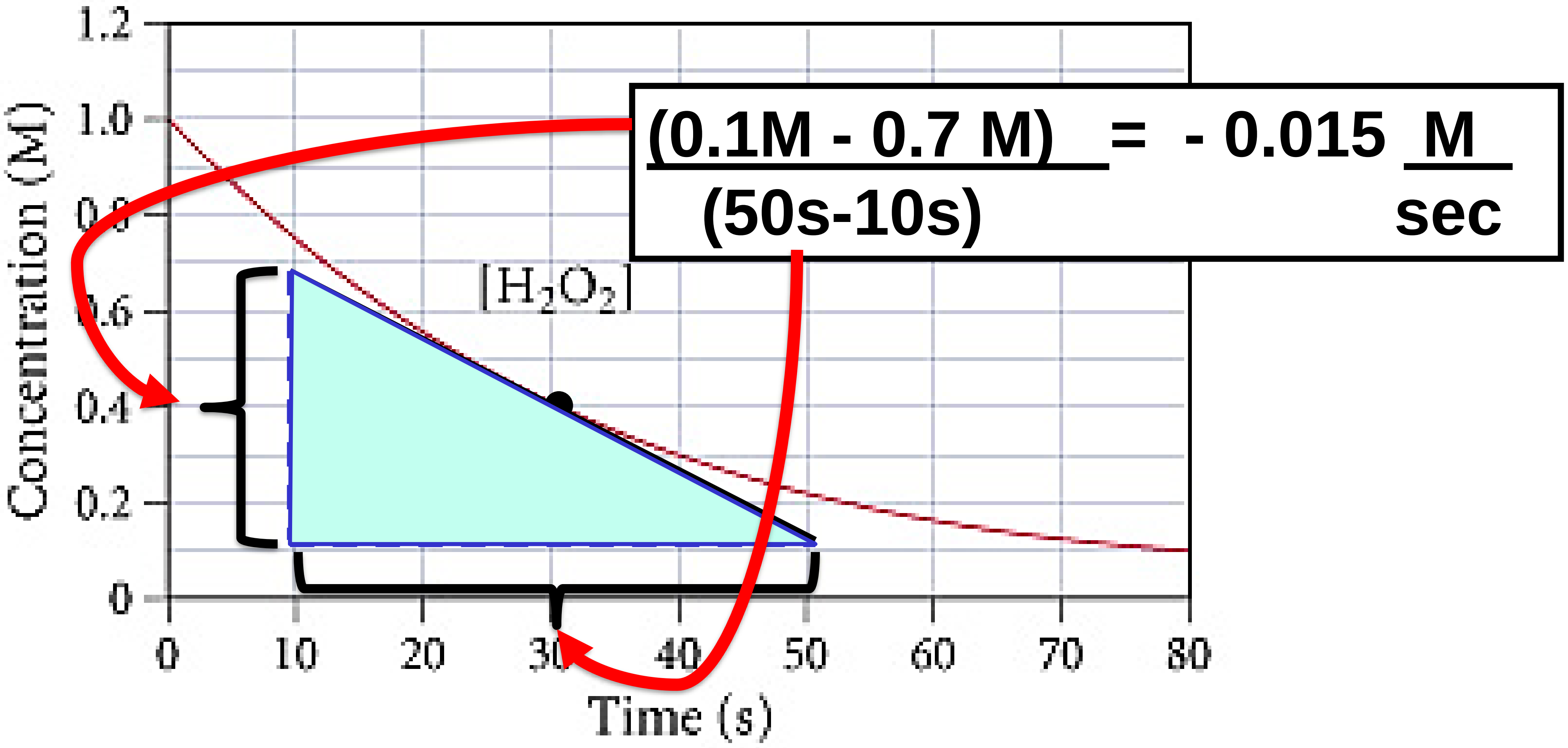
What is the instantaneous rate at 30 seconds for the decomposition of hydrogen peroxide?



Tangent Line

Practice Problem

What is the instantaneous rate at 30 seconds for the decomposition of hydrogen peroxide?



$$\frac{(0.1M - 0.7\ M)}{(50s-10s)} = -\ 0.015\ \frac{M}{sec}$$

Rate Laws

The Rate Law

The **rate law** (really just an equation) expresses the mathematical relationship between the ***rate*** of a chemical reaction and the ***concentration of reactants***

$$aA + bB \longrightarrow cC + dD$$

$$\boxed{\text{Rate} = k\,[A]^{x}[B]^{y}}$$

Notice **ONLY** reactants are used in the rate law!

What is this "k" thing?

$aA + bB \rightarrow cC + dD$ Rate = $k\,[A]^x[B]^y$

k is called the "rate constant"

- A numerical value that relates reaction rate and concentration of reactants at a given temperature
- Different for different reactions!
- Different for different temperatures!
- Large value of *k* means the reaction proceeds quickly

What would small value for k indicate?

Reaction Orders

$aA + bB \rightarrow cC + dD$ Rate = $k\,[A]^{\boxed{x}}\,[B]^{\boxed{y}}$

BUT WHAT DOES THAT EVEN MEAN???

Exponents in the rate law tell us:

- The "**order**" with respect to the concentration of that reactant
- The mathematical **effect** an individual reactant's concentration has on the overall rate – how much does a Δ[ ] affect the overall rate

How do we talk about it?

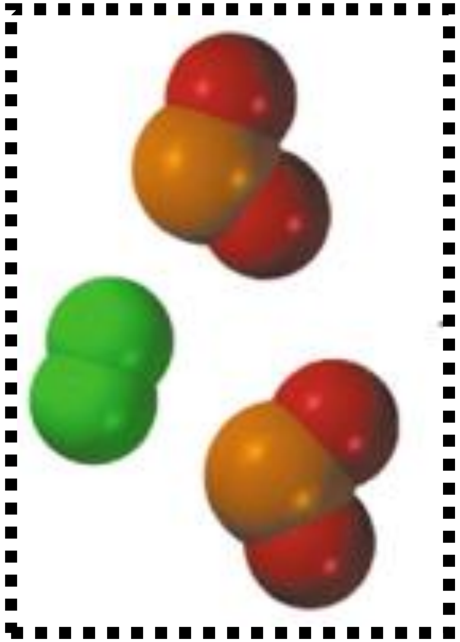
- The reaction is **xth order with respect to A**
- The reaction is **yth order with respect to B**
- The reaction is **(x+y)th order overall**

Rate Orders…Where do they come from?

- Rate laws are **always** determined experimentally.

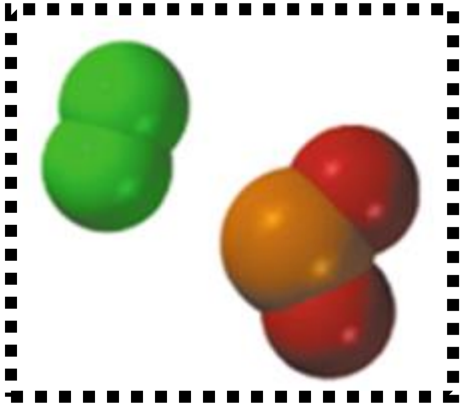
$$F_2\,(g) + \textcircled{2}\,ClO_2\,(g) \longrightarrow 2FClO_2\,(g)$$

$$\text{rate} = k\,[F_2][ClO_2]^{\textcircled{1}}$$



Exponents are NOT the coefficients from the *overall* balanced reaction!

They are coming from the *rate determining step* of the reaction!



What if it is a single step reaction?

$$\text{rate} = k\,[F_2][ClO_2]$$

See how the coefficients don’t match the exponents? That means that this must not have been a single step reaction!

So…if only a SINGLE step reaction…the overall equation IS the rate determining step, then yes the coefficients are the exponents.

Steps for Determining Rate Order

1. Write your “skeleton rate law”
2. Look at your experimental data (chart)
3. Find two trials in which:
   - The [ ] of one substance is held constant
   - The [ ] of another substance is being changed
4. Look to see how the rate changes when you vary the [ ] of ONLY one substance.

Practice Question #1

$F_2\ (g) + 2ClO_2\ (g) \rightarrow 2FClO_2\ (g)$

$$\boxed{\text{rate} = k\,[F_2]^x[ClO_2]^y}$$

Skeleton rate law

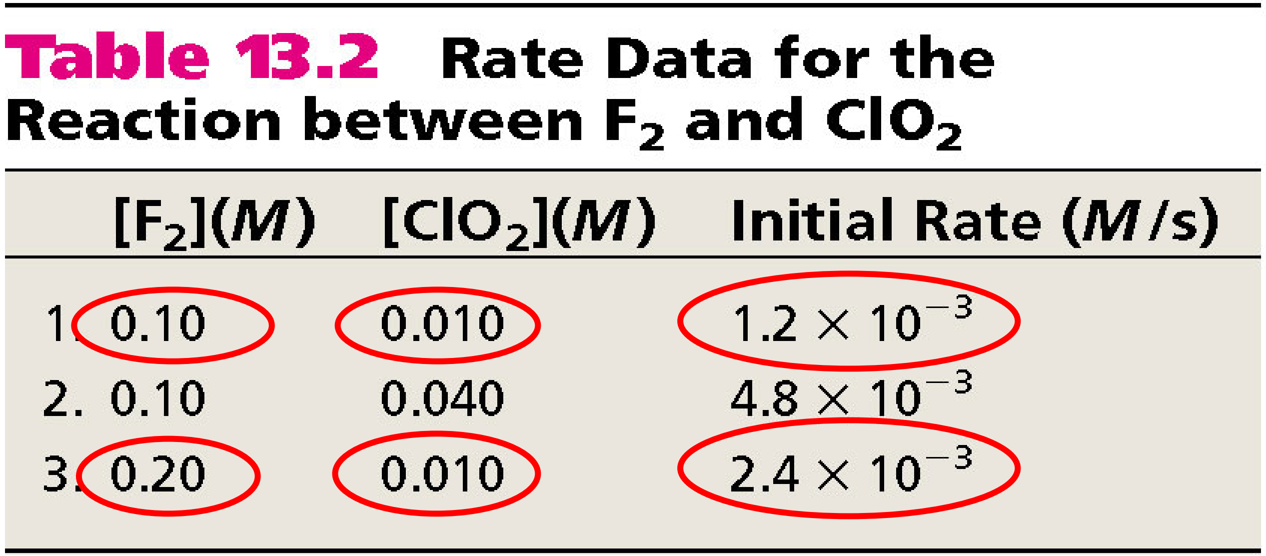


Table 13.2 **Rate Data for the Reaction between F_2 and ClO_2**

	$[F_2]$(M)	$[ClO_2]$(M)	Initial Rate (M/s)
1.	0.10	0.010	1.2×10^{-3}
2.	0.10	0.040	4.8×10^{-3}
3.	0.20	0.010	2.4×10^{-3}

Compare Trials 1 and 3:

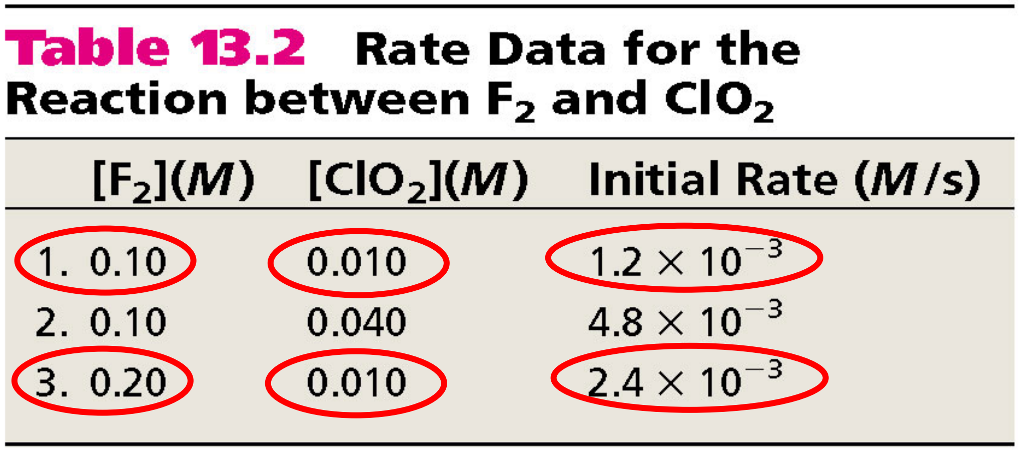
- $[ClO_2]$ stays constant
- $[F_2]$ doubles
- Rate doubles

Steps for Determining Rate Order

1. Write your “skeleton rate law”
2. Look at your experimental data (chart)
3. Find two trials in which:
   - The [ ] of one substance is held constant
   - The [ ] of another substance is being changed
4. Look to see how the rate changes when you vary the [ ] of ONLY one substance.
5. **Figure out what exponent on the [ ] change would result in the observed change to rate – that is the “order”**

OR you could do it the long way…

$F_2\,(g) + 2ClO_2\,(g) \rightarrow 2FClO_2\,(g)$



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3.	0.20	0.010	2.4×10^{-3}

$$\frac{\text{Rate Law Trial 3}}{\text{Rate Law Trial 1}}$$

$$\downarrow$$

$$\frac{2.4 \times 10^{-3} = \cancel{k}\ [0.20]^x\ [\cancel{0.010}]^y}{1.2 \times 10^{-3} = \cancel{k}\ [0.10]^x\ [\cancel{0.010}]^y}$$

$$\downarrow$$

$$2 = [2]^x \longrightarrow x = 1$$

Yuck…why would you want to?!

If you don't have "nice" numbers, or if you don't have a set of trials where things are held constant. Thankfully that is rare!

Practice Question #1

$\text{rate} = k\,[F_2]^x[ClO_2]^y$

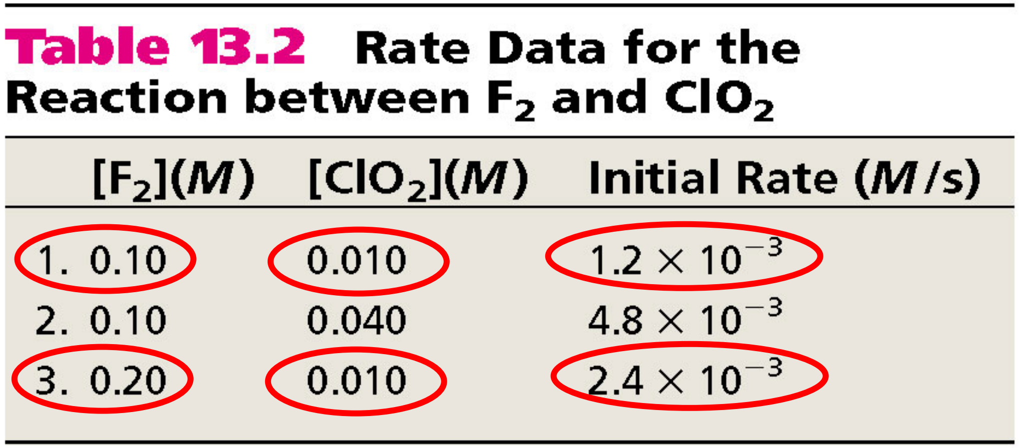
Rate doubles so put a 2

$2 = k\,[F_2]^x[ClO_2]^y$

[F_2] doubles so put a 2

$2 = k\,[2]^x[ClO_2]^y$

$F_2\,(g) + 2ClO_2\,(g) \rightarrow 2FClO_2\,(g)$



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2.	0.10	0.040	4.8×10^{-3}
3.	0.20	0.010	2.4×10^{-3}

[ClO_2] is constant so get rid of it,

$2 = k\,[2]^x$

k is constant so get rid of it

$$2 = [2]^x$$

Order with respect to [F_2] is 1!

Steps for Determining Rate Order

1. Write your “skeleton rate law”
2. Look at your experimental data (chart)
3. Find two trials in which:
    - The [ ] of one substance is held constant
    - The [ ] of another substance is being changed
4. Look to see how the rate changes when you vary the [ ] of ONLY one substance.
5. Figure out what exponent on the [ ] change would result in the observed change to rate – that is the “order”
6. **Repeat for each additional reactant**

Practice Question #1

$F_2\,(g) + 2ClO_2\,(g) \rightarrow 2FClO_2\,(g)$

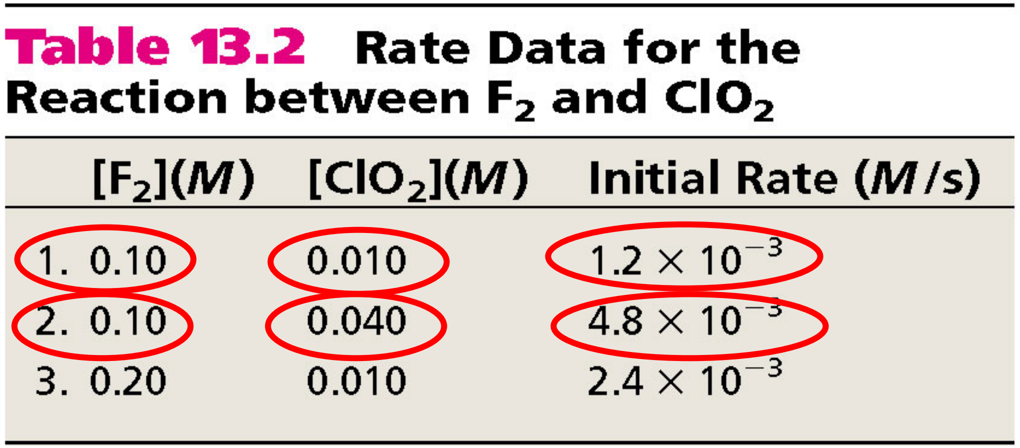


Table 13.2 Rate Data for the Reaction between F_2 and ClO_2

	$[F_2](M)$	$[ClO_2](M)$	Initial Rate (M/s)
1.	0.10	0.010	1.2×10^{-3}
2.	0.10	0.040	4.8×10^{-3}
3.	0.20	0.010	2.4×10^{-3}

$$\text{rate} = k\,[F_2]^1[ClO_2]^y$$

Rate quadruples so put a 4

$$4 = k\,[F_2]^1[ClO_2]^y$$

$[ClO_2]$ quadruples so put a 4

$$4 = k\,[F_2]^1[4]^y$$

$[F_2]$ is constant so get rid of it, k is constant so get rid of it

$$4 = [4]^y$$

Order with respect to $[ClO_2]$ is 1!

$$\textbf{rate} = k\,[F_2]^1[ClO_2]^1$$

What counts as "showing my work?"

Trials being used	Which [ ] is held constant	Which [ ] is being changed and by what factor is it changed by	What factor is the rate changed by	Logic time! (optional to write this)	Order based on rate data
1 & 3	$[H_2]$	$[O_2]$ x 2	x 2	$2 = [2]^x$	1

- *Doesn't need to be in chart format, just needs to somehow convey how you got your answer!*
- *Do not need to show the math to show doubling, tripling, etc unless you need to*
- *When calculating the rate constant you DO need to show the math*
- *Do not need to show the canceling for figuring out units, ok to memorize them.*

Practice Question #2

Run #	Initial [A] ($[A]_0$)	Initial [B] ($[B]_0$)	Initial Rate (v_0)
1	1.00 M	1.00 M	1.25×10^{-2} M/s
2	1.00 M	2.00 M	2.5×10^{-2} M/s
3	2.00 M	2.00 M	2.5×10^{-2} M/s

- What is the order with respect to A? **0**
  - *Trials 2 & 3*
- What is the order with respect to B? **1**
  - *Trials 1 & 2*
- What is the overall order of the reaction? **1**
- What is the rate law? **Rate = k $[B]^1$**

A

$1 = [2]^x$

$x = 0$

Means that A is not participating in the rate determining step!

B

$2 = [2]^y$

$y = 1$

Practice Question #3

$[NO_{(g)}]$ (mol dm^{-3})	$[Cl_{2(g)}]$ (mol dm^{-3})	Initial Rate (mol dm^{-3} s^{-1})
0.250	0.250	1.43×10^{-6}
0.250	0.500	2.86×10^{-6}
0.500	0.500	1.14×10^{-5}

- What is the order with respect to Cl_2? **1**
  - *Trials 1 & 2*
- What is the order with respect to NO? **2**
  - *Trials 2 & 3*
- What is the overall order of the reaction? **3**

$\underline{Cl_2}$

$2 = [2]^x$

$x = 1$

$\underline{NO}$

$4 = [2]^y$

$y = 2$

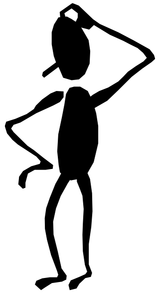
- What is the rate law? **Rate = k $[NO]^2$ $[Cl_2]^1$**

OR **Rate = k $[Cl_2]^1$ $[NO]^2$**

Practice Question #4

Determine the rate law ***AND*** calculate the rate constant for the following reaction from the following data:

$S_2O_8^{2-}\,(aq) + 3I^-\,(aq) \rightarrow 2SO_4^{2-}\,(aq) + I_3^-\,(aq)$



Experiment	$[S_2O_8^{2-}]$	$[I^-]$	Initial Rate (M/s)
1	0.08	0.034	2.2×10^{-4}
2	0.08	0.017	1.1×10^{-4}
3	0.16	0.017	2.2×10^{-4}

$$\text{rate} = k\,[S_2O_8^{2-}]^x[I^-]^y$$

$$x = 1 \qquad y = 1$$

$$\boxed{\text{rate} = k\,[S_2O_8^{2-}][I^-]}$$

To solve for k, rearrange your rate law then plug in values!*

Double [I⁻], rate doubles
(experiment 2 & 1)

Double $[S_2O_8^{2-}]$, rate doubles
(experiment 2 & 3)

$$k = \frac{\text{rate}}{[S_2O_8^{2-}][I^-]} = \frac{2.2 \times 10^{-4}\,M/s}{(0.08\,M)(0.034\,M)}$$

$$\boxed{= 0.08\ \frac{1}{Ms}}$$

Careful with units for k! They depend on order!

***Doesn't matter which trial you use!**

How on earth do you get the units????

$$\frac{(M/s)}{(M)(M)} = \frac{(\cancel{M})}{(\cancel{M})(M)(s)} = \boxed{\frac{1}{(M)(s)}}$$

$$= \boxed{M^{-1}s^{-1}}$$

$$= \frac{1}{(mol/L)(s)}$$

All the same answer!

Same process for any order rxn

$$= \boxed{\frac{L}{(mol)(s)}} = \boxed{L\ mol^{-1}\ s^{-1}}$$

Can't see it?

Then you need to memorize it or actually do the math in your calculator ☹

Change factor to Rate = [Change factor for Concentration]^x

Examples of determining the orders by actually plugging in			
rate doesn't change	$1 = 2^x$	*concentration doubles*	$x = 0$
rate doubles	$2 = 2^x$	*concentration doubles*	$x = 1$
rate quadruples	$4 = 2^x$	*concentration doubles*	$x = 2$
rate increases x8	$8 = 2^x$	*concentration doubles*	$x = 3$
rate is cut in half	$\frac{1}{2} = 2^x$	*concentration doubles*	$x = -1$
rate doesn't change	$1 = 3^x$	*concentration triples*	$x = 0$
rate triples	$3 = 3^x$	*concentration triples*	$x = 1$
rate increases by x9	$9 = 3^x$	*concentration triples*	$x = 2$
rate is cut in thirds	$\frac{1}{3} = 3^x$	*concentration triples*	$x = -1$
rate quadruples	$4 = 4^x$	*concentration quadruples*	$x = 1$
Etc…etc…etc…			

Units for k based on overall order of reaction

$$k = \frac{M}{M^{(x+y+etc\ldots)} \cdot s}$$

Overall Order	Example of Units Plugged In	Final Units for k
0	$k = \frac{M}{M^{(0)} \cdot s} = \frac{M}{1 \cdot s}$	$\frac{M}{s} = Ms^{-1}$
1	$k = \frac{M}{M^{(1)} \cdot s} = \frac{\cancel{M}}{\cancel{M} \cdot s}$	$\frac{1}{s} = s^{-1}$
2	$k = \frac{M}{M^{(2)} \cdot s} = \frac{\cancel{M}}{\cancel{M} \cdot M \cdot s}$	$\frac{1}{M \cdot s} = M^{-1}s^{-1}$
3	$k = \frac{M}{M^{(3)} \cdot s} = \frac{\cancel{M}}{\cancel{M} \cdot M \cdot M \cdot s}$	$\frac{1}{M^2 \cdot s} = M^{-2}s^{-1}$
4	$k = \frac{M}{M^{(4)} \cdot s} = \frac{\cancel{M}}{\cancel{M} \cdot M \cdot M \cdot M \cdot s}$	$\frac{1}{M^3 \cdot s} = M^{-3}s^{-1}$
Etc…etc…etc…		

Remember: $M = \frac{mol}{L}$ $\quad \frac{1}{M} = M^{-1} = \frac{L}{mol}$

↑

You may see this substituted into k units.

For example: $M^{-1}s^{-1} = \frac{L}{mol \cdot s}$

Steps for Determining Rate Order

1. Write your “skeleton rate law”
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    - The [ ] of one substance is held constant
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4. Look to see how the rate changes when you vary the [ ] of ONLY one substance.
5. Figure out what exponent on the [ ] change would result in the observed change to rate – that is the “order”
6. Repeat for each additional reactant

***REMINDER* If you don’t have two trials that hold everything but one reactant constant, solve for the orders you can, then pick two trials and plug in the values you do know to determine what you couldn’t figure out! I think this type of problem is the most difficult. But thankfully, doesn’t happen very often! ☺**

YouTube Link to Presentation

- https://youtu.be/oMjg7QlSP8k