Rate

Change over time.
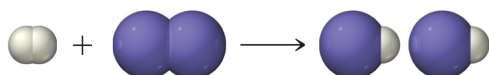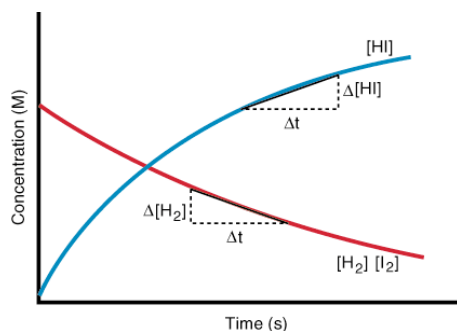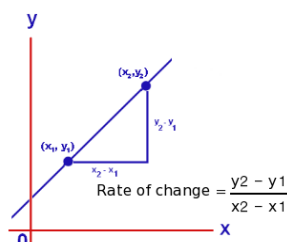
Measuring how fast change occurs.

version 1.6

Rate

- Rate
  - Change (ΔX)
  - Rate (ΔX/Δt)
  - Reaction Rate
    - Definitions
    - Measurement
      - Continuous
      - Difference
    - Avg vs Instantaneous
  - Rate Acceleration
    - Nature of Reaction
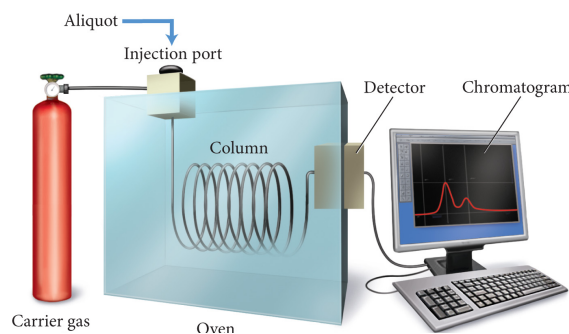   - Experimental Factors

$$\Delta X = X_{final} - X_{initial}$$

$$Rate = \frac{\Delta[A]}{\Delta t} = k[A]$$

Rate of change $= \frac{y2 - y1}{x2 - x1}$

- Rate Laws
  - Differences/Classifications
    - Rate Order
    - Integrated Rate Laws
    - Half Life
      - Finding k
  - Overview of Laws
 - Finding Rate Laws
    - by Inspection
   - by Ratio

2

Measurements of Size & Position

▸ Properties can be intensive or extensive.

  ▸ Measurements of extensive properties answer the question "how much?"

    ▸ These are measurements of size (extent).

    ▸ They say how many units are contained in the sample.

    ▸ Example:

      ▸ Mass, contains 50.0 grams

      ▸ Volume, contains 32 mL

  ▸ Measurements of intensive properties answer the question "how far?"

    ▸ These are measurements of position.

    ▸ They say how many units are between that value and a reference point.

      ▸ Measurements of position can be positive or negative.

      ▸ They require a reference point.

    ▸ Example:

      ▸ Speed, 55 mph faster (than another object)

      ▸ Brightness, 0.23 lumen brighter (than another source)

      ▸ Hardness, 7.0 Moh (70% the hardness of diamond)

      ▸ Density, 19.3 g/mL (19.3 times as dense as water)

B

A

C   D

-10 -9 -8 -7 -6 -5 -4 -3 -2 -1 0 1 2 3 4 5 6 7 8 9 10
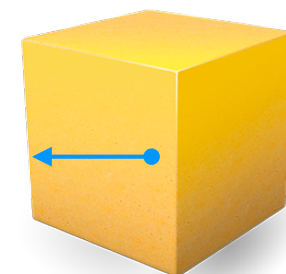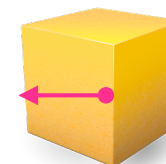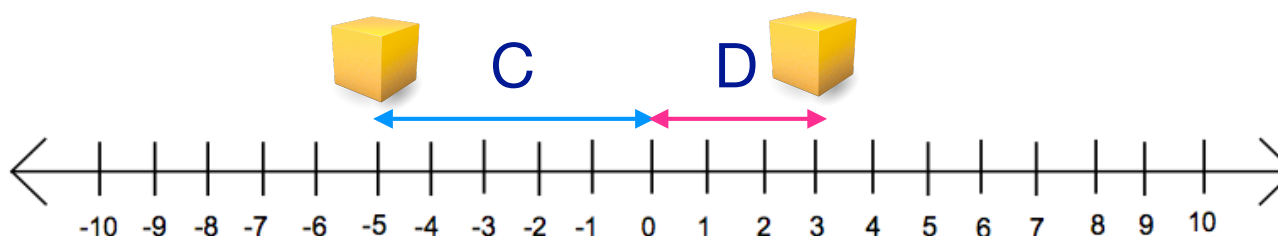
Change (ΔX)

▸ Change is the difference between two measurements.

▸ Change is often between two measurements at different times.
  ▸ We assume time always moves forward.
  ▸ So change is always final minus initial.

▸ The change of a value is represented with the delta symbol (Δ).

$$ΔX = X_{final} - X_{initial}$$

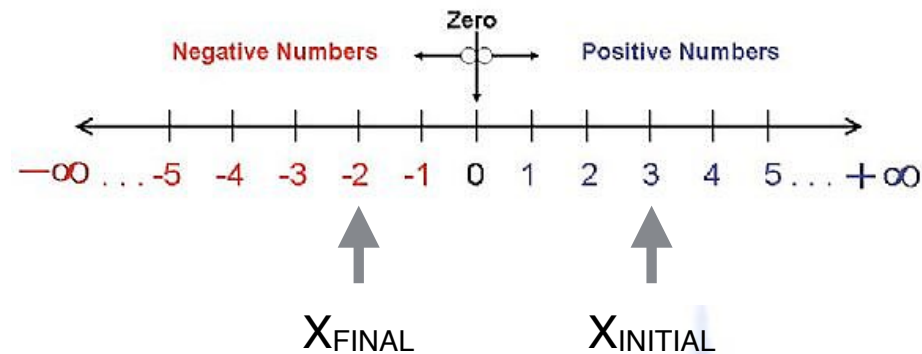▸ Change can be represented by:
  ▸ A single value (which can be positive or negative)

$$ΔX = -5$$

  ▸ A size and a direction (example: decreased)

X decreased by +5
(the size of the change is +5)

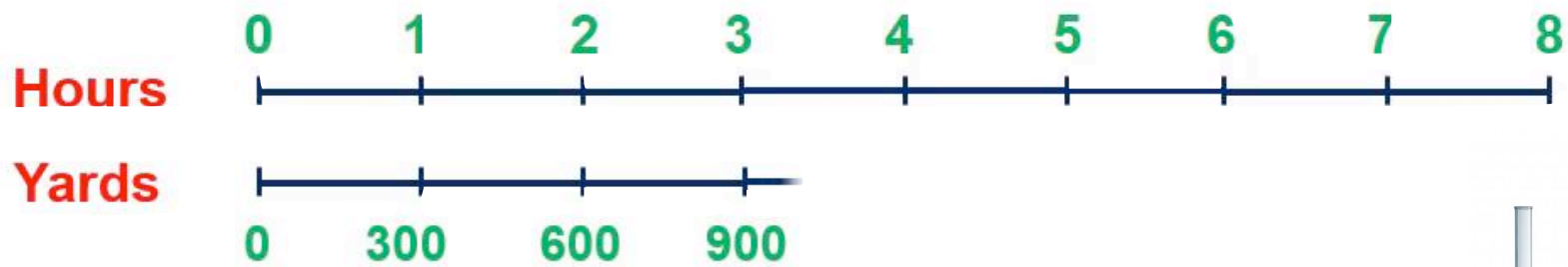X_{FINAL} is -2.

$X_{INITIAL}$ is +3.

Zero

Negative Numbers ←——○——→ Positive Numbers

−∞ …-5 -4 -3 -2 -1 0 1 2 3 4 5…+∞

X_{FINAL} $X_{INITIAL}$

The change in X is
(-2) - (+3) = -5

$$ΔX = -5$$

Rate (ΔX/Δt)

▸ **Rate** is how much a quantity changes per a change in time.

▸ The speed you drive your car is a rate
  —the distance your car travels (miles) in a given period of time (1 hour).

  ▸ The rate of your car has units of mi/hr.

  ▸ 55 mi/hr.

▸ A machine may produce 900 yards of yarn in 3 hours
  —it's rate can be given in yards per hour.

  ▸ The rate of the machine has units of yards/hr.

  ▸ 300 yd/hr.

	0	1	2	3	4	5	6	7	8
Hours									

	0	300	600	900
Yards				

Rate

- Rate
  - Change (ΔX)
  - Rate (ΔX/Δt)
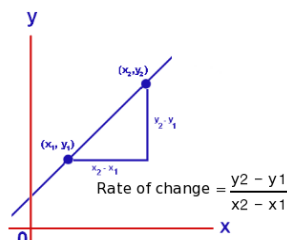
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- Reaction Rate
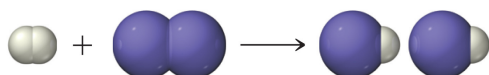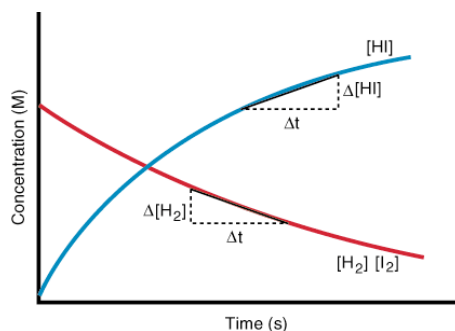 - Definitions
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$$Rate = \frac{\Delta[A]}{\Delta t} = k[A]$$

- Rate Acceleration
  - Nature of Reaction
  - Experimental Factors

- Rate Laws
  - Differences/Classifications
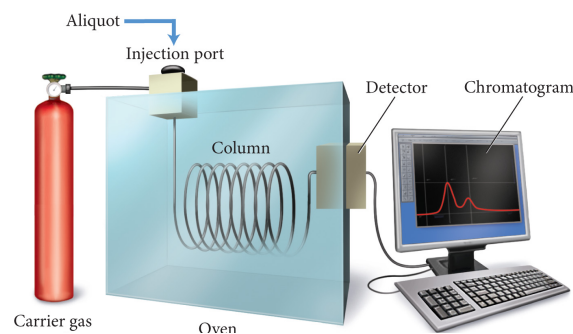   - Rate Order
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$$\text{Rate of change} = \frac{y2 - y1}{x2 - x1}$$

6

Reaction Rates

▸ Reaction rate is the speed of a chemical reaction.

▸ Kinetics is the study of factors that affect the reaction rates, such as temperature, physical state or concentration.

▸ The rate of a reaction is a measure of how fast the reaction makes products or uses reactants.

  ▸ How fast iron rusts.

  ▸ How quickly sugar metabolizes.

  ▸ The speed at which propane burns.

▸ The ability to control the speed of a chemical reaction is important.

  ▸ If you slow rusting, ships last longer.

  ▸ If you speed up metabolism, you loose weight faster.
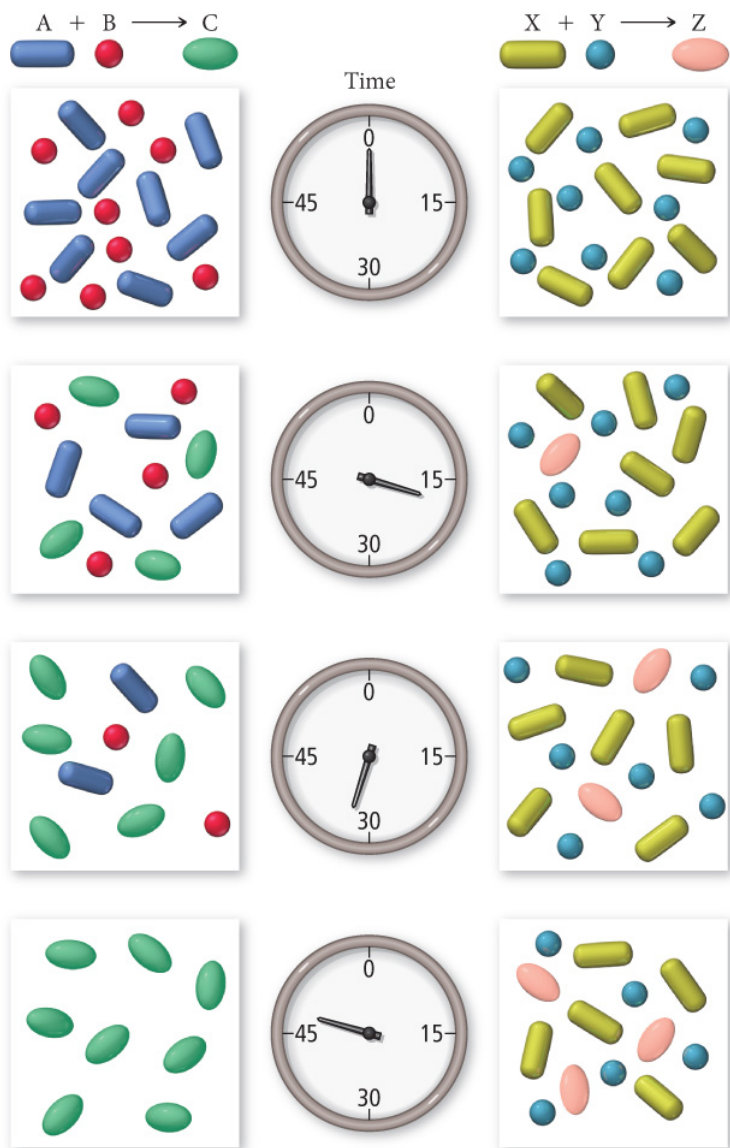
  ▸ Faster burning, creates more intense heat.

H_2
+
I_2

Reaction Rates

‣ The rate of a chemical reaction is generally measured in terms of how much of a reactant decreases (or product increases) per period of time.

‣ For a fixed volume of solution, this can be observed by changes in concentration.

Reaction Rates

A + B ⟶ C   X + Y ⟶ Z

Time

- ‣ The rate of a chemical reaction is generally measured in terms of how much of a reactant decreases (or product increases) per period of time.

- ‣ For a fixed volume of solution, this can be observed by changes in concentration.

- ‣ For reactants, a negative sign in the equation shows decrease.

H_2

$+$

I_2

$$\text{Rate} = -\frac{\Delta[I_2]}{\Delta t}$$

Rate

- Rate
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  - Rate (ΔX/Δt)

$$\Delta X = X_{final} - X_{initial}$$

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  - → Definitions

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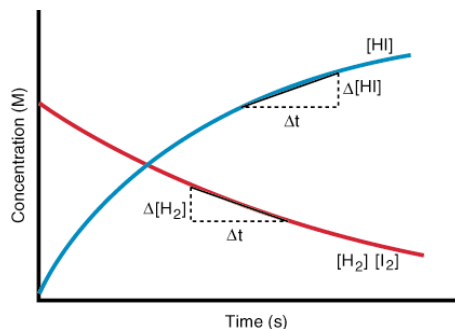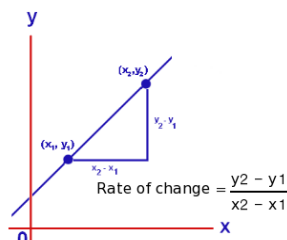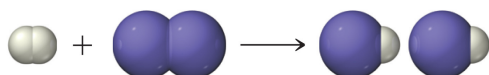
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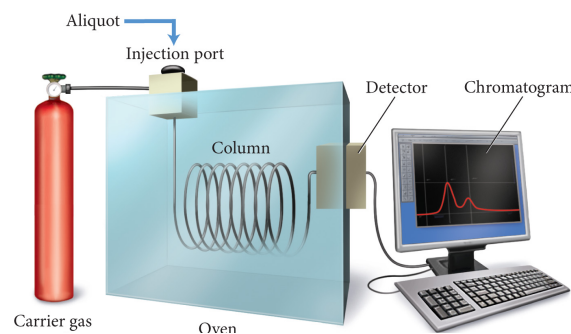   - Rate Order
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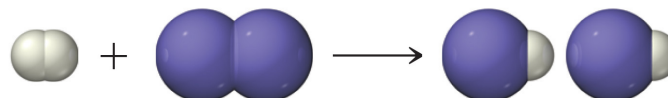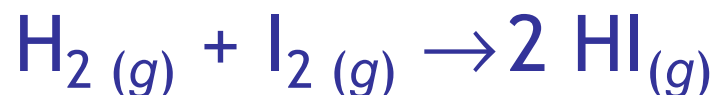   - Half Life
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Reaction Rate

▸ In most reactions, the coefficients of the balanced equation are not all the same.

$$H_{2\,(g)} + I_{2\,(g)} \rightarrow 2\,HI_{(g)}$$

▸ For these reactions, the change in the number of molecules of one substance is a multiple of the change in the number of molecules of another.

▸ For the above reaction, for every 1 mole of H_2 used, 1 mole of I_2 will also be used and 2 moles of HI made.

▸ Therefore, the rate of change will be different for each component ([x]) as

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

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

▸ To be consistent, the change in the concentration of each substance ([A]) is multiplied by 1 over it's coefficient (a). This defines the reaction rate.

Reaction Rate

‣ In most reactions, the coefficients of the balanced equation are not all the same.

$$H_{2\,(g)} + I_{2\,(g)} \rightarrow 2\,HI_{(g)}$$

‣ The rate of H_2 is how fast H_2 is consumed.

‣ The rate is how fast I_2 is consumed.

‣ The rate is half of how fast HI is produced.

  ‣ HI is produced twice as fast as H_2 is consumed.

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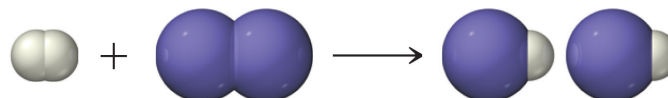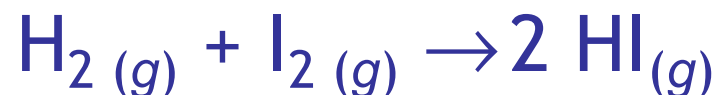
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Question

▸ Hydrogen peroxide (H_2O_2) can be used as a disinfectant; it decomposes as:

$$2\ H_2O_2 \rightarrow 2\ H_2O + O_2$$

▸ If the rate of change of O_2 is +0.0014 Ms^{-1}

...what is the rate of change of H_2O_2?

...what is the rate of change of H_2O?

...what is the *rate of reaction*?

a) +0.0014 Ms^{-1}

b) - 0.00070 Ms^{-1}

c) +0.0028 Ms^{-1}

e) - 0.0014 Ms^{-1}

f) + 0.00070 Ms^{-1}

g) - 0.0028 Ms^{-1}

h) None of the above.

Rate

- Rate
  - Change (ΔX)
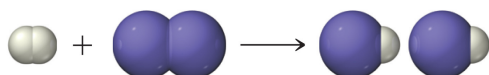 - Rate (ΔX/Δt)
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Measuring Rate

‣ We can measure the rate, by looking at how concentration changes.

Determine the rate of disappearance of NO in the first 100 seconds.

a) 3.4×10^{-4} M/s
b) 5.9×10^{-4} M/s
c) 4.1×10^{-4} M/s
d) 1.6×10^{-4} M/s
e) 2.1×10^{-4} M/s

[NO]	time (s)
0.100	0
0.078	50
0.059	100
0.043	150
0.031	200

Measuring Rate

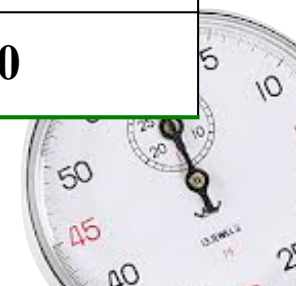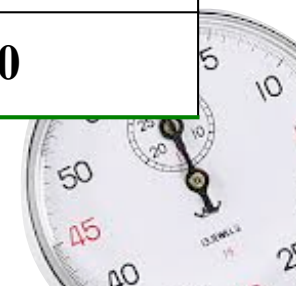▸ We can measure the rate, by looking at how concentration changes.

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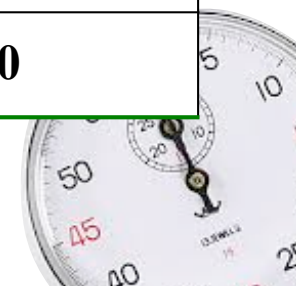| [NO]	time (s)
0.100	0
0.078	50
0.059	100
0.043	150
0.031	200

Measuring Rate

‣ Rates often change as reactions proceed.

Is that the same as the rate after the second 100 seconds?

a) 3.4×10^{-4} M/s
b) 5.9×10^{-4} M/s
c) **4.1×10^{-4} M/s**
d) 1.6×10^{-4} M/s
e) 2.1×10^{-4} M/s

[NO]	time (s)
0.100	0
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0.031	200

Reaction Rate Overtime

A + B ⟶ C
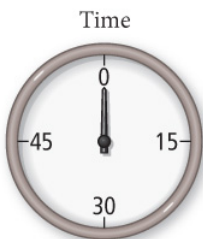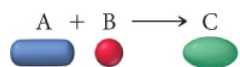
Time

‣ As time progresses, the rate of a reaction generally slows down because the concentration of the reactants decreases.

‣ At some time the reaction stops, either because the reactants run out or because the system has reached equilibrium.

Reaction Rate Overtime

A + B → C
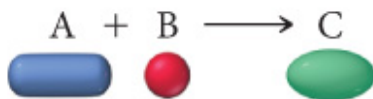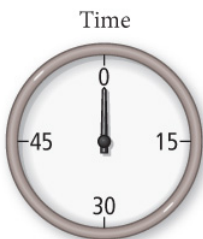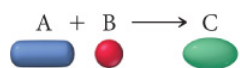
	change			change/time
8 8 0				
4 4 4	-4 -4 +4			fast
2 2 6	-2 -2 +2			slow
0 0 8	0 0 0			zero

19

Most Reactions Slow Over Time

change/time

change

$H_{2\,(g)} + I_{2\,(g)} \rightarrow 2\,HI_{(g)}$
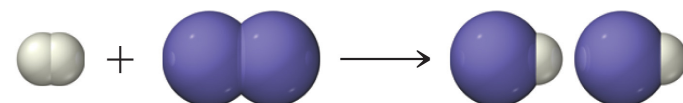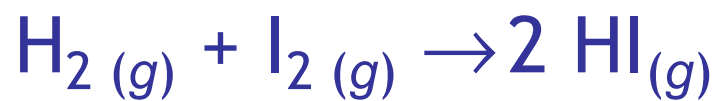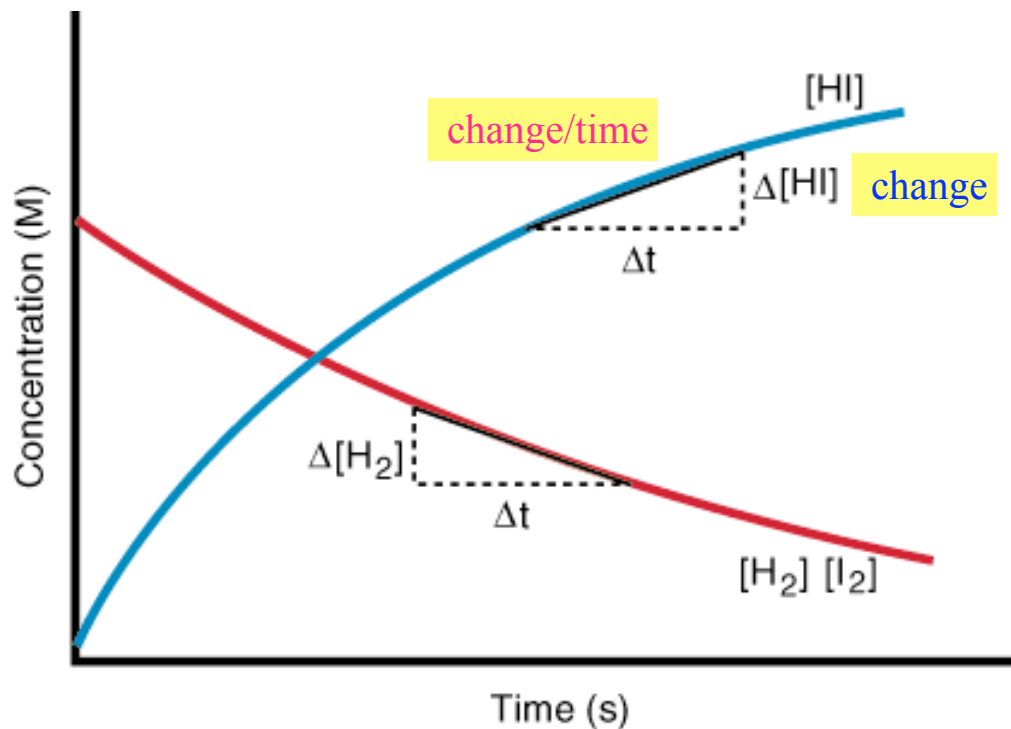
fast   slow   zero

Rate

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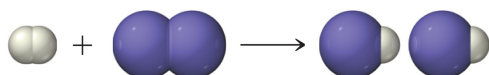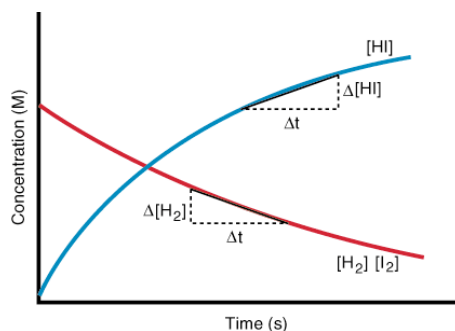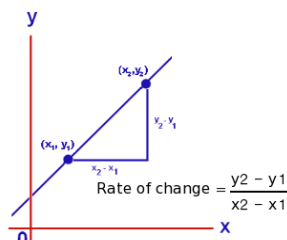
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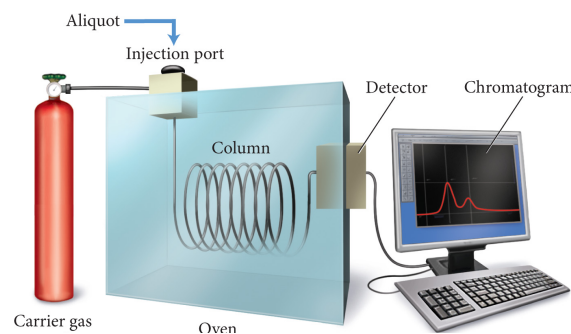
Measuring Reaction Rate

▸ To produce that plot, you need to measure the concentration of at least one component in the mixture at many points in time.

▸ There are two ways of approaching this problem:

  ▸ For reactions that are complete in less than 1 hour, it is best to use continuous monitoring of the concentration.

    ▸ Automatically sampling the concentration at regular intervals.

  ▸ For reactions that happen over a very long time, sampling of the mixture at various times can be used.

  ▸ When sampling is used, often the reaction in the sample must be stopped by a quenching technique.

    ▸ So you get a measure of the concentration when the sample is taken.
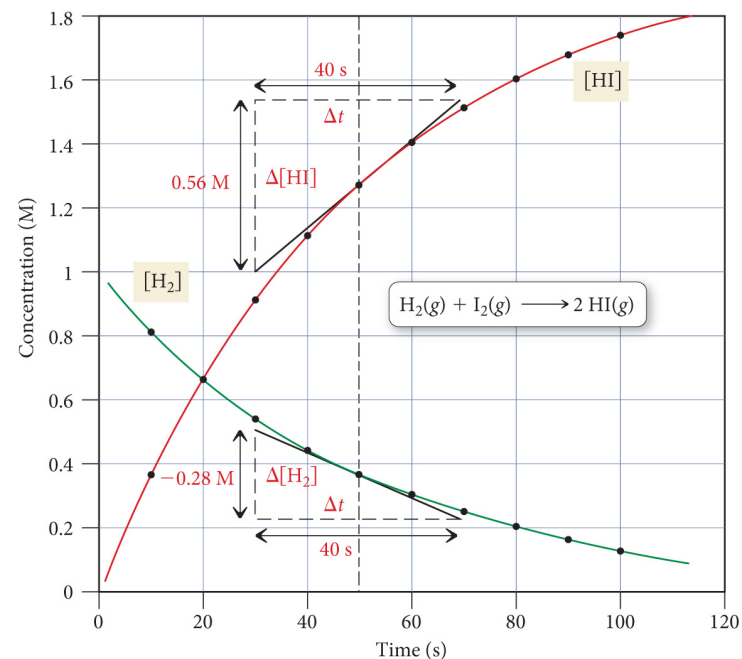
Continuous Monitoring

▸ Methods of continuous monitoring include:

  ▸ Polarimetry – this measures the change in the degree of rotation of plane-polarized light caused by one of the components over time.

  ▸ Spectrophotometry – this measures the amount of light of a particular wavelength absorbed by one component over time.

    ▸ The component absorbs its complementary color.

  ▸ Total pressure – the total pressure of a gas mixture is stoichiometrically related to partial pressures of the gases in the reaction.

| Source | Slit | Monochromator | Sample | Detector | Computer |
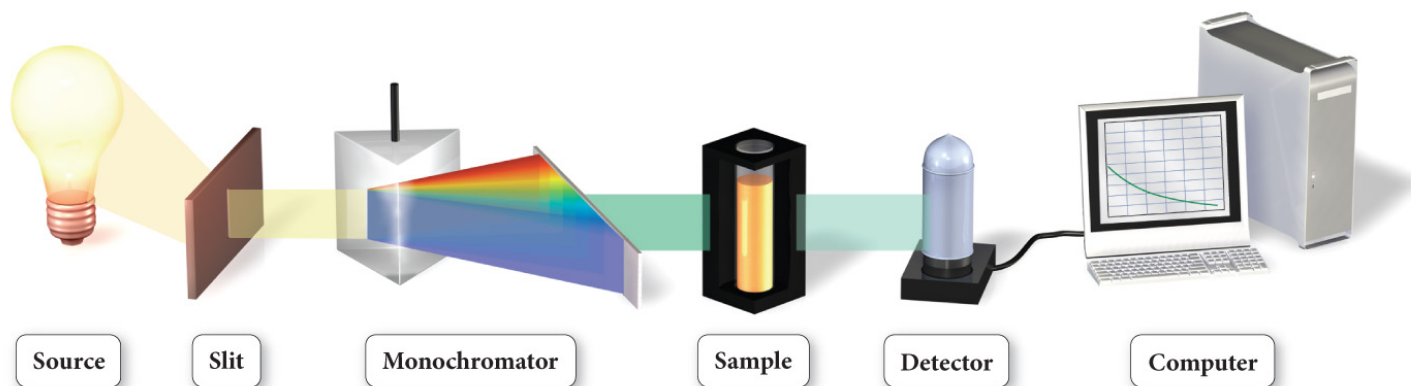
$$\text{Rate} = -\frac{\Delta[\text{H}_2]}{\Delta t} = -\frac{[\text{H}_2]_{t_2} - [\text{H}_2]_{t_1}}{t_2 - t_1}$$

Rate

- Rate
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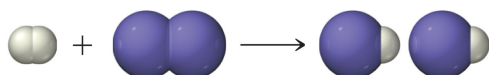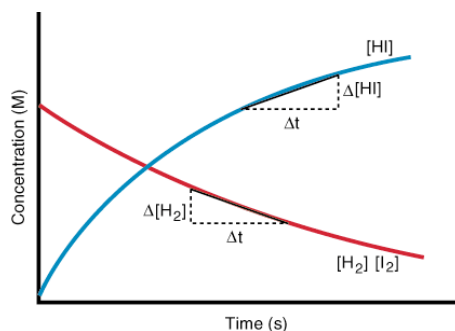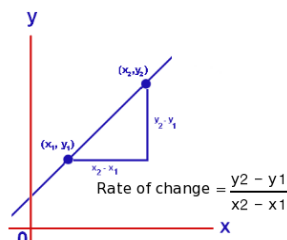
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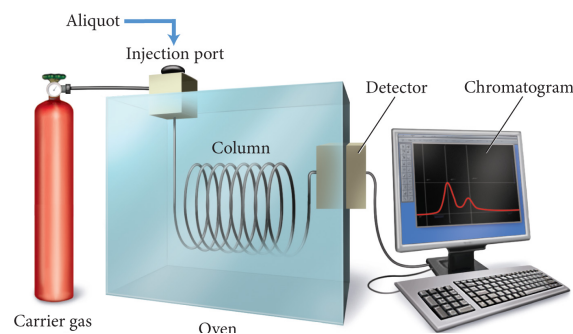
Monitoring by Sampling

▸ Monitoring by sampling can be accomplished with different instrumentation and techniques.

▸ Aliquots (samples from the reaction mixture) are drawn off at specific times during the reaction, and quantitative analysis is performed.

  ▸ Titration for one of the components
  ▸ Gravimetric analysis

▸ Gas chromatography can measure the concentrations of various components in a mixture.

  ▸ For samples that have volatile components
  ▸ Separates mixture by adherence to a surface

$$\text{Rate} = -\frac{\Delta[H_2]}{\Delta t} = -\frac{[H_2]_{t_2} - [H_2]_{t_1}}{t_2 - t_1}$$
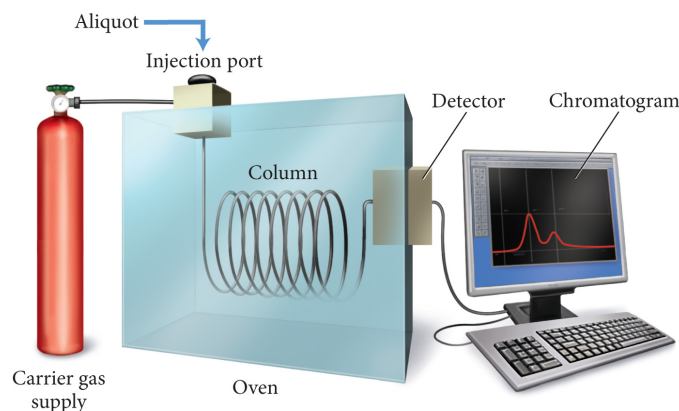
Aliquot

Injection port

Detector   Chromatogram

Column

Carrier gas supply

Oven

Rate

- Rate
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    - by Ratio

Average Rate & Instantaneous Rate

▸ Reaction rates may change during a reaction.

▸ Some reactions move faster at the beginning and slow as they progress.

▸ When we describe the rate of a reaction, it's important to be clear what rate we are talking about.

▸ Instantaneous rate is the rate of change at one moment.

▸ Average rate is the rate of change over an interval of time.
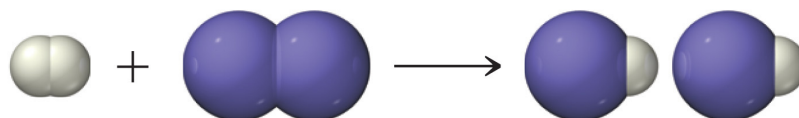
▸ The larger the time interval, the more the average rate deviates from the instantaneous rate.

Average Rate & Instantaneous Rate

- Both types of rates can be determined by plotting how concentration changes over time.

- Instantaneous rate is the rate of change at one moment.
  - The slope of the line tangent to the graph at any point is the instantaneous rate.

$$\text{Rate} = -\frac{\Delta[H_2]}{\Delta t}$$

- Average rate is the rate of change over an interval of time.
  - The distance between any two points on the graph is the magnitude of the average rate (over that interval).

$$\text{Rate} = -\frac{[H_2]_{t_2} - [H_2]_{t_1}}{t_2 - t_1}$$
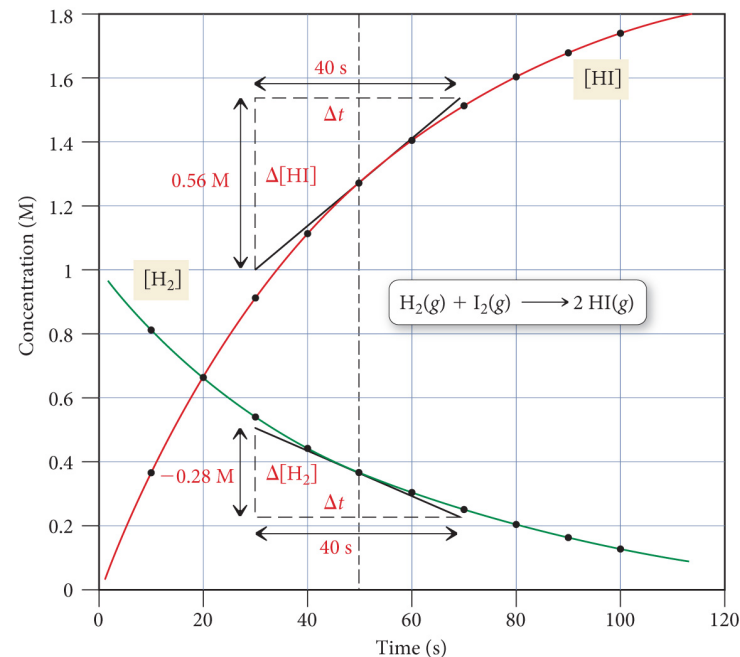
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Rate

- Rate
  - Change (ΔX)
  - Rate (ΔX/Δt)
- Reaction Rate
  - Definitions
  - Measurement
    - Continuous
    - Difference
  - Avg vs Instantaneous
- **Rate Acceleration**
  - Nature of Reaction
  - Experimental Factors

$$\Delta X = X_{final} - X_{initial}$$

$$Rate = \frac{\Delta[A]}{\Delta t} = k[A]$$

Rate of change $= \dfrac{y2 - y1}{x2 - x1}$

- Rate Laws
  - Differences/Classifications
    - Rate Order
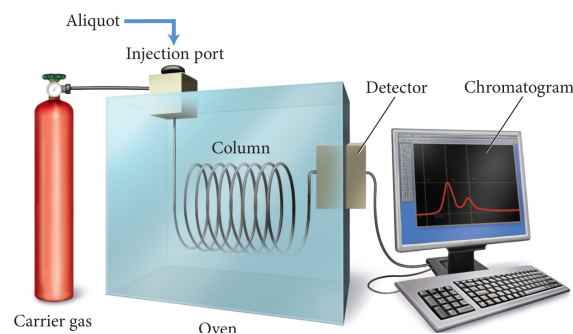   - Integrated Rate Laws
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29
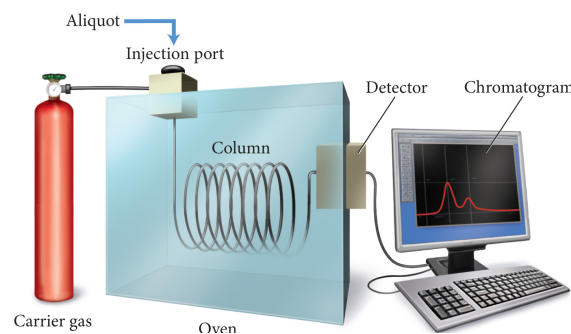
What causes differences in rates?

‣ Differences in the substances themselves or how they combine can produce different rates (we'll talk about mechanisms in a future discussion).

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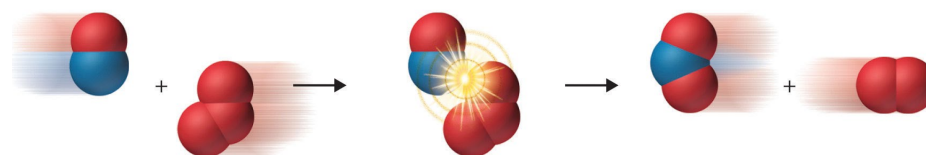
‣ What factors that can influence these events and therefore the rate of chemical reactions?

  ‣ Temperature
  ‣ Physical State
  ‣ Exposes Surface Area
  ‣ Solvent
  ‣ Dispersion
  ‣ Catalysts
  ‣ Concentration of Reactants

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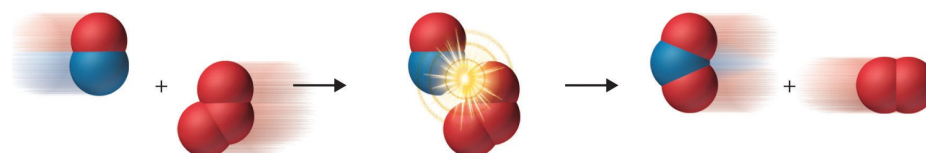
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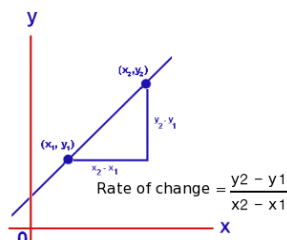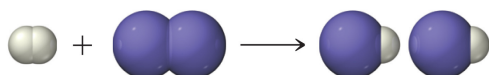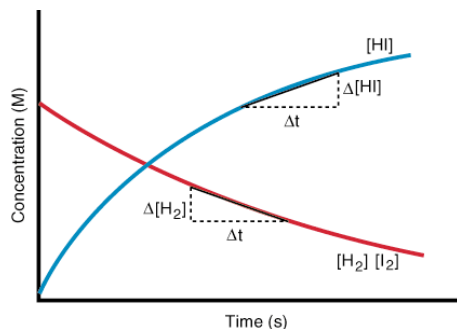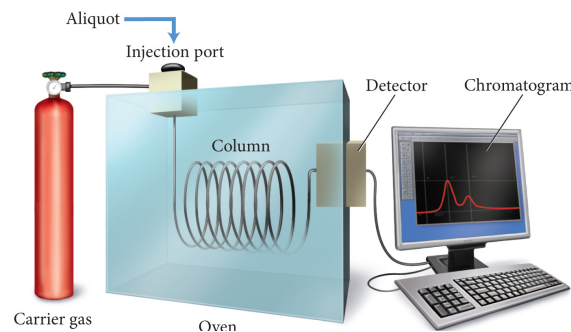
Rate Law

▸ The rate of a reaction is directly proportional to the concentration (liquid phase) or partial pressure (gas phase) of each reactant raised to a power.

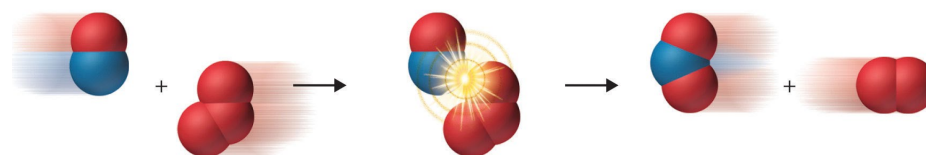▸ The relationship of concentration or pressure to reaction rate can be expressed as an equation called a rate law.

▸ The rate law must be determined experimentally.

▸ For the reaction aA → bB products the rate law would have the form given below.

  ▸ **n** is the orders for each reactant.

  ▸ **k** is the rate constant.

$$\text{Rate} = k[\text{A}]^n$$

▸ Rate order results from the mechanism of the rate limiting step.

▸ Reactions are classified by rate order:

  ▸ n = 1 is first order; n = 2 is second order; n = 0 is zero order

Rate Laws

- Reactions may have any rate order (even fractions).

- Most reactions are first, second or third order.

- Rate most often varies:
  - Independant of concentration
    - Zero Order
  - Linearly with concentration
    - First Order
  - Exponentially with concentration
    - Second Order (most often)

- Rate laws can only be determined by experiment.

- Experimental data can be analyzed by inspection (initial rates) or an algebraic solution (ratio method).

Order	Rate
0	$r = k[A]^0 = k$
1	$r = k[A]$
2	$r = k[A]^2$

Rate Order

$$\text{Rate} = k[\text{A}]^n$$

‣ Reaction order is a function of what type of event controls the rate of reaction.

    ‣ Zero order reactions are limited by something other than the reactant.

    ‣ First order reactions are limited by how much of the reactant exists.

    ‣ Second order reactions are limited by how fast a reactant can find another reactant.

$$\text{CH}_2\text{CH}_2 \xrightarrow[\text{H}_2]{10\%\ \text{Pd/C}} \text{CH}_3\text{CH}_3 \qquad \text{Cu(OH)}_2 \rightarrow \text{CuO} + \text{H}_2\text{O} \qquad \text{HI} \rightarrow \text{I}_2 + \text{H}_2$$

Zero Order — Rate is constant

First Order — Rate changes as [A] changes

Second Order — Rate changes as $[\text{A}]^2$ changes

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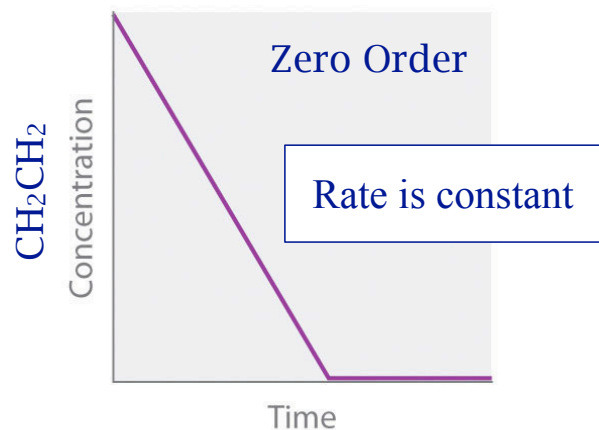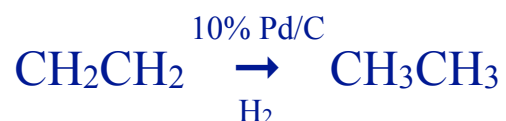
$$\text{Rate} = -\frac{\Delta[\text{A}]}{\Delta t} = k[\text{A}]$$

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Rate $\propto$ catalyst
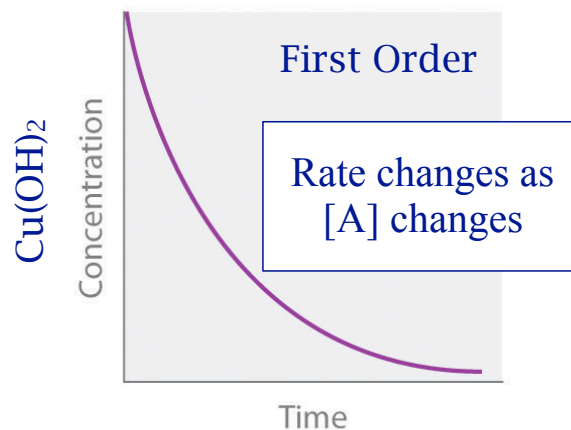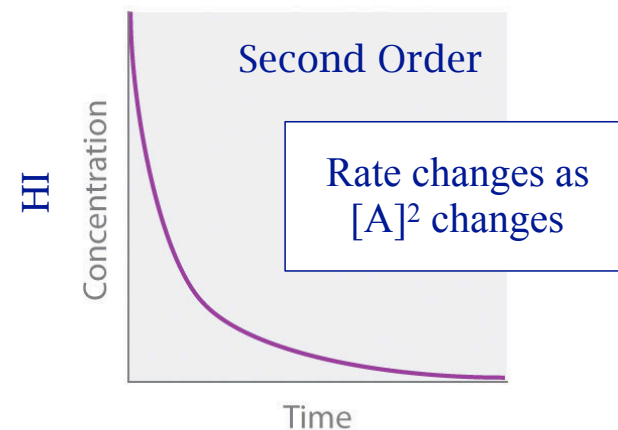
Rate $\propto$ [A]

Rate $\propto$ [A] finding [A]

Overall Rate Order

‣ The rate order is relative to reactants, individually and overall.

‣ If the rate determining event involves no reactants the reaction is zero order.

‣ If the rate determining event involves one reactant molecule A

  ‣ the reaction is first order overall.

  ‣ the reaction is first order in A.

$$A \rightarrow products \qquad Rate = k[A]$$

First order overall
First order in A

‣ If the rate determining event involves two reactant molecules the two molecules may be of different reactants.

  ‣ the reaction is second order overall.

  ‣ and <u>may be</u> second order in substance A.

$$A + A \rightarrow products \qquad Rate = k[A]^2$$

Second order overall
Second order in A

… or may be first order each in different substances.

$$A + B \rightarrow products \qquad Rate = k[A][B]$$

Second order overall
First order in A
First order in B

Overall Rate Order

‣ The rate order is relative to reactants, individually and overall.

‣ Higher order events are possible, although less likely.

$A + A + B \longrightarrow$ products
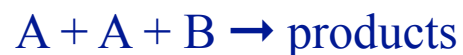
$\text{Rate} = k[A]^2[B]$

Third order overall
Second order in A
First order in B

$A + B + C \longrightarrow$ products

$\text{Rate} = k[A][B][C]$

Third order overall
First order in A
First order in B
First order in C

$A + A + A \longrightarrow$ products

$\text{Rate} = k[A]^3$

Third order overall
Third order in A

Question

‣ What is the order of [A], of [B] and the overall reaction order in each of the following rate laws?

‣ What are the units for k?

$$\text{Rate} = k\,[A]$$

$$\text{Rate} = k\,[B]^2$$

$$\text{Rate} = k\,[A]^3[B]$$

$$\text{Rate} = k\,[A][B][C][D]^2$$

$$\text{Rate} = k\,[A]^{2\frac{1}{2}}[B][C]^{\frac{1}{2}}$$

Rate

▸ Rate
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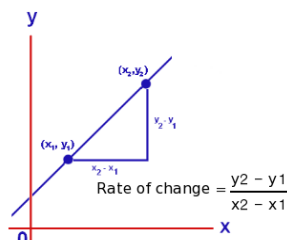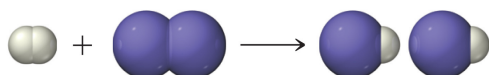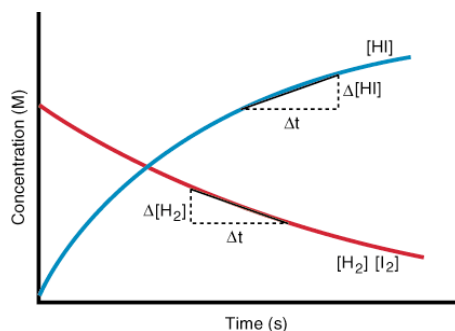
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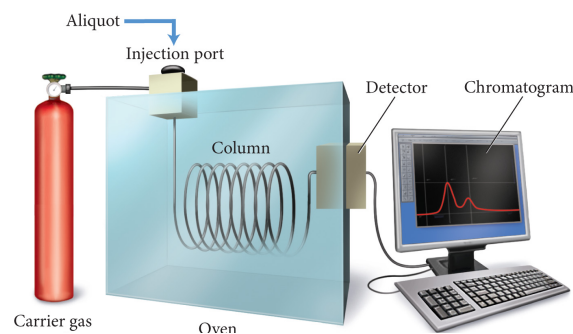
Integrated Rate Laws

▸ Differential rate laws

  ▸ relate the
    change in concentration (Δ[A])
    to a
    change in time (Δt)

$$Rate = \frac{\Delta[A]}{\Delta t} = k[A]$$

Integrating these differential equations produces integrated forms of those same rate laws.

▸ Integrated rate laws

  ▸ relate the
    concentration ([A])
    to a
    time (t)

$$[A] = [A]_0 - kt$$

Integrated Rate Laws

▸ The rate law is a differential equation, it describes the change in concentration of reactants per change in time (difference over time).

▸ Using calculus, the rate law can be integrated to obtain an integrated rate equation that links concentrations of reactants or products directly to time.

	Zeroth Order	First Order	Second Order
Differential rate law	$\text{Rate} = -\dfrac{\Delta[A]}{\Delta t} = k$	$\text{Rate} = -\dfrac{\Delta[A]}{\Delta t} = k[A]$	$\text{Rate} = -\dfrac{\Delta[A]}{\Delta t} = k[A]^2$
Integrated rate law	$[A] = [A]_0 - kt$	$[A] = [A]_0 e^{-kt}$ or $\ln[A] = \ln[A]_0 - kt$	$\dfrac{1}{[A]} = \dfrac{1}{[A]_0} + kt$

▸ Using the integrated rate laws we can predict concentration at any time, provided we know the order, rate constant and initial concentration of the reaction.

Integrated Rate Laws

	Zeroth Order	First Order	Second Order
Integrated rate law	$[A] = [A]_0 - kt$	$[A] = [A]_0 e^{-kt}$ or $\ln[A] = \ln[A]_0 - kt$	$\dfrac{1}{[A]} = \dfrac{1}{[A]_0} + kt$

$$y = b + mx$$

‣ The integrated rate laws each have a linear relationship between time and either [A], the natural log of [A], or the inverse of [A].

Zero Order
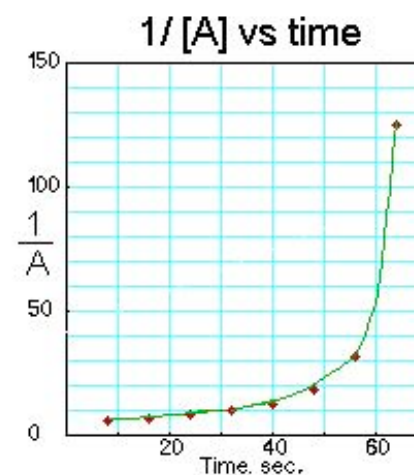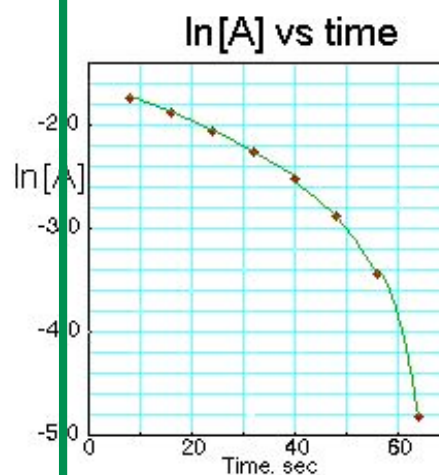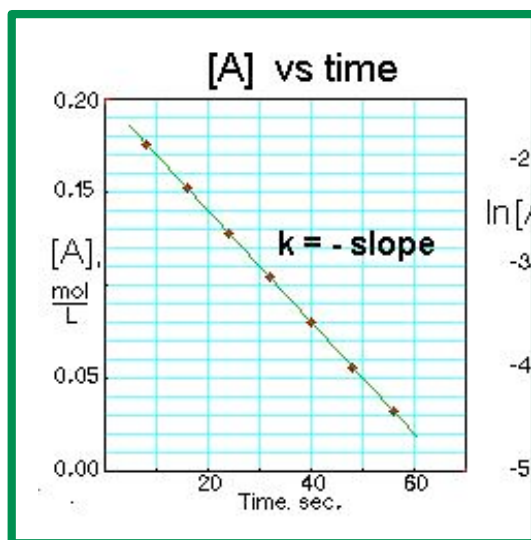
Integrated Rate Laws

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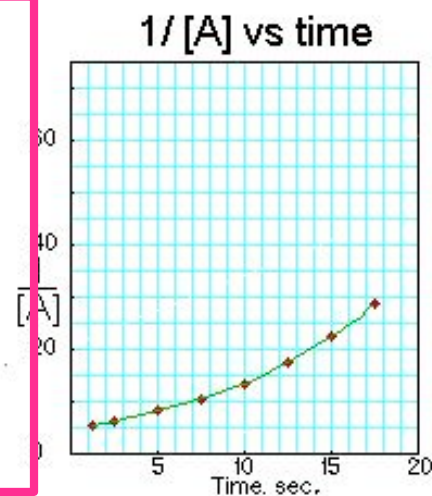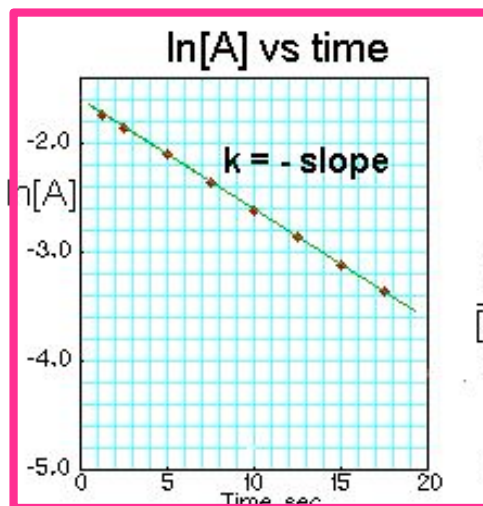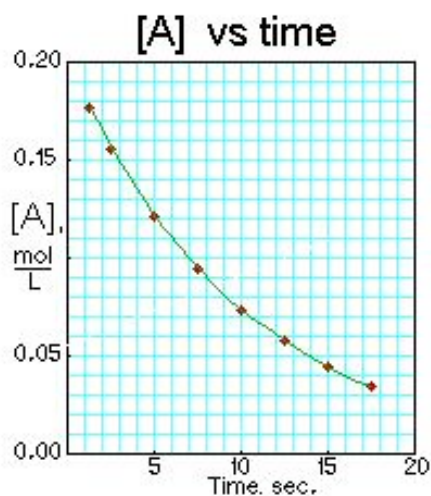
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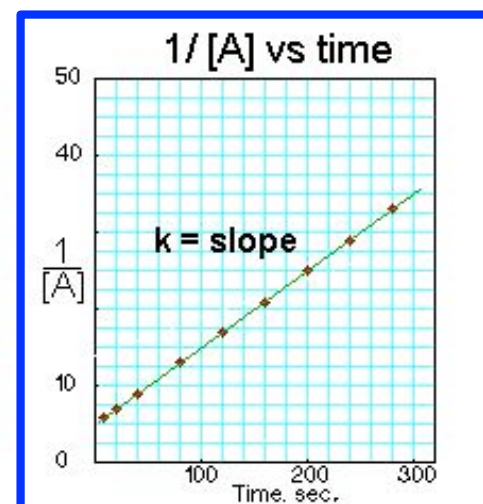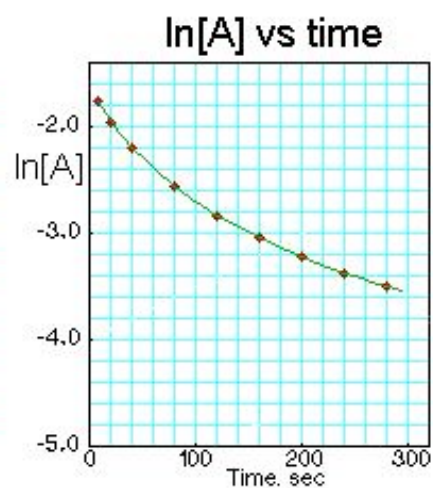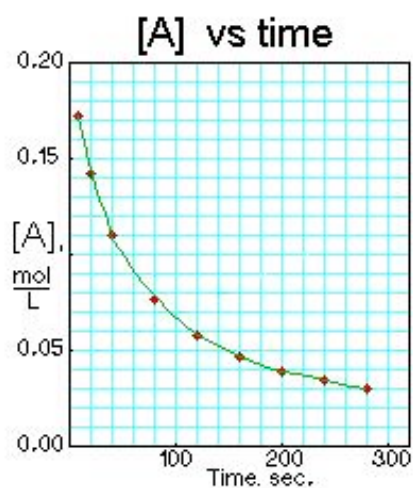
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Integrated Rate Laws

	Zeroth Order	First Order	Second Order
Integrated rate law	$[A] = [A]_0 - kt$	$[A] = [A]_0 e^{-kt}$ or $\ln[A] = \ln[A]_0 - kt$	$\dfrac{1}{[A]} = \dfrac{1}{[A]_0} + kt$

$$y = b + mx$$

▸ The integrated rate laws each have a linear relationship between time and either $[A]$, the natural log of $[A]$, or the inverse of $[A]$.

▸ You can determine the order of a reaction, by plotting time against each of these values and identifying which one produces a straight line.

▸ The slope (m) of that line will be the rate constant (-k or k) for your reaction.

Try this...

▸ Given the following plots of concentration against time, what is the rate order of [A] in this reaction?

	Zeroth Order	First Order	Second Order
Integrated rate law	$[A] = [A]_0 - kt$	$[A] = [A]_0 e^{-kt}$ or $\ln[A] = \ln[A]_0 - kt$	$\dfrac{1}{[A]} = \dfrac{1}{[A]_0} + kt$
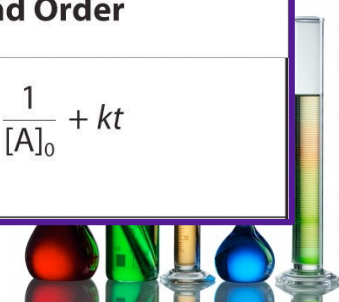
Try this...

‣ Given the following plots of concentration against time, what is the rate order of [A] in this reaction?

Ans: The linear relationship is to natural log [A], this reaction is first order in [A].

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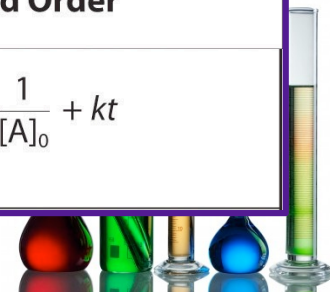
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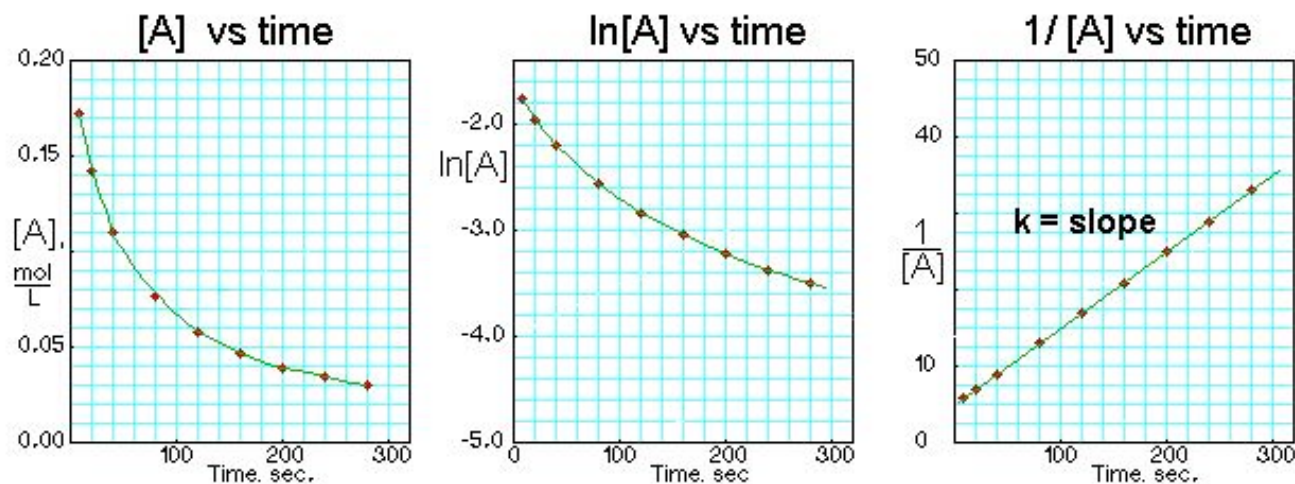
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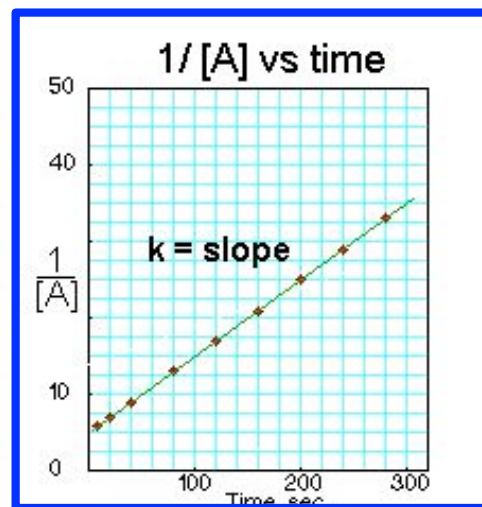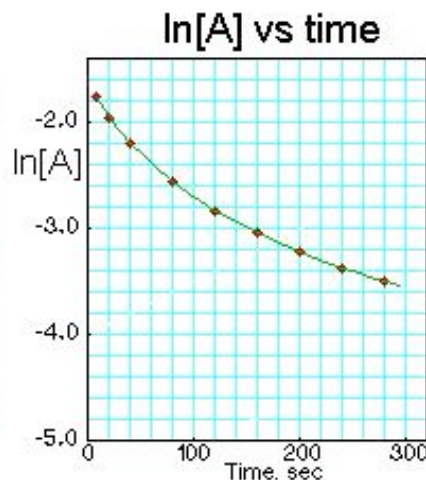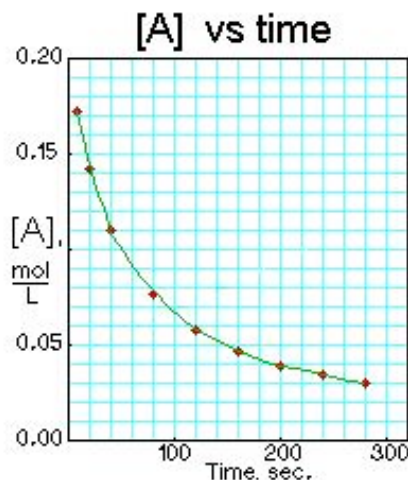
Ans: The linear relationship is inverse [A], this reaction is second order in [A].

	Zeroth Order	First Order	Second Order
Integrated rate law	$[A] = [A]_0 - kt$	$[A] = [A]_0 e^{-kt}$ or $\ln[A] = \ln[A]_0 - kt$	$\dfrac{1}{[A]} = \dfrac{1}{[A]_0} + kt$
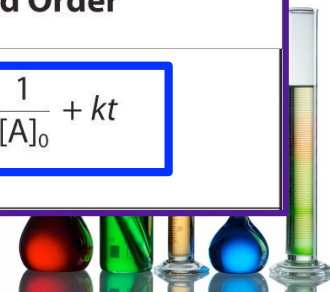
Try this...

▸ The first-order decomposition of N_2O at 1000 K has a rate constant of 0.76 s^{-1}.

If the initial concentration of N_2O is 10.9 M, what is the concentration of N_2O after 9.6 s?

A) 7.4×10^{-3} M

B) 1.0×10^{-3} M

C) 1.4×10^{-3} M

D) 3.6×10^{-3} M

E) 8.7×10^{-3} M

	Zeroth Order	First Order	Second Order
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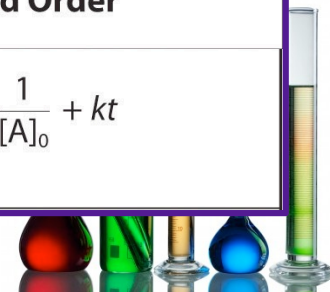
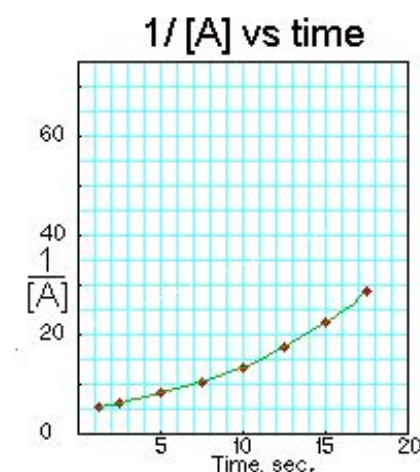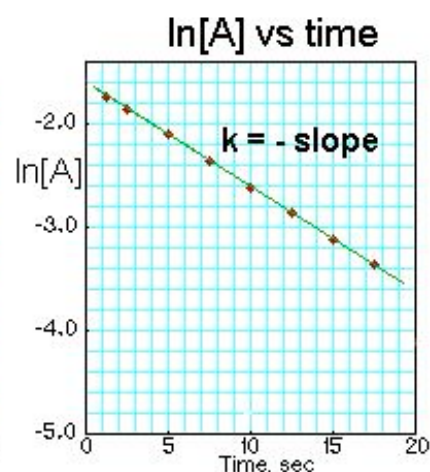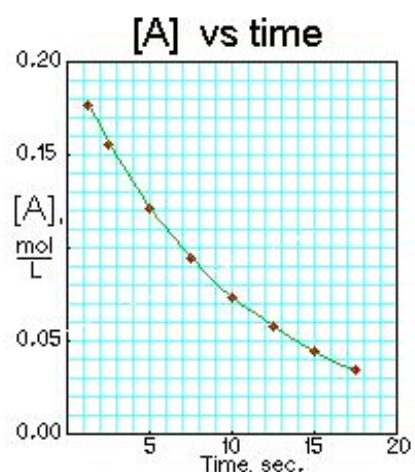# Try this...

- The second-order decomposition of HI has a rate constant of 1.80×10^{-3} $M^{-1}s^{-1}$. How much HI remains after 27.3 s if the initial concentration of HI is 4.78 M?

A) 4.55 M

B) 0.258 M

C) 3.87 M

D) 2.20 M

E) 2.39 M

	Zeroth Order	First Order	Second Order
Integrated rate law	$[A] = [A]_0 - kt$	$[A] = [A]_0 e^{-kt}$ or $\ln[A] = \ln[A]_0 - kt$	$\dfrac{1}{[A]} = \dfrac{1}{[A]_0} + kt$
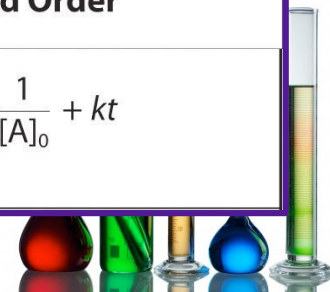
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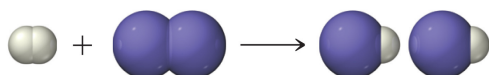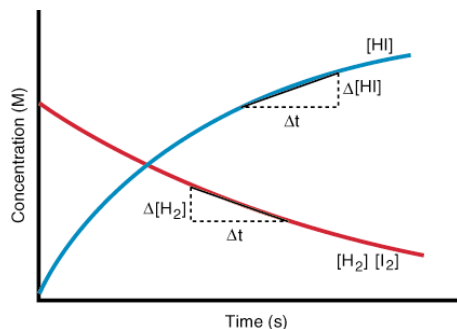
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    - by Inspection
    - by Ratio
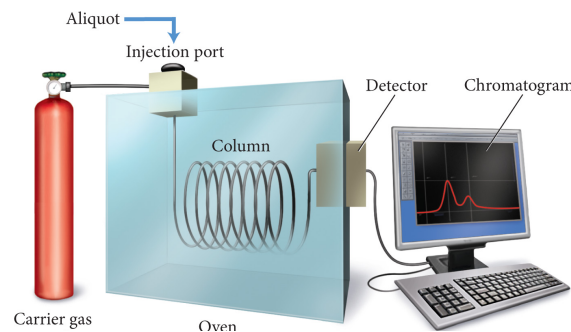
Half-Life

▸ The half life of a reaction is the time it takes for the concentration to drop to 50% of it's current value.

▸ For first order reactions half life is constant.

[A] vs time for a 0 order reaction — Half life decreases with decreasing concentration. 1st half life, 2nd half life, 3rd half life

[A] vs time for a 1st order reaction — Length of half life is constant. 1st half life, 2nd half life, 3rd half life

[A] vs time for a 2nd order reaction — Length of half life increases with decreasing concentration. 1st half life, 2nd half life, 3rd half life
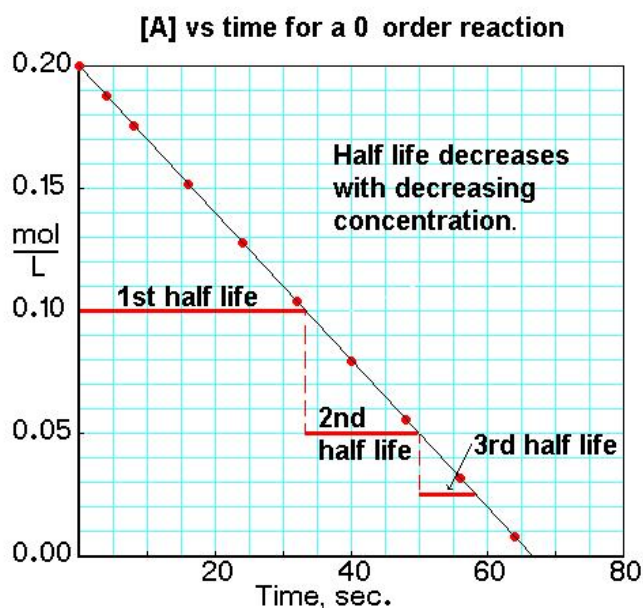
▸ With second order reactions the half life slows down as the reaction progresses.

▸ With zero order reactions the half life speeds up as the reaction progresses.

Half Life

- For a zero order reaction, the lower the initial concentration of the reactants, the shorter the half-life.
  - $t_{1/2} = [A]_{init}/2k$

- For a first order reaction, the half-life is independent of the concentration.
  - $t_{1/2} = \ln(2)/k = 0.693 / k$

- For a second order reaction, the half-life is inversely proportional to the initial concentration, increasing the initial concentration shortens the half-life.
  - $t_{1/2} = 1/(k[A]_{init})$

[A] vs time for a 0 order reaction

Half life decreases with decreasing concentration.

1st half life
2nd half life
3rd half life

mol/L

Time, sec.

[A] vs time for a 1st order reaction

Length of half life is constant.

[A], M

1st half life
2nd half life
3rd half life

Time, sec.

[A] vs time for a 2nd order reaction

Length of half life increases with decreasing concentration.

1st half life
2nd half life
3rd half life

mol/L

Time, sec.

55
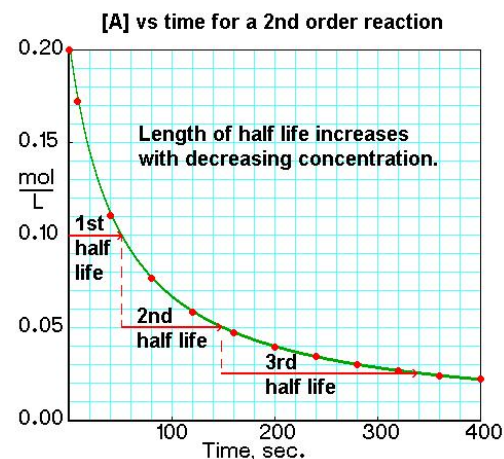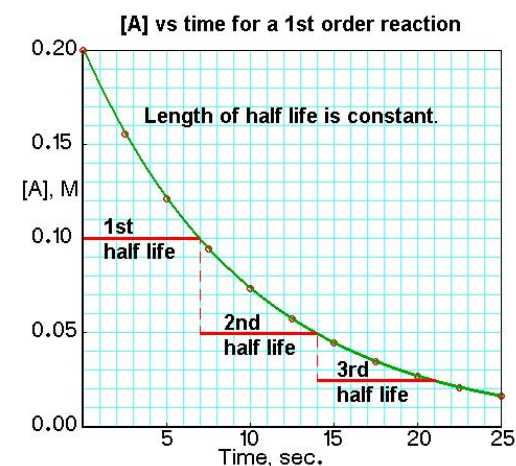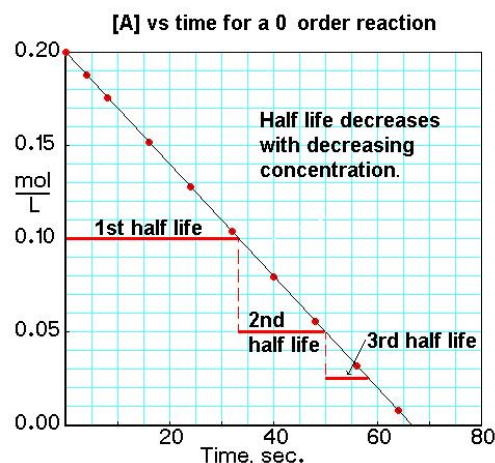
Half Life

Measuring half life allows you to calculate k!

▸ For a zero order reaction, the lower the initial concentration of the reactants, the shorter the half-life.

  ▸ $t_{1/2} = [A]_{init} / 2k$

  ▸ $k = [A]_{init} / (2\, t_{1/2})$

▸ For a first order reaction, the half-life is independent of the concentration.

  ▸ $t_{1/2} = \ln(2)/k = 0.693 / k$

  ▸ $k = 0.693 / t_{1/2}$

▸ For a second order reaction, the half-life is inversely proportional to the initial concentration, increasing the initial concentration shortens the half-life.

  ▸ $t_{1/2} = 1/(k[A]_{init})$

  ▸ $k = 1/(t_{1/2} * [A]_{init})$

[A] vs time for a 0 order reaction

Half life decreases with decreasing concentration.

1st half life

2nd half life   3rd half life

[A] vs time for a 1st order reaction

Length of half life is constant.

1st half life

2nd half life

3rd half life

[A] vs time for a 2nd order reaction

Length of half life increases with decreasing concentration.

1st half life

2nd half life

3rd half life

56
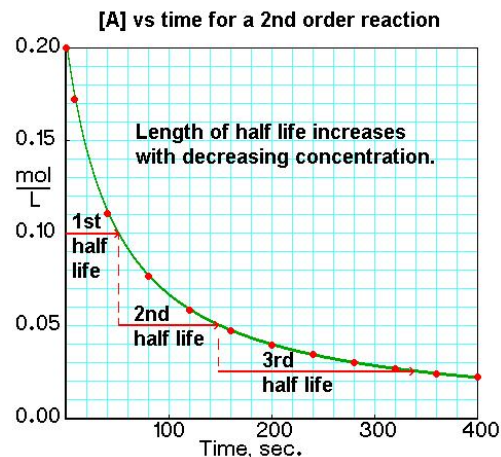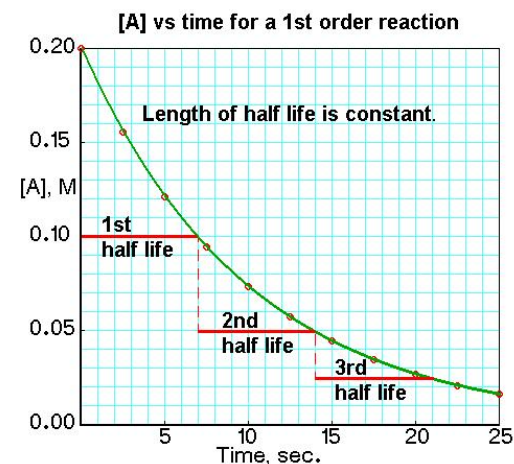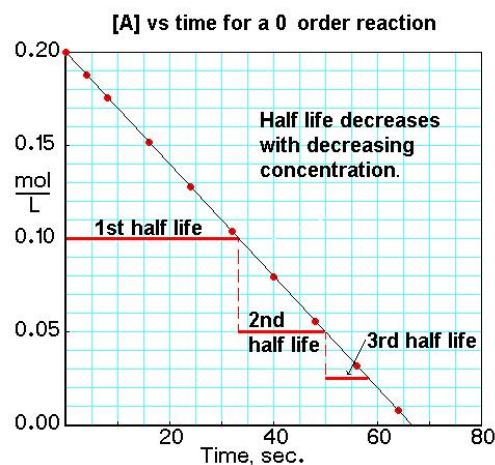
Try this...

▸ The first-order decay of radon has a half-life of 3.823 days. How many grams of radon decompose after 5.55 days if the sample initially weighs 100.0 grams?

A) 83.4 g

B) 16.6 g

C) 50.0 g

D) 36.6 g

E) 63.4 g

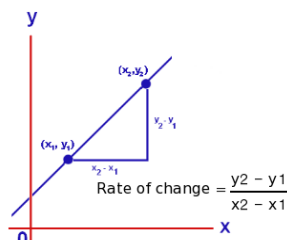|	Zeroth Order	First Order	Second Order
Integrated rate law	$[A] = [A]_0 - kt$	$[A] = [A]_0 e^{-kt}$ or $\ln[A] = \ln[A]_0 - kt$	$\dfrac{1}{[A]} = \dfrac{1}{[A]_0} + kt$
Half-life	$t_{1/2} = \dfrac{[A]_0}{2k}$	$t_{1/2} = \dfrac{0.693}{k}$	$t_{1/2} = \dfrac{1}{k[A]_0}$
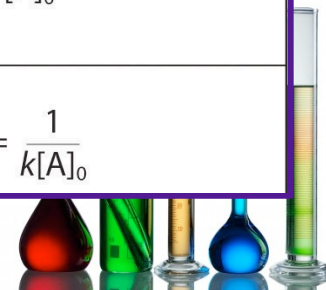
Rate

- Rate
  - Change (ΔX)
  - Rate (ΔX/Δt)

$$\Delta X = X_{final} - X_{initial}$$

- Reaction Rate
  - Definitions
  - Measurement
    - Continuous
    - Difference

$$Rate = \frac{\Delta[A]}{\Delta t} = k[A]$$

  - Avg vs Instantaneous
- Rate Acceleration
  - Nature of Reaction
  - Experimental Factors

- Rate Laws
  - Differences/Classifications
   - Rate Order
    - Integrated Rate Laws
    - Half Life
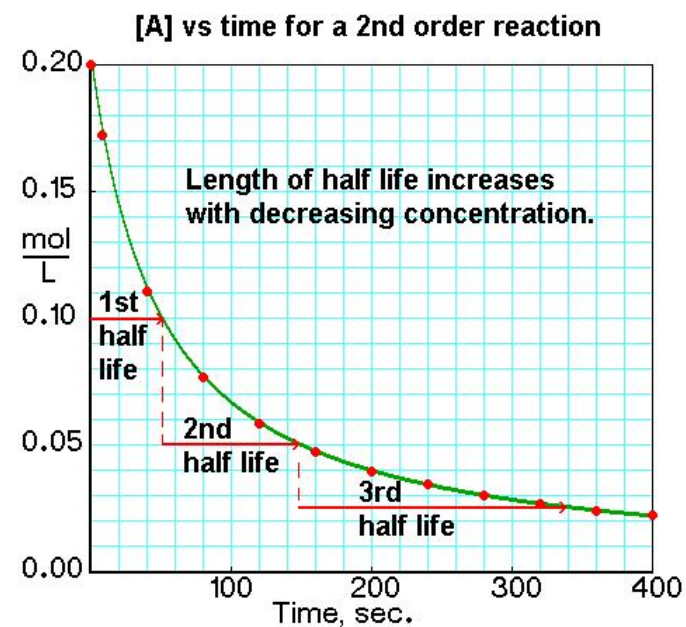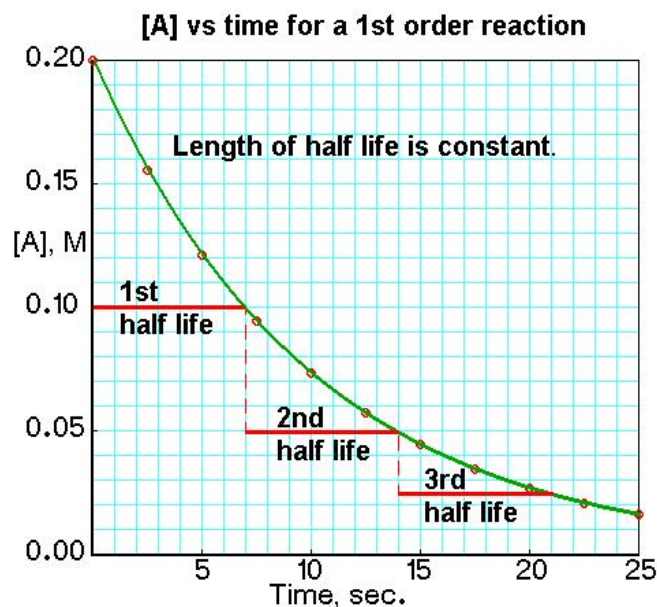   - Finding k
  - Overview of Laws
  - Finding Rate Laws
    - by Inspection
    - by Ratio

$$\text{Rate of change} = \frac{y2 - y1}{x2 - x1}$$
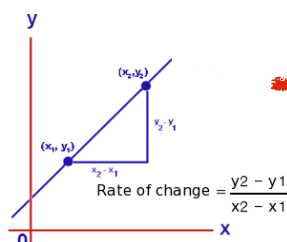
Zero Order Reactions

Zeroth Order

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

Concentration vs Time graph

$$[A] = [A]_0 - kt$$

Concentration vs Time graph, Slope $= -k$
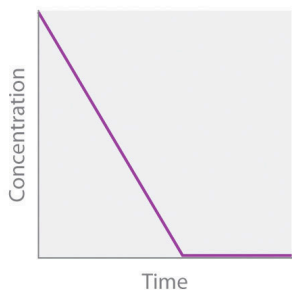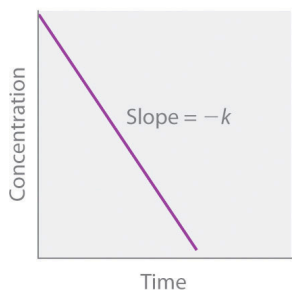
[A], M	Rate, M/s
1	1
2	1
3	1

▸ *Rate of reaction is constant.*

▸ Rate $= k[A]_0 = k$
  ▸ Constant rate reactions
▸ $[A] = -kt + [A]_{initial}$
▸ Graph of [A] versus time – straight line with slope $= -k$ and y-intercept $= [A]_{initial}$
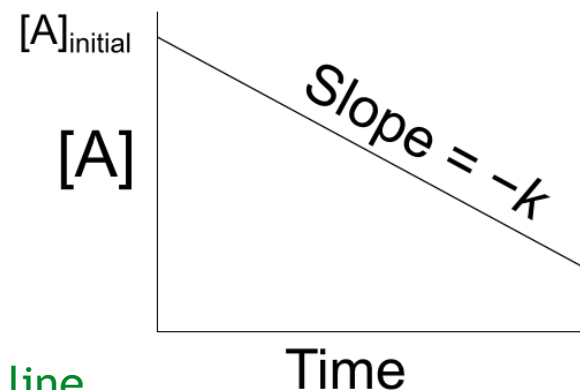
▸ Half life equations
  ▸ $t_{1/2} = [A]_{init}/2k$
  ▸ $k = [A]_{init}/(\,2\,t_{1/2}\,)$

▸ Units for zero order reactions
  ▸ When Rate = M/sec, k = M/sec

$[A]_{initial}$

$[A]$ Slope $= -k$

Time

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First Order Reactions

First Order

$$Rate = -\frac{\Delta[A]}{\Delta t} = k[A]$$

Concentration vs Time (decaying curve)

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

ln concentration vs Time (straight line, Slope = $-k$)
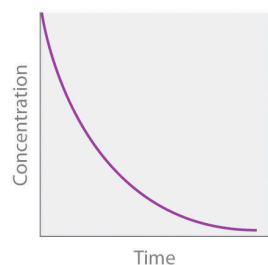
[A], M	Rate, M/s
1	1
2	2
3	3

‣ Rate = k[A]^1 = k[A]

‣ ln[A] = −kt + ln[A]$_{initial}$

‣ Graph ln[A] versus time – straight line with slope = −k and y-intercept = ln[A]$_{initial}$

  ‣ Used to determine the rate constant

‣ Half life is

  ‣ t$_{½}$ = ln(2)/k = 0.693 / k

  ‣ The half-life of a first order reaction is constant.

  ‣ $k = 0.693 / t_{½}$
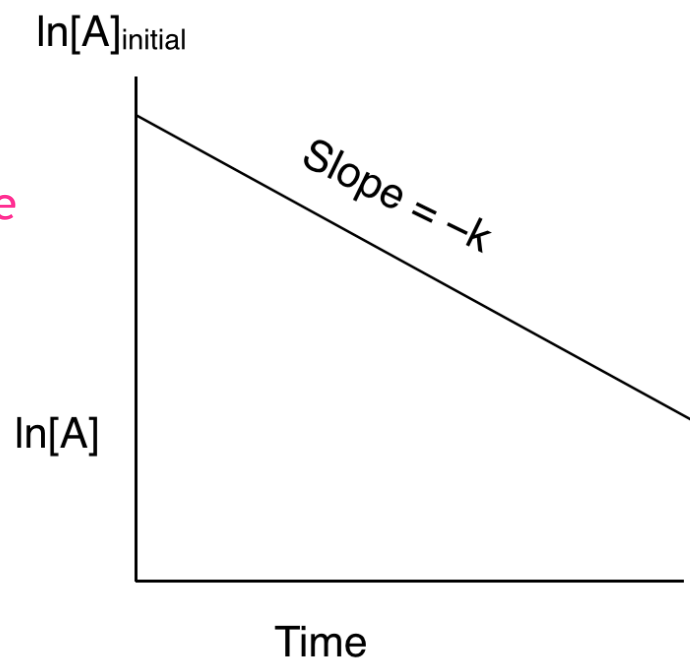
‣ Units for first order reactions

  ‣ When Rate = M/sec, k = s^{-1}

ln[A]$_{initial}$

Slope = −k

ln[A]

Time

Second Order Reactions

Second Order

$$\text{Rate} = -\frac{\Delta[A]}{\Delta t} = k[A]^2$$

Concentration vs Time

$$\frac{1}{[A]} = \frac{1}{[A]_0} + kt$$

1/concentration vs Time, Slope = k
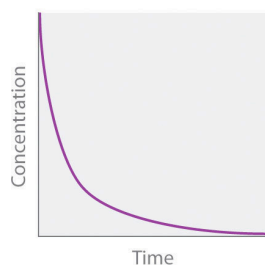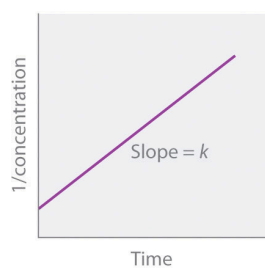
[A], M	Rate, M/s
1	1
2	4
3	9

▸ Rate = k[A]^2

▸ 1/[A] = kt + 1/[A]$_{initial}$

▸ Graph 1/[A] versus time – straight line with slope = k and y-intercept = 1/[A]$_{initial}$
  ▸ Used to determine the rate constant

▸ Half life is
  ▸ $t_{1/2}$ = 1/(k[A]$_{init}$)
  ▸ k = 1/($t_{1/2}$ * [A]$_{init}$)

▸ Units for second order reactions
  ▸ When Rate = M/sec, k = $M^{-1} \cdot s^{-1}$
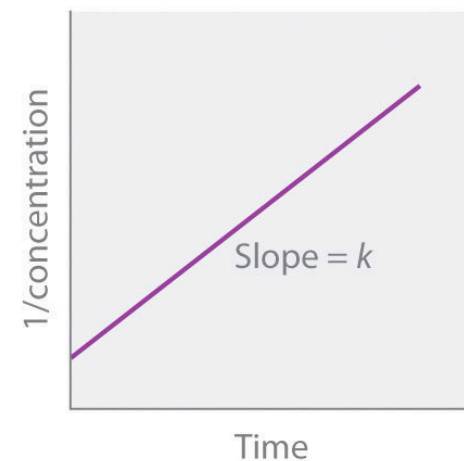
1/concentration vs Time, Slope = k

Rate

- Rate
  - Change (ΔX)
  - Rate (ΔX/Δt)

$$\Delta X = X_{final} - X_{initial}$$

- Reaction Rate
  - Definitions
  - Measurement
    - Continuous
    - Difference
  - Avg vs Instantaneous
- Rate Acceleration
  - Nature of Reaction
  - Experimental Factors

$$Rate = \frac{\Delta[A]}{\Delta t} = k[A]$$

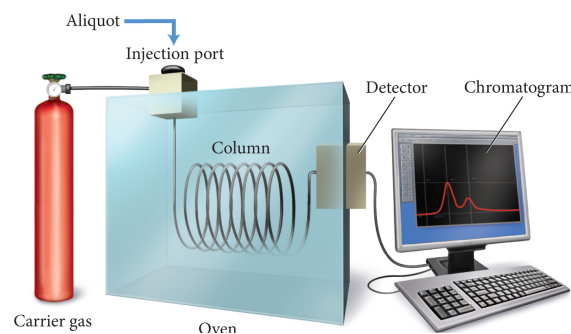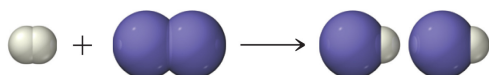Rate of change = $\frac{y2 - y1}{x2 - x1}$

- Rate Laws
  - Differences/Classifications
    - Rate Order
    - Integrated Rate Laws
    - Half Life
      - Finding k
  - Overview of Laws
  - Finding Rate Laws
    - by Inspection
    - by Ratio

$$\text{Rate} = k[A]^n$$

A + 2B ➔ C + 2D
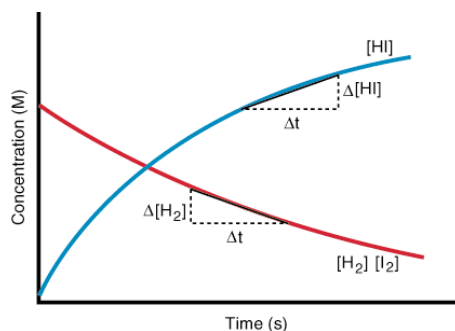
What's the rate law
for this reaction?
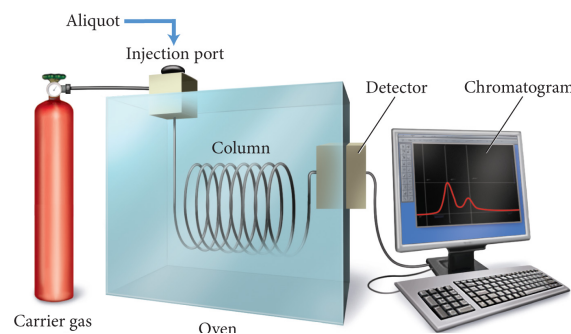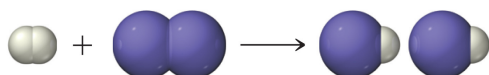
Finding Rate Laws

$$\text{Rate} = k[A]^n$$

A + 2B ➜ C + 2D

What's the rate law for this reaction?

a) rate = $k\,[A][C]$
b) rate = $k\,[A]^2[B]$
c) rate = $k\,[A][B]^2$
d) rate = $k\,[A]$
e) could be any of the above

Finding Rate Laws

You need experimental data!

$$\text{Rate} = k[A]^n$$

$$A + 2B \rightarrow C + 2D$$

Exp.	Initial A (mol/L)	Initial B (mol/L)	Init. Rate of Formation of C (M min^{-1})
1	0.10	0.10	3.0×10^{-4}
2	0.30	0.30	9.0×10^{-4}
3	0.10	0.30	3.0×10^{-4}
4	0.20	0.40	6.0×10^{-4}

What's the rate law for this reaction?

a) rate = k [A][C]
b) rate = k [A]^2[B]
c) rate = k [A][B]^2
d) rate = k [A]
e) could be any of the above

Finding Rate Law
(initial concentrations)

Finding Reaction Orders by Experiment - I

Given the reaction: $O_{2(g)} + 2\ NO_{(g)} \longrightarrow 2\ NO_{2(g)}$

The rate law for this reaction in general terms is: $Rate = k\ [O_2]^m[NO]^n$

To find the reaction orders, we run a series of experiments, each with a different set of reactant concentrations, and determine the initial reaction rates.

Experiment	Initial Reactant Concentrations (mol/l)		Initial Rate (mol/L·s)
	O_2	NO	
1	1.10×10^{-2}	1.30×10^{-2}	3.21×10^{-3}
2	2.20×10^{-2}	1.30×10^{-2}	6.40×10^{-3}
3	1.10×10^{-2}	2.60×10^{-2}	12.8×10^{-3}
4	3.30×10^{-2}	1.30×10^{-2}	9.60×10^{-3}
5	1.10×10^{-2}	3.90×10^{-2}	28.8×10^{-3}

By using the data from experiments 1&2 we can calculate the values of the coefficients m & n for the rate equation:

Finding Rate Law
(initial concentrations)

Determining Reaction Orders by Experiment - II

The oxygen concentration changes for these two experiments but NO is the same and the constant k is the same, they will cancel out.

$$\frac{\text{Rate 2}}{\text{Rate 1}} = \frac{[O_2]_2^m}{[O_2]_1^m} = \left(\frac{[O_2]_2}{[O_2]_1}\right)^m$$

Using the concentrations from the preceding table and the rate:

$$\frac{6.40 \times 10^{-3} \text{ mol/L s}}{3.21 \times 10^{-3} \text{ mol/L s}} = \left(\frac{2.20 \times 10^{-2} \text{ mol/L}}{1.10 \times 10^{-2} \text{ mol/L}}\right)^m$$

$$1.99 = (2.00)^m \qquad m = 1$$

The reaction is first order in O_2, when O_2 doubles, the rate doubles.

To find the order of NO we will compare experiments 3 & 1 in which oxygen is constant, but NO doubles, and the rate between the two experiments goes up substantially.

Finding Rate Law
(initial concentrations)

$$\frac{\text{Rate 3}}{\text{Rate 1}} = \frac{k[O_2]_3{}^m[NO]_3{}^n}{k[O_2]_1{}^m[NO]_1{}^n}$$ As before, k and for this one, the concentration of oxygen is not varying, and will cancel out, leaving only the rate and the concentration of No to consider.

$$\frac{\text{Rate 3}}{\text{Rate 1}} = \frac{[NO]_3}{[NO]_1}$$ Substituting in the values from the table, we get the following:

$$\frac{12.8 \times 10^{-3} \text{ mol/L s}}{3.21 \times 10^{-3} \text{ mol/L s}} = \frac{2.60 \times 10^{-2} \text{ mol/L}}{1.30 \times 10^{-2} \text{ mol/L}}$$

$$3.99 = (2.00)^n \qquad n = 2$$

The reaction is second order in NO: when [NO] doubles, the rate quadruples, Thus the rate law is:

$$\textbf{Rate} = \textbf{\textit{k}} \textbf{[O}_2\textbf{][NO]}^2$$

Use Inspection where Possible

For the reaction A + B ➜ products, the following initial rates were found.

What is the rate law for this reaction?

Trial 1: [A] = 0.50 M; [B] = 1.50 M; Initial rate = 4.2 x 10^{-3} M/min

Trial 2: [A] = 1.50 M; [B] = 1.50 M; Initial rate = 1.3 x 10^{-2} M/min

Trial 3: [A] = 3.00 M; [B] = 3.00 M; Initial rate = 5.2 x 10^{-2} M/min

Solve for k

The following data was obtained for this chemical reaction: A + B → products.

(a) Determine the rate law for this reaction.

(b) Find the rate constant.

Exp.	Initial A (mmol/L)	Initial B (mmol/L)	Init. Rate of Formation of products (mM min^{-1})
1	4.0	6.0	1.60
2	2.0	6.0	0.80
3	4.0	3.0	0.40

Solve for k and then rate at a given time

The following data was obtained for the chemical reaction: A + B → products.
(a) Determine the rate law for this reaction and find the rate constant.
(b) What is the initial rate of reaction when $[A]_o$ = 0.12 M and $[B]_o$ = 0.015?

Exp.	Initial A (mol/L)	Initial B (mol/L)	Init. Rate of Formation of products (M s^{-1})
1	0.040	0.040	9.6×10^{-6}
2	0.080	0.040	1.92×10^{-5}
3	0.080	0.020	9.6×10^{-6}

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Solve for k and then rate at a given time

When a ClO_2 solution and a solution containing hydroxide ions (OH^{1-}) are mixed, the following reaction occurs. the following rate data were obtained.

(a) Write the rate equation for the chemical reaction & calculate the rate constant, k.

(b) Calculate the reaction rate for the reaction when $[ClO2]_o = 8.25 \times 10^{-3}$ M and $[OH^{-1}]_o = 5.35 \times 10^{-2}$ M.

$$2ClO_{2(aq)} + 2OH^-_{(aq)} \rightarrow ClO3^-_{(aq)} + ClO2^-_{(aq)} + H2O_{(l)}$$

Determination #1: $[ClO2]o = 1.25 \times 10^{-2}$ M; $[OH^-]o = 1.30 \times 10^{-3}$ M

Initial rate for formation of $ClO3^- = 2.33 \times 10^{-4}$ M s^{-1}

Determination #2: $[ClO2]o = 2.50 \times 10^{-2}$ M; $[OH^-]o = 1.30 \times 10^{-3}$ M

Initial rate for formation of $ClO3^- = 9.34 \times 10^{-4}$ M s^{-1}

Determination #3: $[ClO2]o = 2.50 \times 10^{-2}$ M; $[OH^-]o = 2.60 \times 10^{-3}$ M

Initial rate for formation of $ClO3^- = 1.87 \times 10^{-3}$ M s^{-1}

Find the Rate Law

Determine the proper form of the rate law for:

$CH_3CHO(g) \rightarrow CH_4(g) + CO(g)$

Exp.	[CH₃CHO]	[CO]	Rate (M s⁻¹)
1	0.30	0.20	0.60
2	0.10	0.30	0.067
3	0.10	0.20	0.067
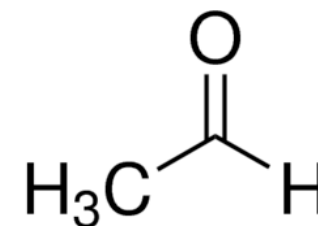
Solving for Rate Law by Algebra

The following data about the reaction shown were obtained from three experiments.
Calculate the rate expression in terms of [A] for experiment 1.

$$2A + B \rightarrow C + D$$

Exp.	[A]	[B]	Initial rate of formation of C
1	0.6	0.15	6.3×10^{-3}
2	0.2	0.6	2.8×10^{-3}
3	0.2	0.15	7.0×10^{-4}

Solving for Rate Law by Algebra

Determine the proper form of the rate law for the reaction shown.

$$CH_3CHO(g) \rightarrow CH_4(g) + CO(g)$$

Exp.	$[CH_3CHO]$	$[CO]$	Rate (M s^{-1})
1	0.30	0.20	0.60
2	0.10	0.30	0.067
3	0.10	0.20	0.067

Solving for Rate Law by Algebra

Determine the rate law, including the values of the orders and rate law constant, for the following reaction using the experimental data provided.

$$Q + X \rightarrow products$$

Trial	[Q]	[X]	Rate
1	0.12 M	0.10 M	1.5×10^{-3} M/min
2	0.24 M	0.10 M	3.0×10^{-3} M/min
3	0.12 M	0.20 M	1.2×10^{-2} M/min

Solving for Rate Law by Algebra

Determine the rate law, including the values of the orders and rate law constant, for the following reaction using the experimental data provided.

$$Q + X \rightarrow products$$

Trial	[Q]	[X]	Rate
1	0.12 M	0.10 M	1.5×10^{-3} M/min
2	0.24 M	0.10 M	3.0×10^{-3} M/min
3	0.12 M	0.20 M	1.2×10^{-2} M/min

For Q: Examine trials 1 and 2. [X] is held constant while [Q] is doubled (from 1 to 2). As a result, the rate doubles. We conclude that the reaction is first order in Q.

For X: Compare the ratios of trial 1 and 3:

$$rate_3 / rate_1 = k_3[Q_3]^x[X_3]^y / k_1[Q_1]^x[X_1]^y$$

k's will cancel and [Q] will cancel

$$rate_3 / rate_1 = [X_3]^x / [X_1]^x$$

$$0.012 / 0.0015 = (0.20)^x / (0.10)^x$$

$$8 = 0.20^x / 0.10^x$$

$$8 = 2^x$$

$$x = 3$$

Solving for Rate Law by Algebra

With the following data, use the method of initial rates to find the reaction orders with respect to NO and O_2.

Trial	$[NO]_o$	$[O_2]_o$	Initial reaction rate, M/s
1	0.020	0.010	0.028
2	0.020	0.020	0.057
3	0.040	0.020	0.227

Find the Rate Law

Determine the rate law and the value of k for the following reaction using the data provided.

$$S_2O_8^{2-}{}_{(aq)} + 3\,I^-{}_{(aq)} \rightarrow 2\,SO_4^{2-}{}_{(g)} + I_3^-{}_{(aq)}$$
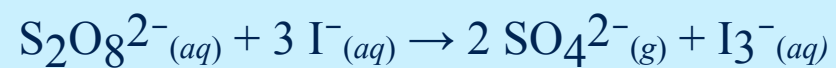
$[S_2O_8^{2-}]_i$	$[I^-]_i$ (M)	Initial Rate ($M^{-1}s^{-1}$)
0.30	0.42	4.54
0.44	0.42	6.65
0.44	0.21	3.33

Find the Rate Law

Determine the rate law and the value of k for the following reaction using the data provided.

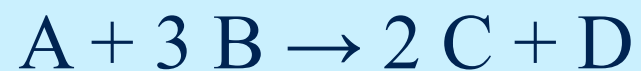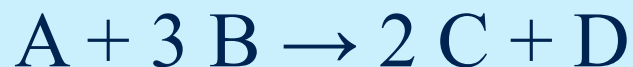$$A + 3\,B \longrightarrow 2\,C + D$$

[A]$_i$ (M)	[B]$_i$ (M)	Initial Rate (M^{-1}s^{-1})
0.30	0.20	3.06 x10^{-3}
0.54	0.20	9.91x10^{-3}
0.54	0.48	1.37 x10^{-1}

Determine the rate law and the value of *k* for the following reaction using the data provided.

$$A + 3\,B \rightarrow 2\,C + D$$

[A]i (M)	[B]i (M)	Initial Rate (M⁻¹s⁻¹)
0.30	0.20	3.06 x10⁻³
0.54	0.20	9.91x10⁻³
0.54	0.48	1.37 x10⁻¹

For [A] choose 1 & 2

$$\frac{RATE_1}{RATE_2} = \frac{k[A]^x[B]^y}{k[A]^x[B]^y} = \frac{[A_1]^x}{[A_2]^x}$$

$$\frac{3.06\times10^{-3}}{9.9\times10^{-3}} = \frac{[.30]^x}{[.54]^x}$$

$$.309 = \left(\frac{.30}{.54}\right)^x = (0.56)^x$$

$$\log(0.309) = \log(0.56^x)$$

$$\log(0.309) = x \cdot \log(0.56)$$

$$x = \frac{\log(0.309)}{\log(0.56)} = \frac{-0.510}{-0.25} = 2.0$$

For B choose 2 & 3

$$\frac{RATE_2}{RATE_3} = \frac{k[A]^x[B_2]^y}{k[A]^x[B_3]^y}$$

$$\frac{RATE_2}{RATE_3} = \frac{[B_2]^y}{[B_2]^y}$$

$$\frac{9.91\times10^{-3}}{1.37\times10^{-1}} = \frac{(0.20)^y}{(0.48)^y} = \left(\frac{0.20}{0.48}\right)^y$$

$$0.0723 = 0.42^y$$

$$\log(0.0723) = \log(0.42^y) = y \cdot \log(0.42)$$

$$y = \frac{\log(0.0723)}{\log(0.42)} = \frac{-1.14}{-0.38} = 3$$

$$RATE = k[A]^2[B]^3$$

$$k = \frac{RATE}{[A]^2[B]^3} = \frac{3.06\times10^{-3}}{[0.30]^2[0.20]^3}$$
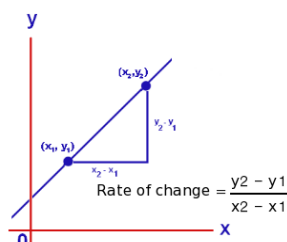
$$\boxed{k = 4.25}$$

Rate

- ▸ Rate
  - ▸ Change (ΔX)
  - ▸ Rate (ΔX/Δt)

$$\Delta X = X_{final} - X_{initial}$$

- ▸ Reaction Rate

$$Rate = \frac{\Delta[A]}{\Delta t} = k[A]$$

  - ▸ Definitions
  - ▸ Measurement
    - ▸ Continuous
    - ▸ Difference
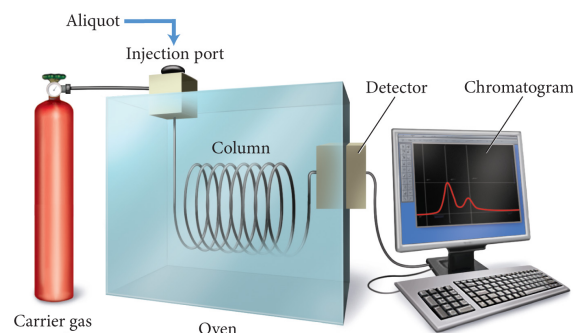 - ▸ Avg vs Instantaneous
- ▸ Rate Acceleration
  - ▸ Nature of Reaction
  - ▸ Experimental Factors

- ▸ Rate Laws
  - ▸ Differences/Classifications
    - ▸ Rate Order
    - ▸ Integrated Rate Laws
    - ▸ Half Life
      - ▸ Finding k
  - ▸ Overview of Laws
  - ▸ Finding Rate Laws
    - ▸ by Inspection
    - ▸ by Ratio

Rate of change $= \frac{y2 - y1}{x2 - x1}$

Questions?