Chapter 16:

Chemical Kinetics

16.1 **Factors that influence reaction rates**

16.2 **Expressing the reaction rate**

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16.3 **The rate law and its components**

16.4 **Integrated rate laws: Concentration changes over time**

16.5 **Reaction mechanisms: Steps in the overall reaction**

16.6 **Catalysis: Speeding up a chemical reaction**

Exam 1 Tonight: 6:00PM - 7:30PM
Berchman Hall

Pen and Calculator and toolbox is all you need!

Ch 11 F - B102 - Nestor
Ch 11 E - B03 - JP
Ch 11 D - B104 - Aran
Ch 11B - B105 - Dr Gross
Ch 11C - B106 - Dr. Gross and Michelle

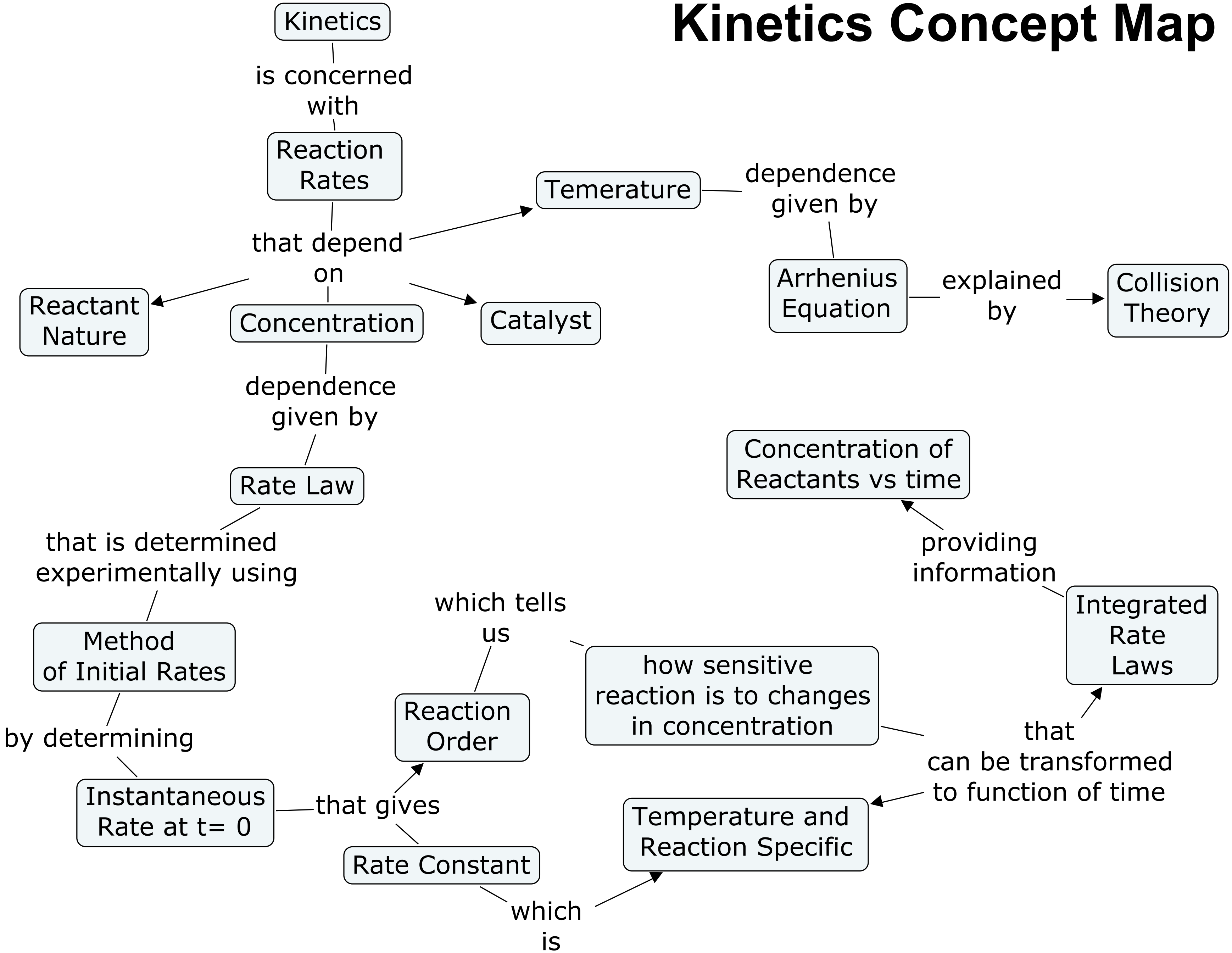
Different theories tell us different things.

Thermodynamic theory gives us information on the ***energetics of a reaction***, and whether a chemical reaction can occur, ***but it has no information on how fast*** a reaction can occur (which kinetic theory tells us).

Kinetic theory provides information on ***how fast or slow a chemical reaction*** is but it can not tell us the energetics or how far a reaction will go (the extent)

Equilibrium theory tells us to what ***extent a chemical reaction occurs*** but not on how fast it will occur.

Kinetics Concept Map



Five factors affect the rate of a chemical reaction.

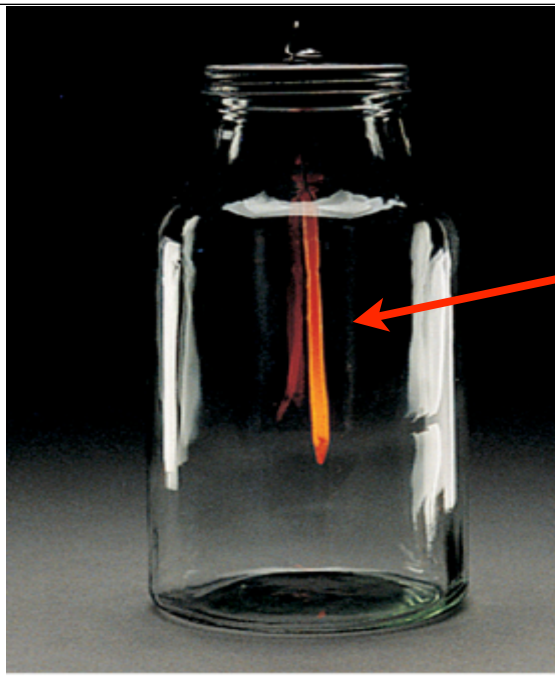
1. **Nature of Reactants**--bonds break and form during a reaction. Element and compounds have "inherent tendencies to react".

2. **Concentration** - molecules must collide to react; the more molecules there are---the faster the reaction.

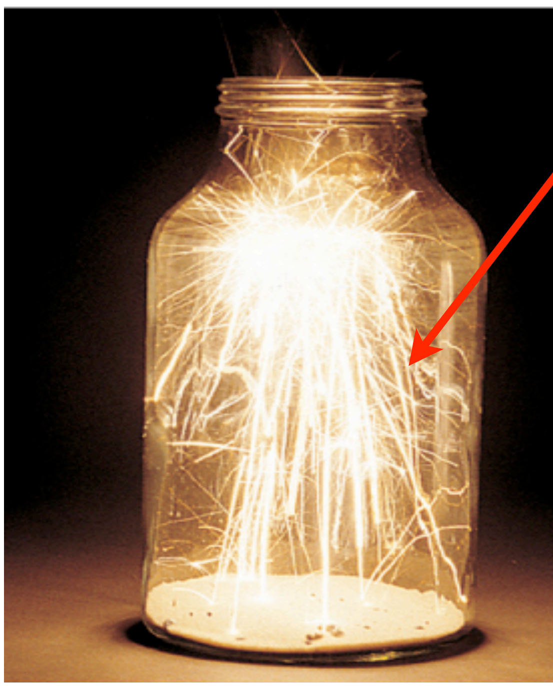
3. **State or Phase of reacting molecules** must mix to collide, gas, liquids and solids have different surface area to volume ratios varying reactivity.

4. **Temperature** - molecules must collide with a minimum energy in order to react. Higher temperatures mean higher KE during a collision.

5. **Presence of a catalyst**: catalyst increase reaction rates without being consumed in the reaction itself.



A hot steel nail glows in O_2 but the same mass of steel wool bursts into flames.



The greater the surface area per unit volume means more metal atoms can react with O_2 and increases the reaction rate.

A *chemical reaction rate* is the change in the concentration (molarity) of a reactant or a product with time. By convention, the reaction rate it is always a *positive number.*

$$A \longrightarrow B$$

$$\text{rate} = -\frac{\Delta[A]}{\Delta t}$$

$\Delta[A] = [A]_t - [A]_{t=0}$ = change in concentration of [A] over a period of time $\Delta t = t - t_0$

Because [A] is a reactant it decreases with time therefore Δ[A] is a negative value so we place a minus sign in the expression!

$$\text{rate} = \frac{\Delta[B]}{\Delta t}$$

Δ[B] = change in concentration of B over time period Δt

Because [B] is a product it increases with time: Δ[B] is a positive value and so does the rate!

To avoid the ambiguity in a reaction rate, we use a "scaled or unified rate" such that one number describes the rate of change of all reactants and all products.

$$C_3H_8\,(g) + 5O_2\,(g) \Longrightarrow 3CO_2\,(g) + 4H_2O(g)$$

$$\textbf{rate} = -\frac{\Delta[C_3H_8]}{\Delta t} = -\frac{1}{5}\frac{\Delta[O_2]}{\Delta t} = \frac{1}{3}\frac{\Delta[CO_2]}{\Delta t} = \frac{1}{4}\frac{\Delta[H_2O]}{\Delta t}$$

stoichiometric coefficients!

notice the - sign for the reactants!

Rate > 0 (it's a positive number)!

A balanced *chemical equation* relates the rates of disappearance of reactants to the rate of appearance of products.

$$C_3H_8\,(g) + 5O_2\,(g) \Longrightarrow 3CO_2\,(g) + 4H_2O(g)$$

For every 1 mol C_3H_8 (M) per unit time requires 5 mol O_2 per unit time
For every 1 mol C_3H_8 (M) per unit time produces 3 mol CO_2 per unit time
For every 1 mol C_3H_8 (M) per unit time produces 4 mol H_2O per unit time

$$\text{rate} = -\frac{\Delta[O_2]}{\Delta t} = -5\frac{\Delta[C_3H_8]}{\Delta t} = 5/3\frac{\Delta[CO_2]}{\Delta t}$$

this is confusing so we avoid it!

We use a "unified rate" such that the stoichiometry is considered and a single positive value rate of reaction can be written.

$$\text{rate} = -\frac{\Delta[C_3H_8]}{\Delta t} = -\frac{1}{5}\frac{\Delta[O_2]}{\Delta t} = \frac{1}{3}\frac{\Delta[CO_2]}{\Delta t} = \frac{1}{4}\frac{\Delta[H_2O]}{\Delta t}$$

Analogy With Sandwich Equation

2 bread slices + 3 sardines + 1 pickle $\longrightarrow$ 1 sandwich

Suppose 4 sandwiches can be made per minute. What is the rate of change of the other ingredients?

$$\text{rate} = \frac{\Delta\text{sandwich}}{\Delta t} = -\frac{1}{2}\frac{\Delta\text{ bread}}{\Delta t} = -\frac{1}{3}\frac{\Delta\text{ sardines}}{\Delta t}$$

$$\text{rate} = \frac{\Delta\text{sardine}}{\Delta t} = -\frac{1}{2}\frac{\Delta\text{ bread}}{\Delta t} = -\frac{1}{3}\frac{\Delta\text{ sardines}}{\Delta t}$$

$$\text{rate} = \frac{\Delta\text{bread}}{\Delta t} = -\frac{1}{2}\frac{\Delta\text{ bread}}{\Delta t} = -\frac{1}{3}\frac{\Delta\text{ sardines}}{\Delta t}$$

Suppose you are given the following generalized reaction.

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

What is the rate of reaction written as a function of change in [A], [B], [C] and [D]?

$$\text{rate} = -\frac{1}{a}\frac{\Delta[A]}{\Delta t} = -\frac{1}{b}\frac{\Delta[B]}{\Delta t} = \frac{1}{c}\frac{\Delta[C]}{\Delta t} = \frac{1}{d}\frac{\Delta[D]}{\Delta t}$$

Suppose the rate of appearance of NO_2 is measured and found to be 2 Molar sec^{-1}. What is the rate of disappearance, $\frac{\Delta[N_2O_5]}{\Delta t}$ and the rate of formation of O_2 ?

$$2\,N_2O_5(g) \longrightarrow 4\,NO_2(g) + O_2(g) \qquad \frac{\Delta[NO_2]}{\Delta t} = 2\text{ M s}^{-1}$$

Method 1

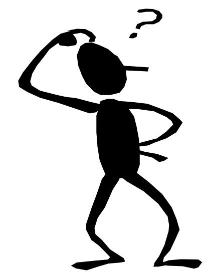
$$-\frac{\Delta[N_2O_5]}{\Delta t} = \frac{2\text{M } NO_2}{\text{sec}} \times \frac{2\text{M } N_2O_5}{4\text{M } NO_2} = \frac{1\text{M } N_2O_5}{\text{sec}}$$

Method 2

$$-\frac{1}{4}\frac{\Delta[NO_2]}{\Delta t} = -\frac{1}{2}\frac{\Delta[N_2O_5]}{\Delta t} = \frac{1}{1}\frac{\Delta[O_2]}{\Delta t}$$

$$-\frac{1}{4}\frac{2\text{M } NO_2}{\text{sec}} = -\frac{1}{2}\frac{\Delta[N_2O_5]}{\Delta t} = \frac{1}{1}\frac{\Delta[O_2]}{\Delta t}$$

Hydrogen gas is used for fuel aboard the space shuttle and may be used by automobile engines in the near future.



$$2H_2(g) + O_2(g) \longrightarrow 2H_2O(g)$$

(a) Express the reaction rate in terms of changes in $[H_2]$, $[O_2]$, and $[H_2O]$ with time.

(b) If $[O_2]$ decreases at 0.23 mol O_2/L/s, at what rate is $[H_2O]$ increasing?

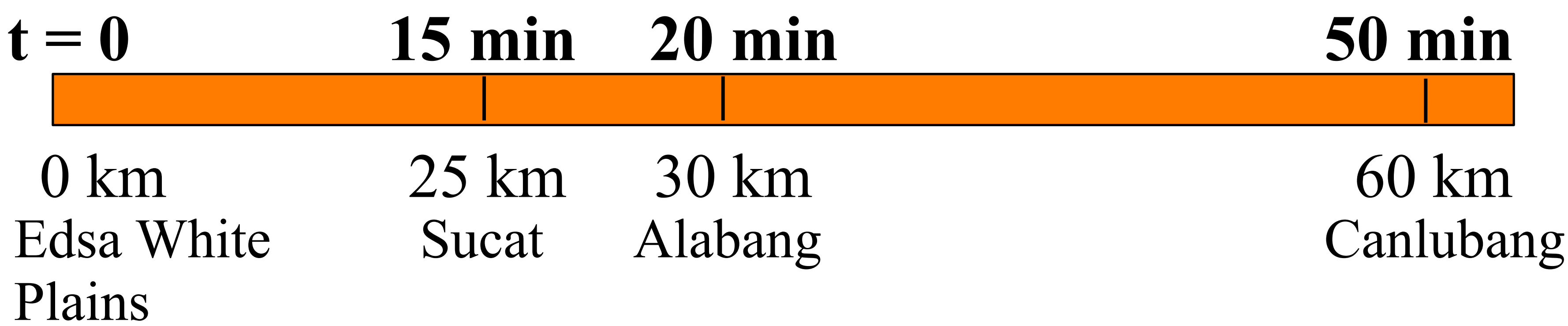
(a) $$\text{rate} = -\frac{1}{2}\frac{\Delta[H_2]}{\Delta t} = -\frac{\Delta[O_2]}{\Delta t} = +\frac{1}{2}\frac{\Delta[H_2O]}{\Delta t}$$

(b) $$-\frac{\Delta[O_2]}{\Delta t} = 0.23\ \text{mol/L}\cdot\text{s} = +\frac{1}{2}\frac{\Delta[H_2O]}{\Delta t}$$

$$\frac{\Delta[H_2O]}{\Delta t} = \mathbf{0.46\ mol/L\cdot s}$$

The "rate" of a phenomenon is the ratio of how some quantity changes with respect to time.

Suppose we have drive to Alabang starting from White Plains



$$Avg\ Rate\ of\ Speed_{Alabang} = \frac{Position_{Alabang} - Position_{Edsa}}{Time_{Alabang} - Time_{Edsa}}$$

$$Avg\ Rate\ of\ Speed_{Alabang} = \frac{\Delta d}{\Delta t} = \frac{30\ km}{20\ min} = \frac{1.5\ km}{min}$$

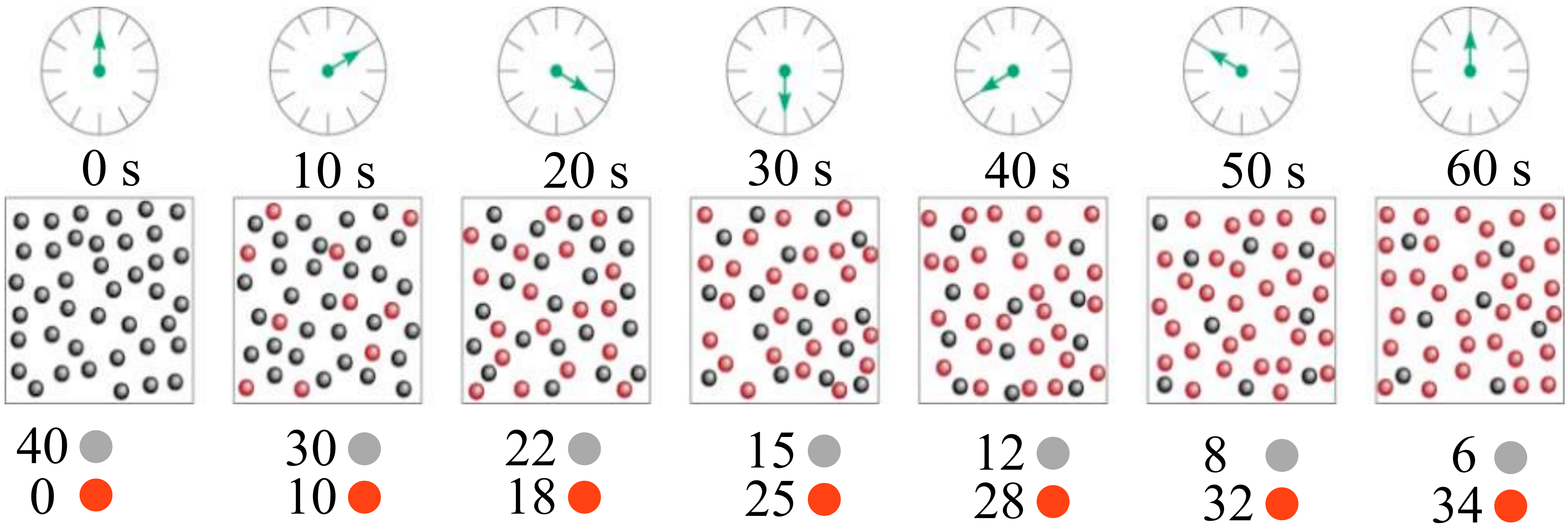
We can measure our distance from a point on Edsa by looking at the odometer of the car and noting the distance & time from the starting point.

$$\text{rate of speed} = \frac{\Delta \text{Distance}}{\Delta \text{time}} = \frac{\Delta D}{\Delta t} = \frac{D_i - D_0}{T_i - T_0}$$

Place	Time (min)	Distance Traveled (km)	Rate of Speed (km/min)
Edsa	0	0	0
Sucat	20	25	1.25 km/min
Alabang	40	30	0.75 km/min
Canalubang	60	60	1.0 km/min

All speeds are relative to starting point but need not be

In chemical reactions we can observe the rate of disappearance of a reactant, or the appearance of a product: Consider a transformation: A ==> B

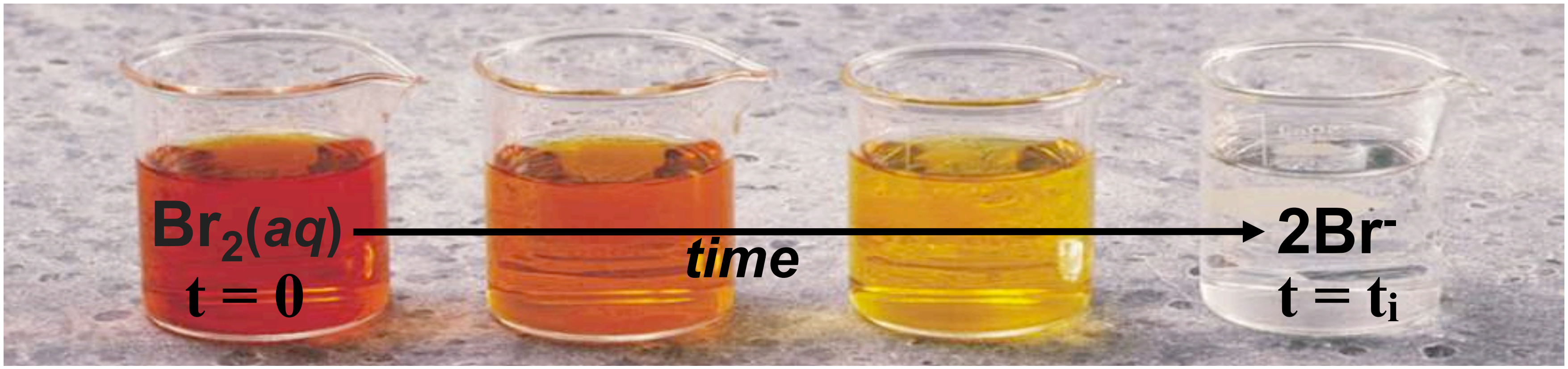


$$\text{rate} = -\frac{\Delta[A]}{\Delta t} = -\frac{\text{Change in Concentration A}}{\text{Change in time}} = -\frac{[A]_t - [A_{t=0}]}{t - t_0}$$

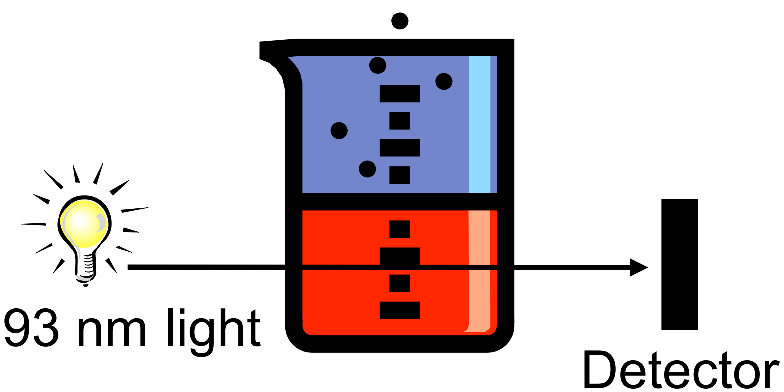
$$\text{rate} = +\frac{\Delta[B]}{\Delta t} = \frac{\text{Change in Concentration B}}{\text{Change in time}} = \frac{[B]_t - [B_{t=0}]}{t - t_0}$$

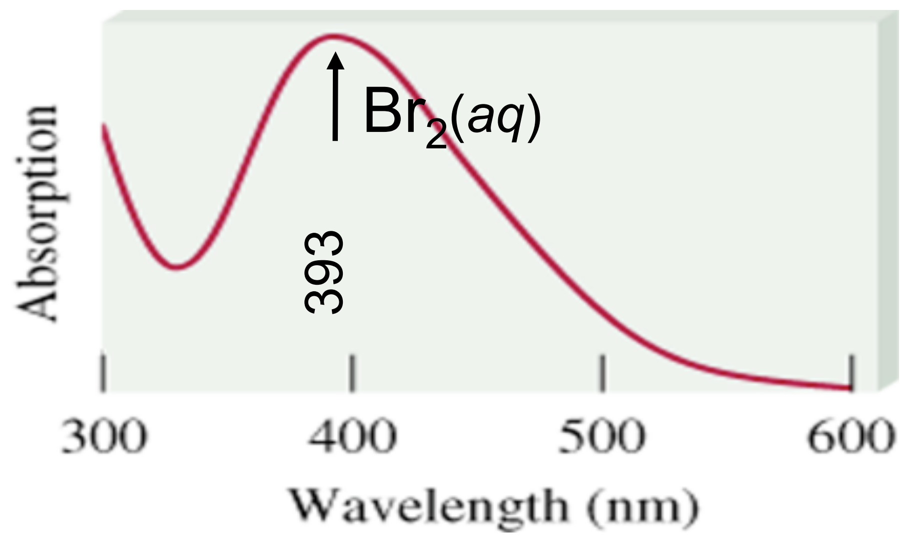
An Example: Reduction of Bromine to Bromide

$$Br_2(aq) + HCOOH\ (aq) \longrightarrow 2Br^-\ (aq) + 2H^+\ (aq) + CO_2\ (g)$$



We can easily monitor the change in [Br_2] with an lab instrument.

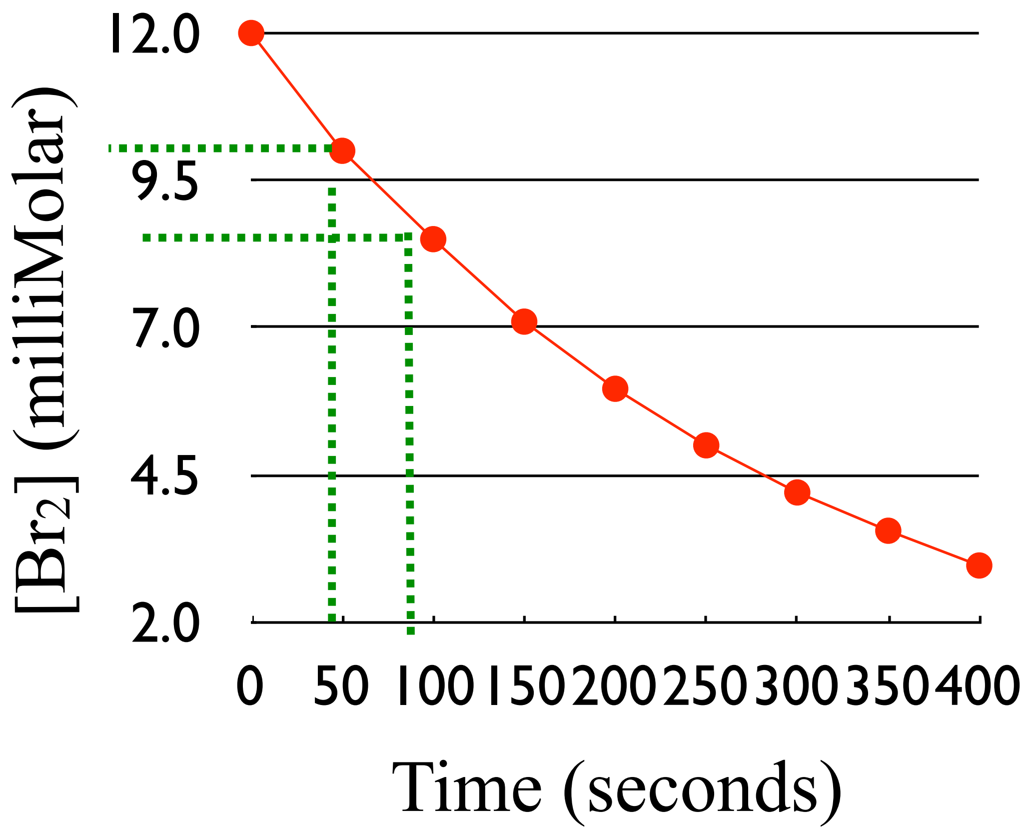




Suppose we monitor the color change and we plot the reaction data:

$$Br_2(aq) + HCOOH\ (aq) \longrightarrow 2Br^-\ (aq) + 2H^+\ (aq) + CO_2\ (g)$$

Time (s)	$[Br_2]$ (mM)
0.0	12.0 mM
50.0	10.0 mM
100.0	8.46 mM
150.0	7.10 mM
200.0	5.96 mM
250.0	5.00 mM
300.0	4.20 mM
350.0	3.55 mM
400.0	2.96 mM

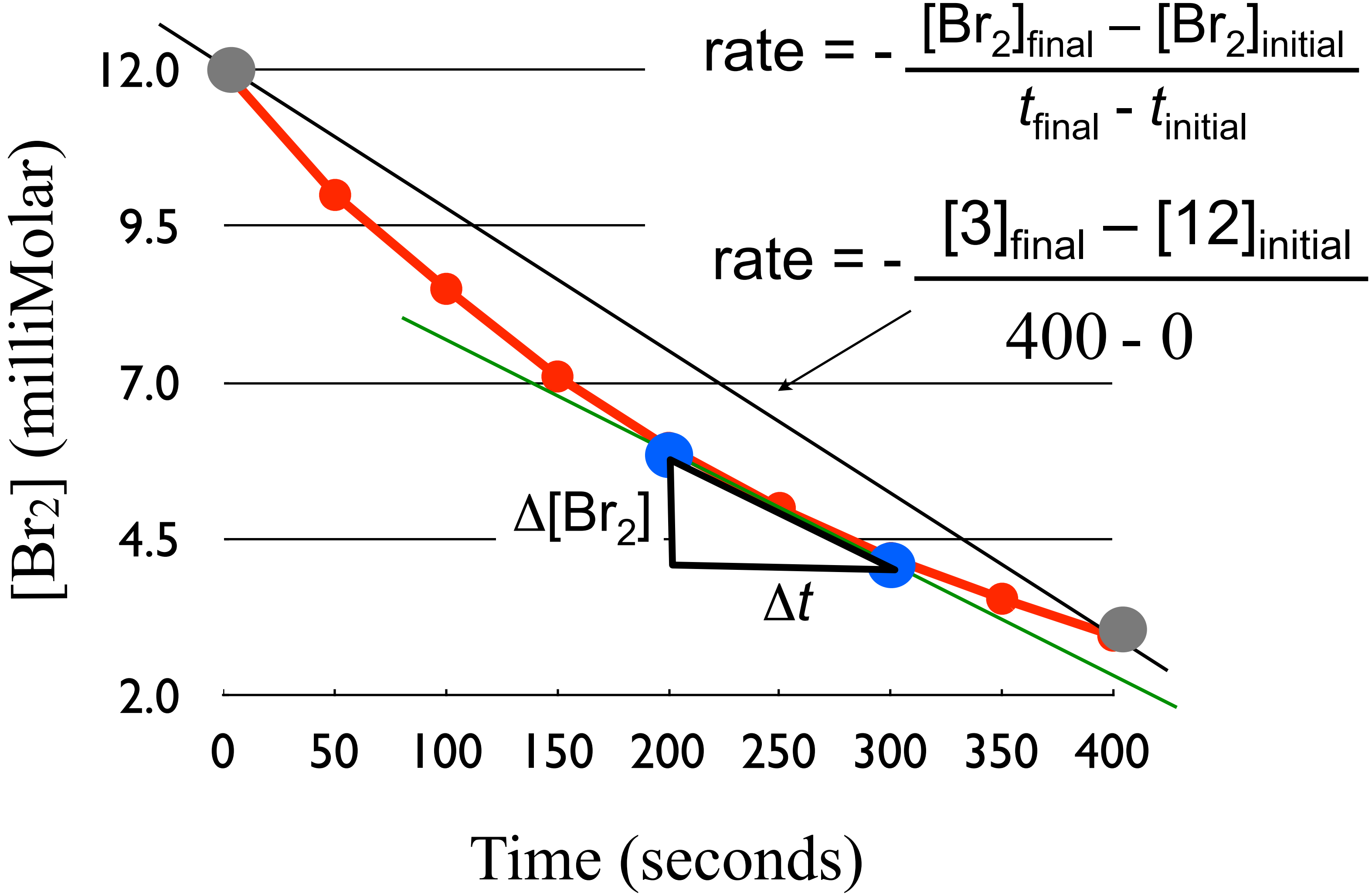


$$\textit{average rate of disappearance} = -\frac{\Delta[Br_2]}{\Delta t} = -\frac{[Br_2]_{final} - [Br_2]_{initial}}{t_{final} - t_{initial}}$$

Time (s)	$[Br_2]$ (mM)	$\Delta[Br_2]$	Avg Rate
0.0	12.0 mM		
		2.00	0.04
50.0	10.0 mM		
		1.54	0.031
100.0	8.46 mM		
		1.36	0.027
150.0	7.10 mM		
		1.14	0.023
200.0	5.96 mM		
		0.96	0.019
250.0	5.00 mM		
		0.80	0.016
300.0	4.20 mM		
		0.65	0.013
350.0	3.55 mM		
		0.59	0.01
400.0	2.96 mM		

Just like driving in a car and sometimes going fast, then slow, then fast again---the average rate of a chemical reaction also varies over time!

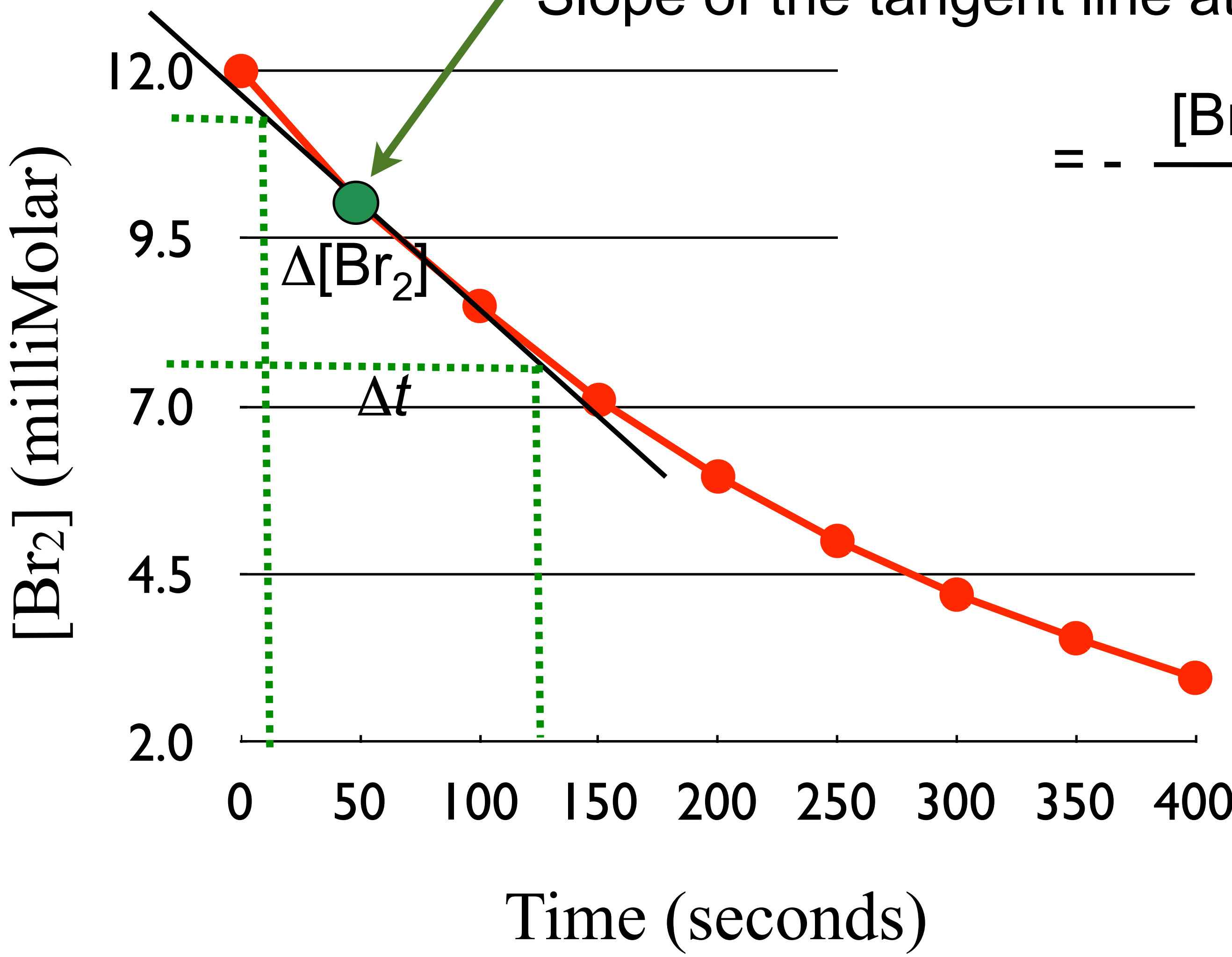
The average rate of disappearance of Br_2 is the slope of the line *between any two points on the curve*. We can pick any two points and get and average rate.



The instantaneous rate of disappearance of Br_2 is the slope of the line tangent *at any point* along the curve.

Instantaneous Rate of Change

Slope of the tangent line at a point



$$= -\frac{[Br_2]_{t+\Delta t} - [Br_2]_t}{\Delta t}$$