Applications of Calculus I

Chemical Kinetics
The Derivative as a Function

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UCF EXCEL

Derivatives

- Recently in class, you have discussed derivatives.
- One way to find the derivative of a function is to find the slope of a tangent line.
- Derivatives (slope of the tangent line) are limits of the average rate of change (slope of the secant line) as the interval gets smaller.
- Chemists use this approach to analyze data in a subject called chemical kinetics.

Chemical Changes Often Occur at Different Rates

- One major factor is concentration

- Let's perform a couple of **Hydrogen Explosions** to demonstrate this

- **$H_2 + O_2 \rightarrow H_2O$ + Boom!!!**

Chemistry Clicker Question 1 Participation

- Which of the balloons had the higher concentration of hydrogen?
- A
- B
- C
- D

What about reactions in solution? Does concentration have an effect on the rate of change?

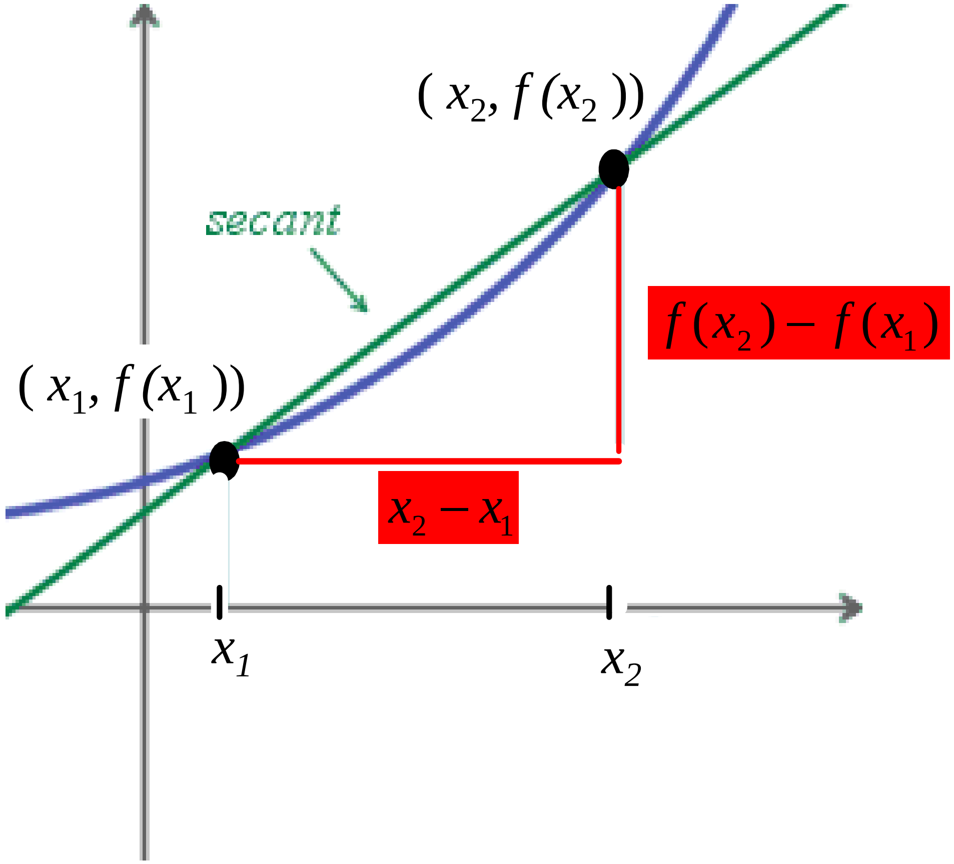
- Let's demonstrate this with a chemical reaction that emits light like a lightning bug.

- CpdM + CpdN $\rightarrow$ CpdZ + Light ($h\nu$)

Physical changes of rate

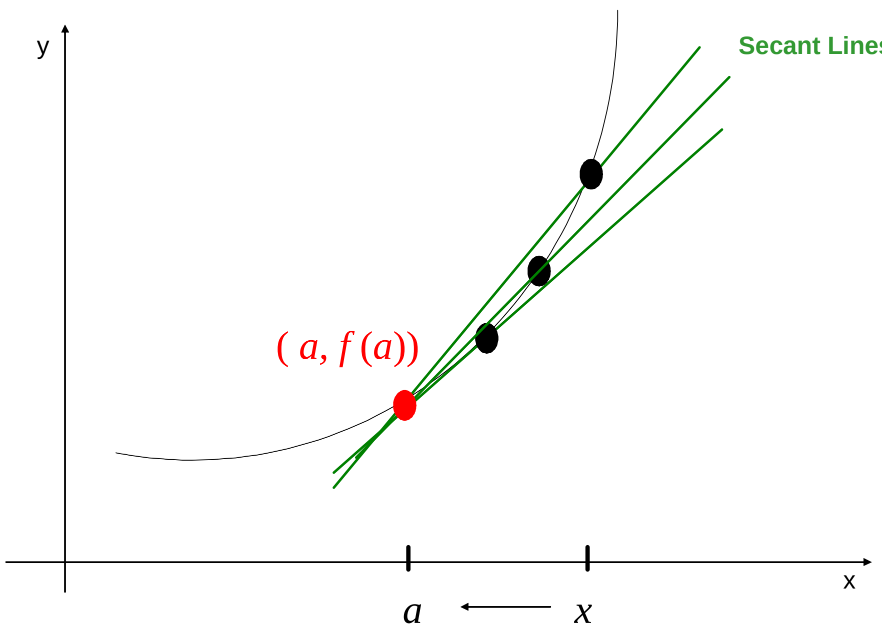
- Observe my changes in Distance Traveled vs Time (i.e. rate of change) as I move across the stage.
- So you can see I will have an average rate of change as I go from one end of the stage to the other
- But my instantaneous rate of change at any given moment might be different

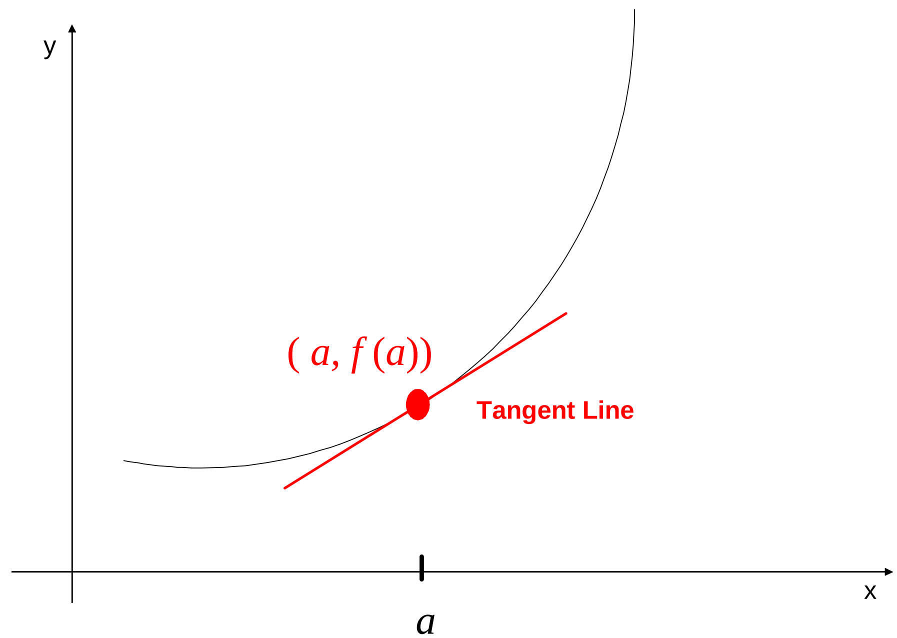
Average Rate of Change = Slope of Secant Line



$$m_{\sec ant} = \text{Average Rate of Change} = \frac{f(x_2) - f(x_1)}{x_2 - x_1}$$

Instantaneous Rate of Change = Slope of Tangent Line





$$f'(x) = m = \lim_{x \to a} \frac{f(x) - f(a)}{x - a}$$

The smaller the interval, the better the average rate of change approximates the instantaneous rate of change

Rates

- Rates of reactions and unemployment rates both measure a change over time.
- For example: Problem
- from your text 3.1 (33)

t	$U(t)$	t	$U(t)$
1991	6.8	1996	5.4
1992	7.5	1997	4.9
1993	6.9	1998	4.5
1994	6.1	1999	4.2
1995	5.6	2000	4.0

This shows the percentage of Americans that were unemployed, U(t), from time=1991 to time= 2000

Finding the Average Rate of Change of Unemployment

- The rate at which the unemployment rate is changing, in percent unemployed per year.
  - Example:

$$U'(1991) \approx \frac{U(1992) - U(1991)}{1\text{yr.}} = \frac{7.5 - 6.8}{1} = 0.70$$

$$U'(1992) \approx \frac{U(1993) - U(1992)}{1\text{yr.}} = \frac{6.9 - 7.5}{1} = -0.60$$

Approximating the derivative

- A more accurate value approximation to U'(1992) is to take the average between U(1992)-U(1991) and U(1993)-U(1992).

$$\therefore U'(1992) \approx \frac{0.70 - 0.60}{2} = 0.05$$

t	U'(t)	t	U'(t)
1991	0.70	1996	–0.35
1992	0.05	1997	–0.45
1993	–0.70	1998	–0.35
1994	–0.65	1999	–0.25
1995	–0.35	2000	–0.20

Application to Chemistry

Chemical Kinetics (what is it?)

The branch of chemistry that is concerned with the rates (or speed) of change in the concentration of reactants in a chemical reaction.

- **Chemists analyze how reaction rates change over time.**
- **The derivative of this function (reaction rate) is commonly used in kinetics .**
- **To find the derivative, the slope of a tangent line can be used.**

Chemical Kinetics

- Why study kinetics?
  - To determine steps in a chemical reaction
  - To develop a mechanism
  - To figure out how and why a reaction occurs
  - Ultimately to learn how to make a reaction go faster or slower

At UCF, the Chemistry courses that cover kinetics are:

CHM 2046- Fundamentals of Chemistry II; CHM 3411-Physical Chemistry II; CHS 6440- Kinetics and Catalysis

This is a problem from a CHM 2046 exam that deals with Chemical Kinetics

Decomposition of Hydrogen Peroxide.

$2H_2O_2(l) \rightarrow H_2O(l) + O_2(g)$

$$\text{Rate of decomposition} = \left|\frac{-d(H_2O_2)}{dt}\right| = k[H_2O_2]$$

The concentration of H_2O_2 changes with time by the following:

$$[H_2O_2]_t = (5.4\times10^{-8})t^2 - (1.0\times10^{-4})t + (9.0\times10^{-3})$$

Calculate the following:

a) The rate of decomposition of H_2O_2 after 10 seconds

b) The rate constant

c) The $[H_2O_2]$ after 10 seconds

$$\text{Rate of decomposition} = \left|\frac{-d(H_2O_2)}{dt}\right| = k[H_2O_2]$$

$$[H_2O_2]_t = (5.4\times10^{-8})t^2 - (1.0\times10^{-4})t + (9.0\times10^{-3})$$

Before we can learn about calculus applied to chemical kinetics, we need to know about Chemical Equations

- In a reaction, reactants are converted to products.

  Reactants → Products

  For example, let's write a simple acid/base reaction: NaOH (a base) + HCl (an acid) → NaCl (a salt) + H_2O (water)

- The speed of the reaction can be determined by:
  - The change of reactants (i.e. NaOH and/or HCl)
  - The change of products (i.e. NaCl and or H_2O)

Let's perform this acid-base reaction with HCl and NaOH here in class.
We will see how fast the reaction can occur. The color change will indicate when the reaction is over.

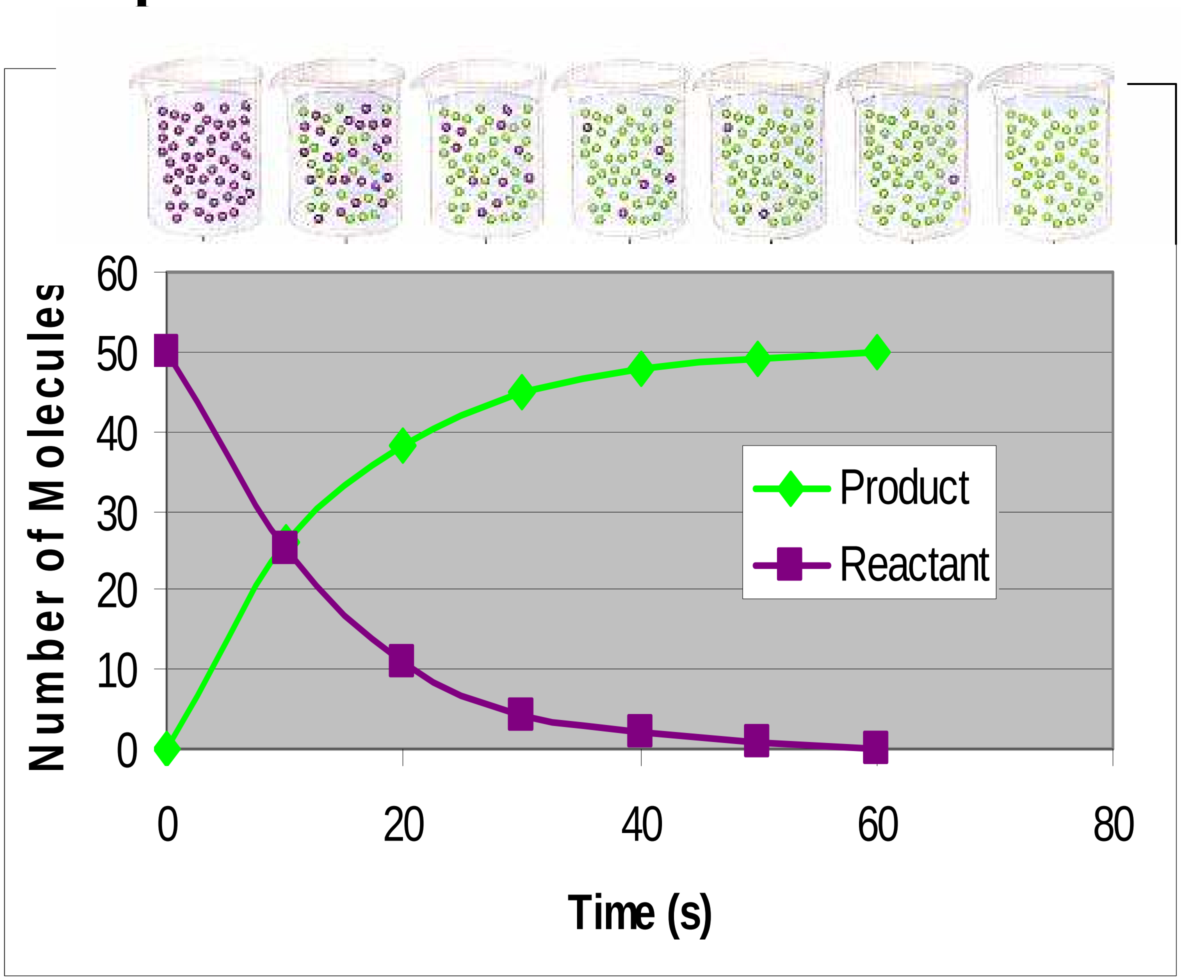
- "As you can see the reaction is very fast."
- Too fast to follow the change visually but with the proper instrumentation, we can follow changes in concentration vs time

When we gather concentration vs time data, we plot it.

- Change in time
  - Denoted as Δtime (x-axis)
- Change in concentration

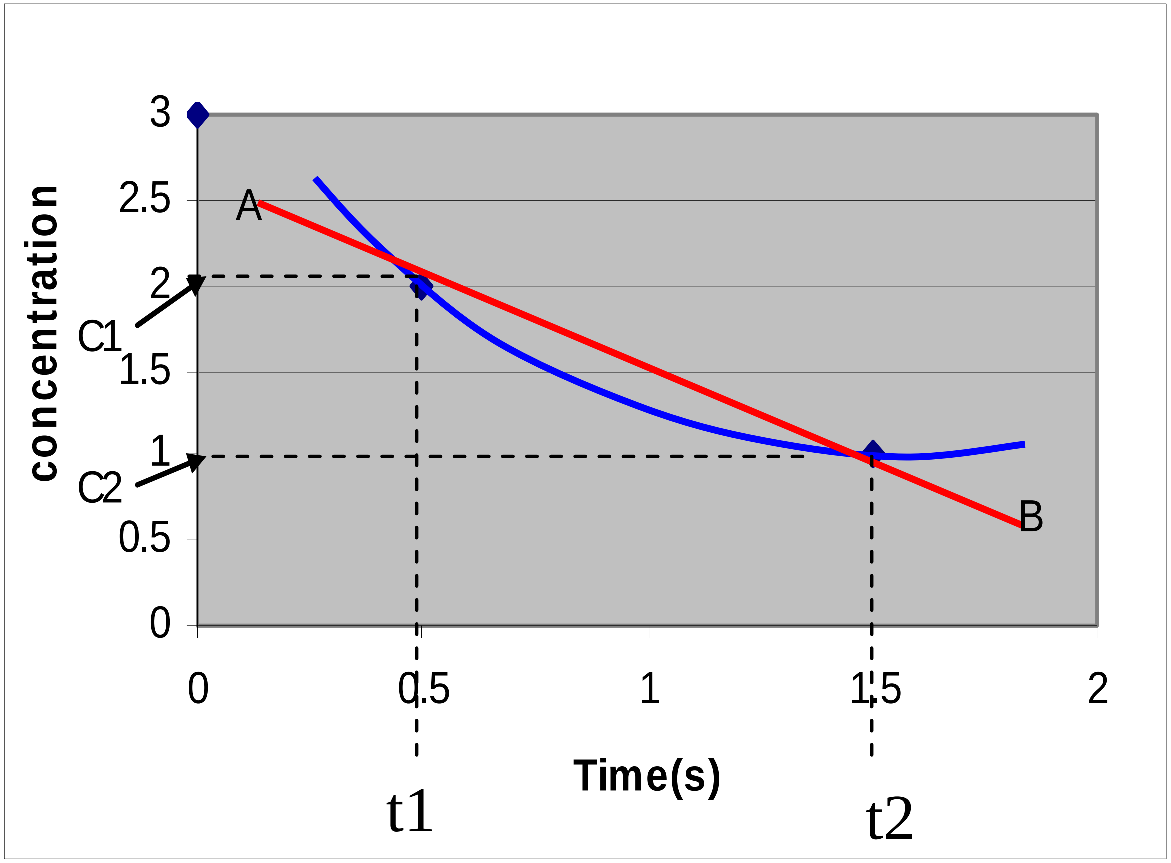
  Denoted as: Δ [reactants] or Δ [products]

  (y-axis)



A plot of concentration vs time shows how the **Rate of Reaction** is changing

- The plot is not linear
  - The rates change over time
- The average rate over the time interval t_1 to t_2 is the change of [reactants] from c_1 to c_2



$$\text{Average rate} = \frac{c_2 - c_1}{t_2 - t_1} = \text{slope of line AB} = \frac{\Delta c}{\Delta t}$$

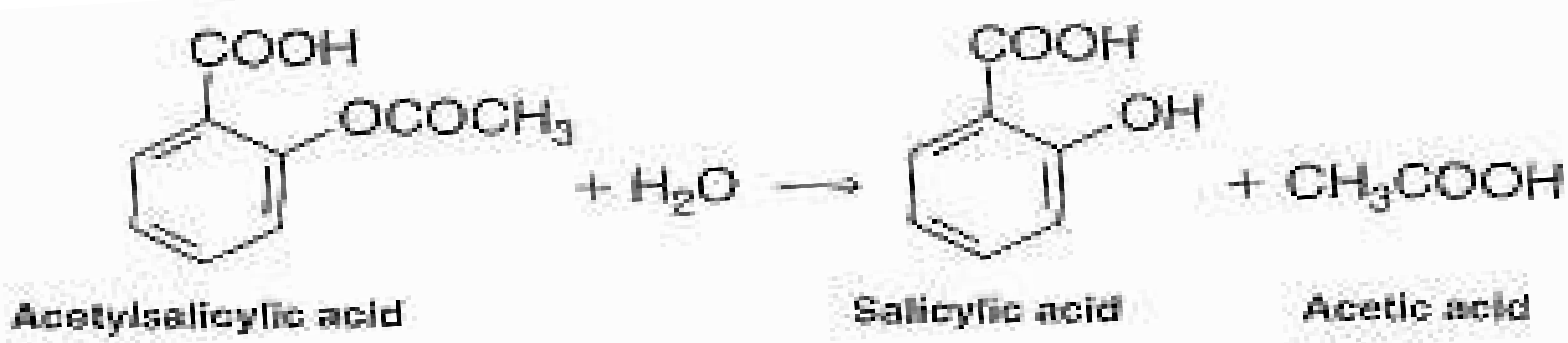
Rate of Reaction

- NOTE: Slope of [reactants] vs. time is always negative
  - Reactants are consumed to form products
  - Notice that the slope of AB is negative

- Rate must always be expressed as positive numbers
- To ensure this, use the absolute value
  - Rate calculated from [reactants] = $\left| \frac{-\Delta C}{\Delta t} \right|$

Let’s look at an example reaction that all of you experienced-the use of aspirin

- Aspirin (acetylsalicylic acid) reacts with water to produce salicylic acid and acetic acid

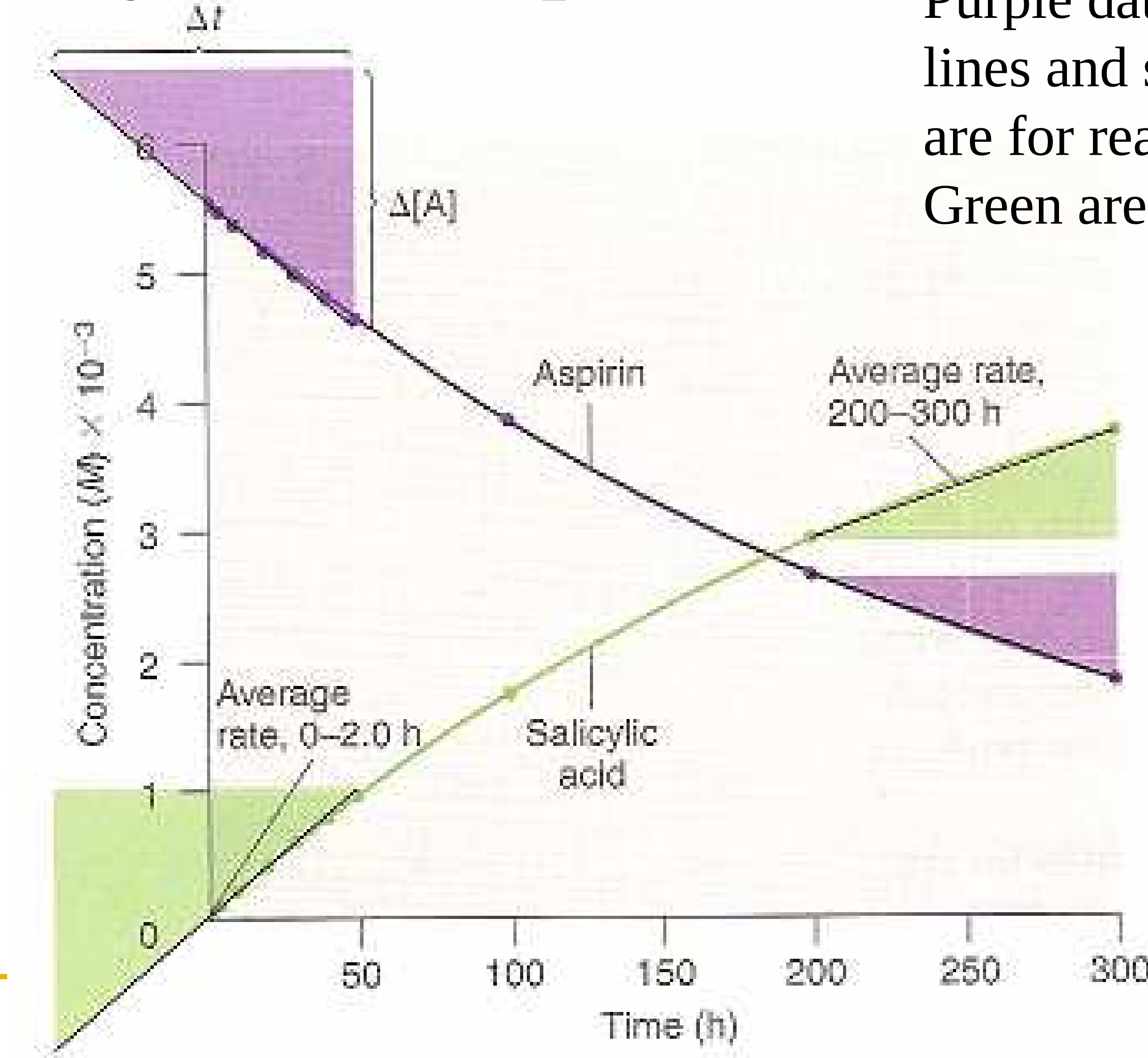


  - The reaction occurs in your stomach and is called an hydrolysis reaction
  - Salicylic acid is the actual pain reliever and fever reducer
  - The reaction was stopped at various points so the concentration of the reactant and product could be observed

Table 1. Data for the hydrolysis of Aspirin in aqueous solution at pH 7 and 37°C

Time (h)	[aspirin]	[Salicylic acid]
0	5.55×10^{-3}	0×10^{-3}
20	5.15×10^{-3}	0.40×10^{-3}
50	4.61×10^{-3}	0.94×10^{-3}
100	3.83×10^{-3}	1.72×10^{-3}
200	2.64×10^{-3}	2.91×10^{-3}
300	1.82×10^{-3}	3.73×10^{-3}

Hydrolysis of Aspirin



Purple data markers,
lines and shading
are for reactants
Green are for products

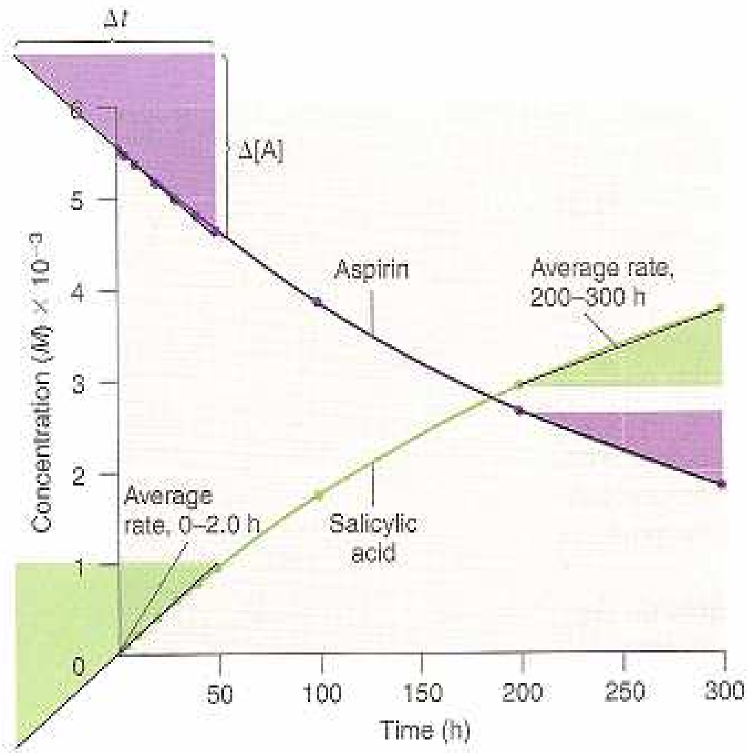
Hydrolysis of Aspirin (rate in terms of the product: salicylic acid)

- We can find the average reaction rate using the reactants or the products.
- For example:

Using salicylic acid from t =0h to t =2.0h

$$rate_{(t=2.0h-0h)} = \frac{[salicylicacid]_2 - [salicylicacid]_0}{2.0h - 0h} =$$

$$\frac{0.040\times10^{-3}M - 0M}{2h} = 2\times10^{-5}M/h$$



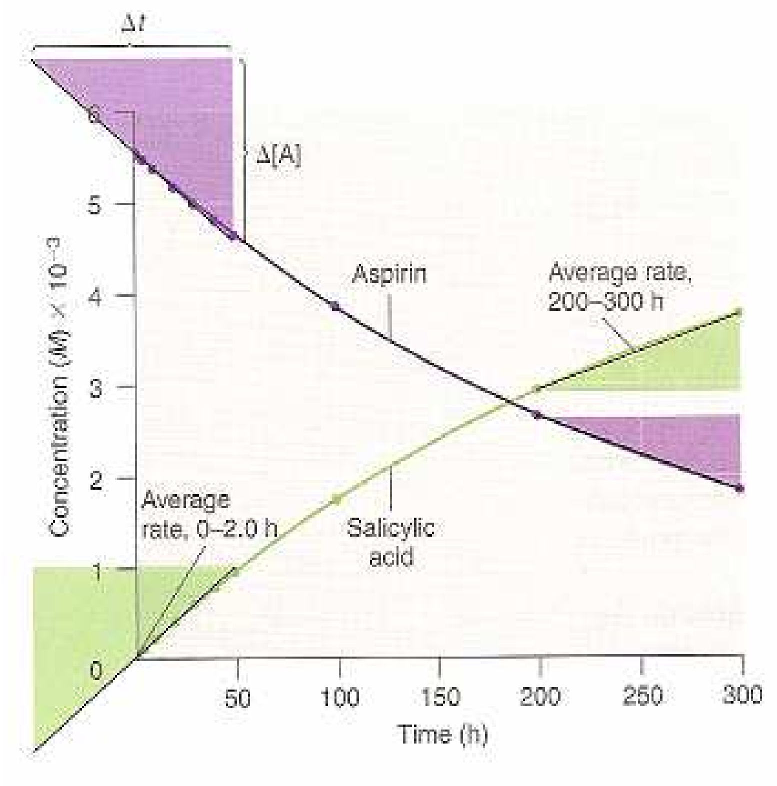
Hydrolysis of Aspirin (rate in terms of the reactant: aspirin)

- You may also look at the Aspirin to get reaction rate
- For example:

Use data for Aspirin from t=0h to t=2h

$$rate_{(t=2h-0h)} = -\frac{[[aspirin]_2 - [aspirin]_0]}{2.0h - 0.0h} =$$

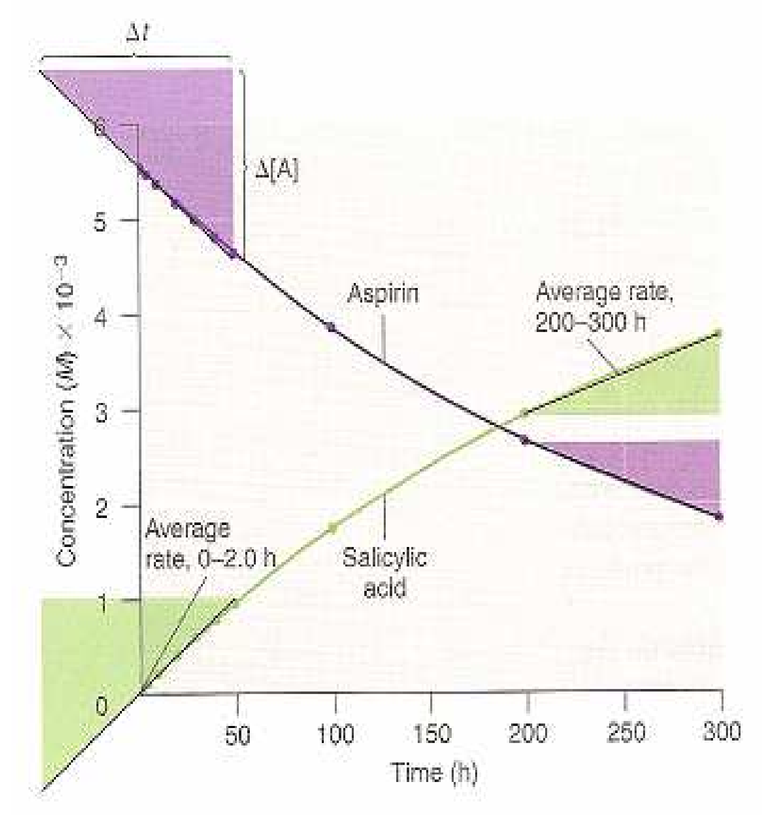
$$- \left| \frac{5.51\times10^{-3}M - 5.55\times10^{-3}M}{2.0h - 0h} \right| = 2.0\times10^{-5} M/h$$



Hydrolysis of Aspirin (near the end of the reaction)

- Towards the end of the reaction, we can figure out how the rate has changed
- For example:

The rate found by the salicylic acid from t=200 to t=300



$$rate_{(t=200\text{h}-300\text{h})} = -\frac{\left[[salicyclic\,acid]_2 - [salicyclic\,acid]_0\right]}{300\text{h} - 200\text{h}} =$$

$$\frac{3.73\times10^{-3}M - 2.91\times10^{-3}M}{100h} = 8.2\times10^{-6}M/h$$

Rates: average vs. instantaneous

- Average rates are over a period of time
  - Gives limited information
- As the time intervals get smaller and smaller, they approach a particular "instance"
- The concentration at that point vs. time is called the **instantaneous rate**

YOU WILL CALCULATE THE INSTANTANEOUS RATE OF CHANGE OF A FUNCTION BY USING A NON-GRAPHICAL PROCEDURE

* Remember that the Instantaneous Rate is when change $\rightarrow 0$ and Δtime $\rightarrow 0$

Finding instantaneous rate

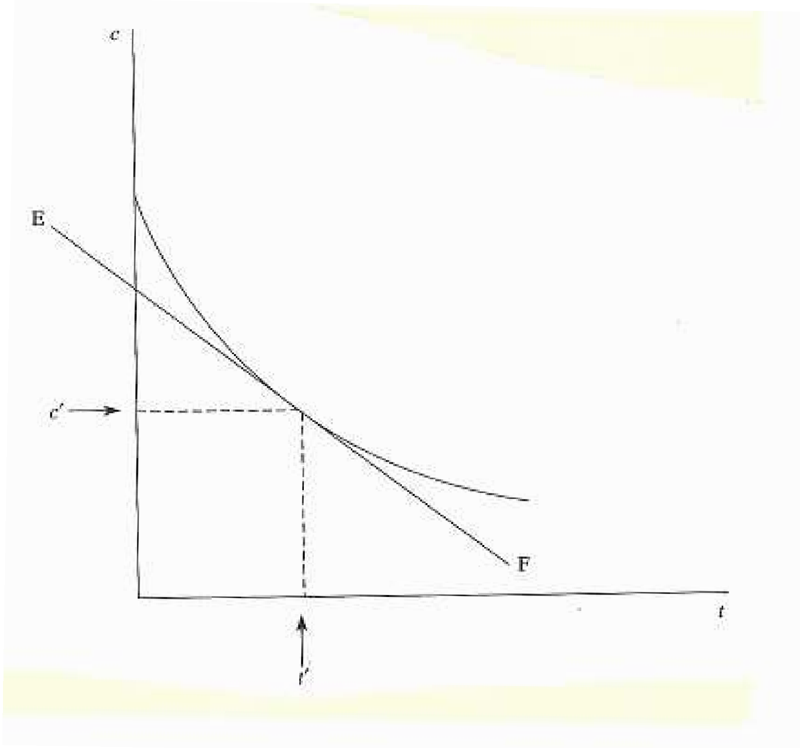
Instantaneous rate:

When the $\Delta c \rightarrow 0$ and $\Delta t \rightarrow 0$

Slope of tangent, EF, hits the curve at c' and t'

(-slope tangent) = instantaneous rate

Since the tangent has a negative slope, you must use a negative sign to express the rate as a positive number.



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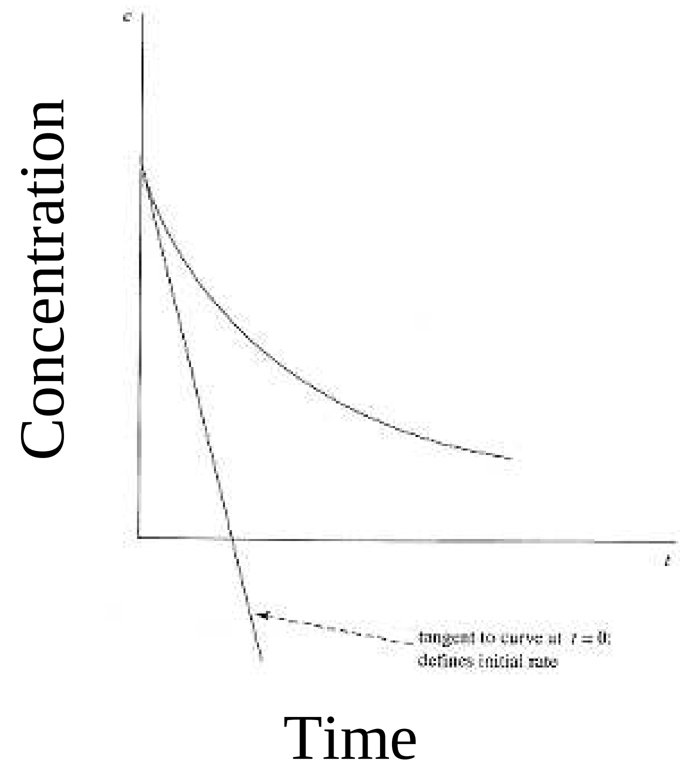
The initial rate of the reaction

- Is very important, especially in complex reactions
- Is at the start of the reaction
- Is the line of steepest slope
  - Fastest rate



In your first class meeting with me (last week), you learned the meaning and difference between average and instantaneous rates, and how to calculate them.

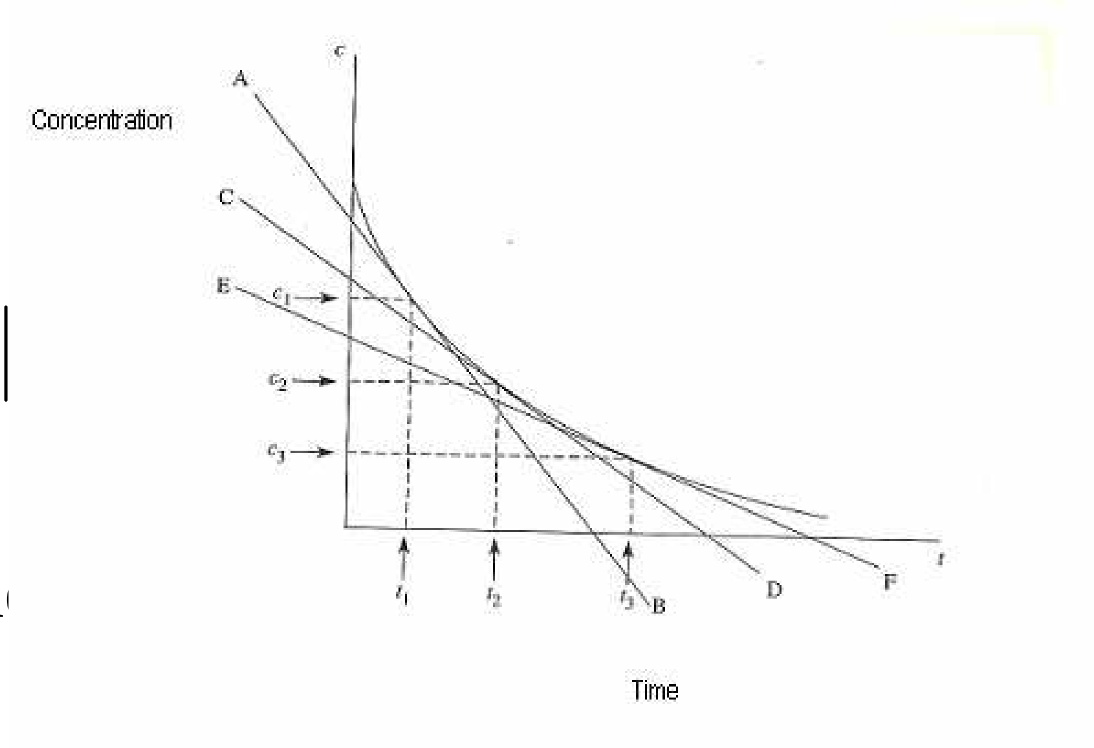
- We will now learn about the importance and use of these concepts in **Chemistry** and another method for calculating an instantaneous rate.

Dependence of rate on [reactants]

- Three tangents are drawn

$$|m_{AB}| > |m_{CD}| > |m_{EF}|$$

- As [reactants] decrease, so does the rate



If you know the equation for a data set such as CONCENTRATION VS TIME, then you can simply take the derivative of it to calculate an instantaneous rate.

That is

$$\left(\frac{d[C]}{dt}\right)$$

For Example, if

$$[C] = (3.5\times10^{-8})t^2 - (2.0\times10^{-5})t + 3.0\times10^{-3}$$

then

$$\frac{dC}{dt} = (7.0\times10^{-8})t - 2.0\times10^{-5}$$

(this is the rate of change of [C] with t)

Let's Compare Chemical Kinetics and Cars

- The **average rate** of a chemical reaction is like the average speed of your car during a trip
- The **instantaneous rate** of the reaction is like the exact speed of your car at a particular instance.

Now back to Chemistry

The Rate equation: Tells us how fast the reaction is occurring at a particular concentration of reactant

- Rate = k [reactant]^n
  - Rate is Δ[M]/Δtime
  - k is the rate constant
  - [reactant] is the concentration of the reactant
    - Usually in Moles solute/Liter solution denoted as M
  - n is called the order of the reaction
    - If n=1, it is “first order”
    - If n=2 it is “second order”
    - If n= 3/2 it is “three halves order”

How does rate equation relate to a chemical reaction equation

Remember the rate equates the rate (i.e. speed) of a reaction to the concentration of reactants.

For a reaction with the general equation

$$aA + bB \rightarrow cC + dD$$

The experimentally determined rate law is

$$\textbf{rate} = k[A]^m[B]^n$$

Notice that the orders, m and n, may or may not be the stoichiometric coeffecients

m and n can only be determined by experiment

Order of the reaction

- Reaction order can only be found experimentally
- Consider the following data

  - We can find the order of the reaction by finding the ratio of two experiments

Experiment	**[A] (*M*)**	**[B] (*M*)**	**Initial Rate (*M*/min)**
1	0.50	0.50	8.3×10^{-3}
2	0.75	0.50	19×10^{-3}
3	1.00	0.50	33×10^{-3}
4	0.50	0.75	8.3×10^{-3}

Experiment	[A] (*M*)	[B] (*M*)	Initial Rate (*M*/min)
1	0.50	0.50	8.3×10^{-3}
3	1.00	0.50	33×10^{-3}

- Pick a pair of experiments where one of the reactant concentrations is the same. In this case we used experiments 1 and 3 ([B] is the same in both).

$$\frac{rate_1}{rate_3} = \frac{k\,[A_1]^m\,[B_1]^n}{k\,[A_3]^m\,[B_3]^n}$$

$$\frac{8.3\times10^{-3}\,M/\min}{33\times10^{-3}\,M/\min} = \frac{k[0.5]^m[0.5]^n}{k[1.0]^m[0.5]^n}$$

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Order of the reaction

- The rate constants, k, and the $[B]^n$ cancel, leaving:

$$.25 = [.5]^m$$

$$m = 2$$

- So, the reaction is second order in terms of A
- Find the order of the reaction in terms of B

Order of reaction in terms of B

Experiment	[A] (*M*)	[B] (*M*)	Initial Rate (*M*/min)
1	0.50	0.50	8.3×10^{-3}
4	0.50	0.75	8.3×10^{-3}

- Experiments 1 and 4 keep [A] constant while changing the [B]:

$$\frac{rate_1}{rate_4} = \frac{k[A_1]^m[B_1]^n}{k[A_4]^m[B_4]^n}$$

$$\frac{8.3 \times 10^{-3}}{8.3 \times 10^{-3}} = \frac{k[0.5]^m[0.5]^n}{k[0.5]^m[0.75]^n}$$

Order of the reaction in terms of B

- The rate constants, k, and the $[A]^m$ cancel, leaving:

$$1 = [0.67]^n$$

$$n = 0$$

- So, the reaction is zero order in terms of B, which means that the rate of the reaction does not depend on the concentration of B
- The overall rate law is:

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

- The overall reaction order is second order because:

$$\mathbf{2 + 0 = 2}$$

In Class Kinetics Experiment

- Beakers with different concentrations of reagents will be set up. You will observe and time the reaction until it is over as indicated by a color change. You will then use this data to calculate a rate law and rate constant.

The End

- You now know how calculus is used in chemical kinetics!