Kinetics

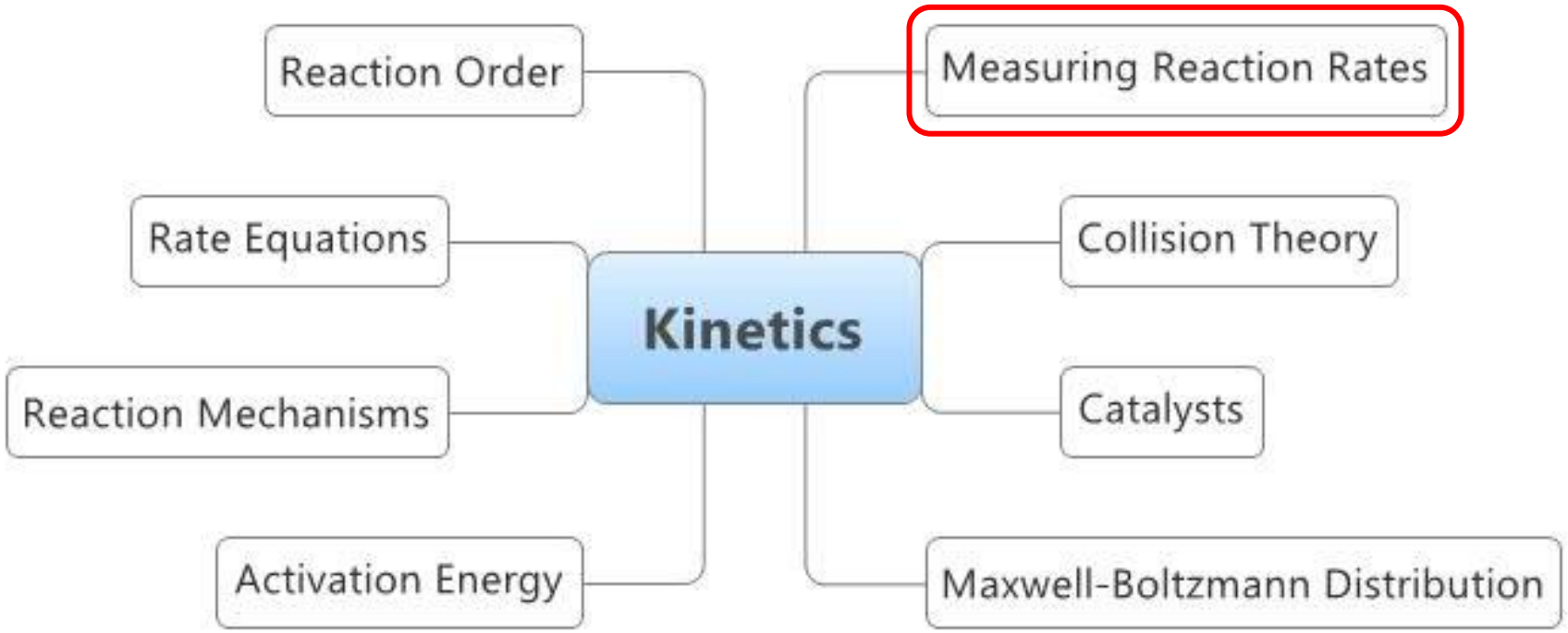
Ms. Peace

Lesson 1

6.1 Collision Theory and Rates of Reactions

Main Menu

We Are Here



Main

The Rate of Reactions

- In simple terms, the rate of a reaction can be thought of as its speed

- Some reactions are very fast

- Some reactions are very slow

Discuss:

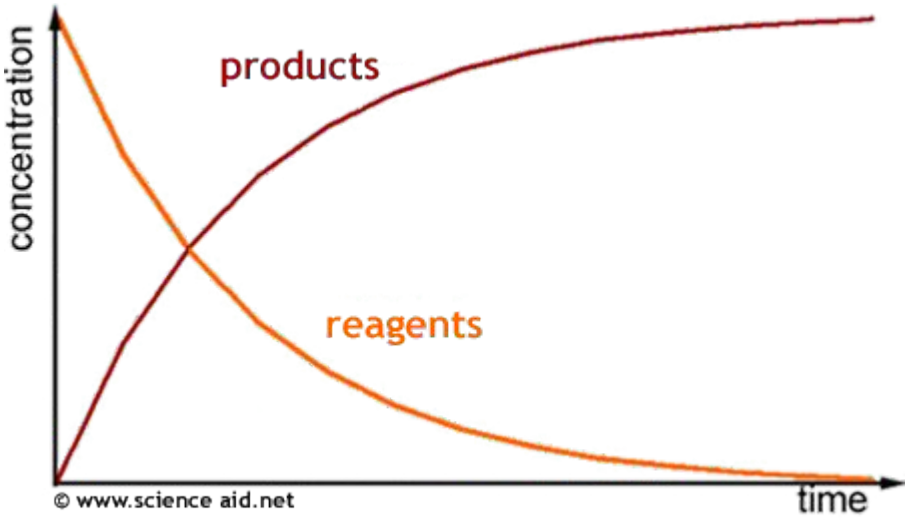
- Think of examples of 'fast' and 'slow' reactions
- Why is 'speed' not a good word to use in this context?

Defining the Rate of Reaction

- The rate of reaction is:

$$Rate = \frac{-\Delta[R]}{\Delta t} = \frac{\Delta[P]}{\Delta t}$$

- Where:
  - Δ[R] is change in concentration of reactants (final-initial)
  - Δ[P] is change in concentration of products (final-initial)
  - Δt is change in time (final-initial)



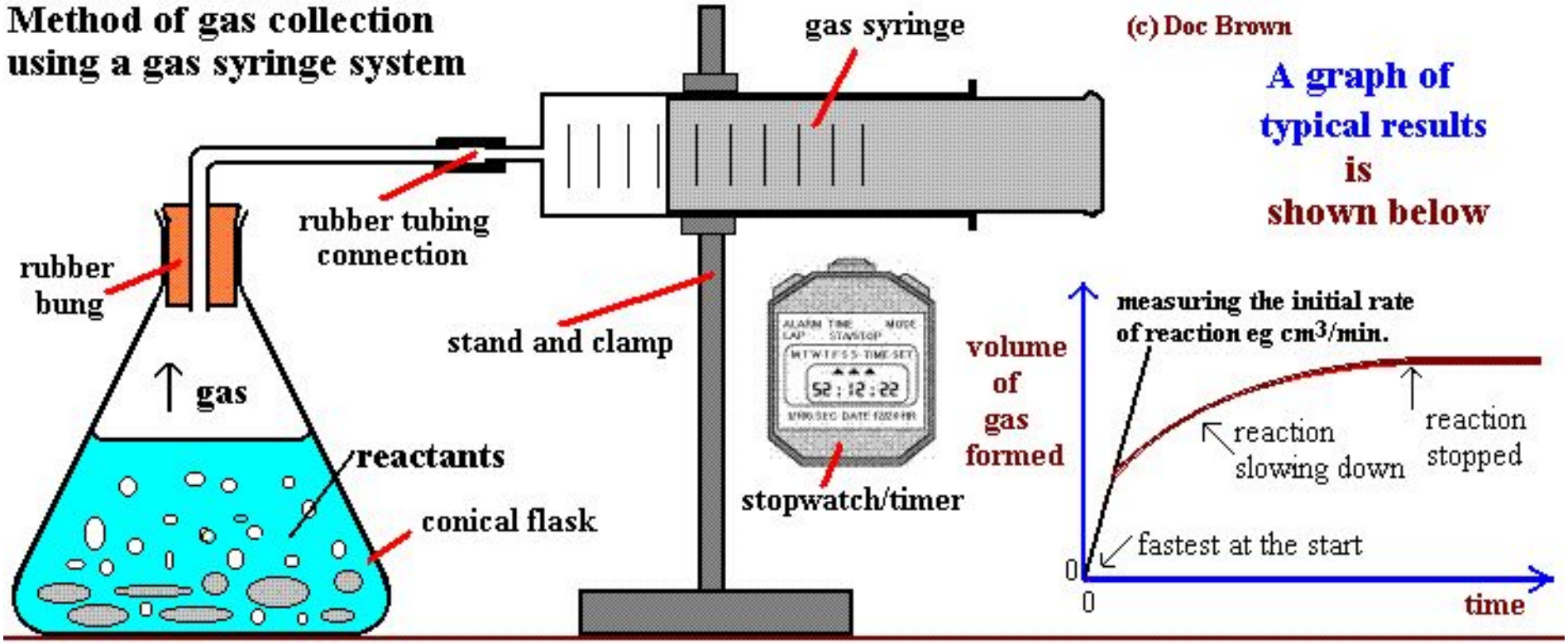
Main

Measuring Reaction Rates

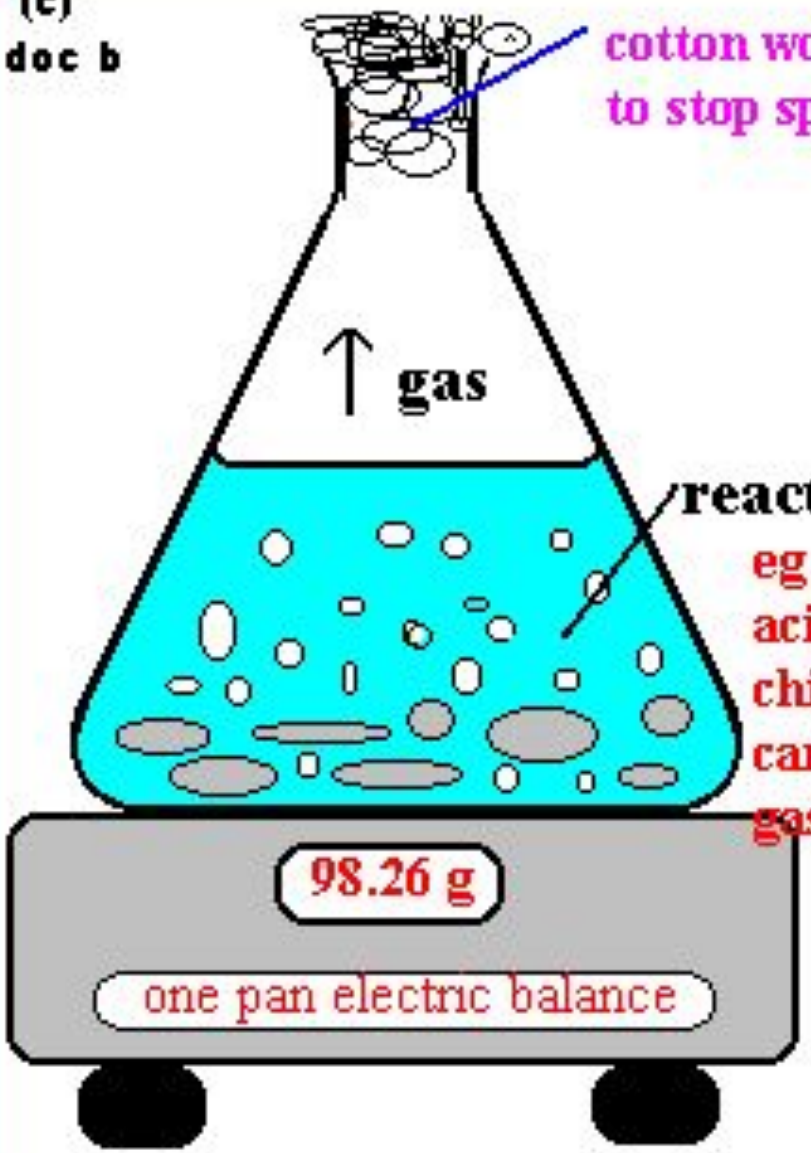
Technique	Apparatus/Notes
Collecting gas	Using a gas syringe or inverted measuring cylinder filled with water
Mass loss	Reaction conducted on a balance…if it produces a gas the mass will decrease
Colour change	Measured using a colorimeter
Obscured cross	Useful if reaction produces a precipitate (for example sodium thiosulphate and acid)
Iodine clock	Produces a sudden colour change from colourless to black….monitors any reaction producing iodine
pH	Monitored using a pH probe
Conductivity	Decrease in ion concentration..measured using a conductivity probe and meter
Temperature change	Not ideal as it is difficult to prevent heat loss

- We then need to work out how the concentration has changed, using our knowledge of stoichiometry

Main

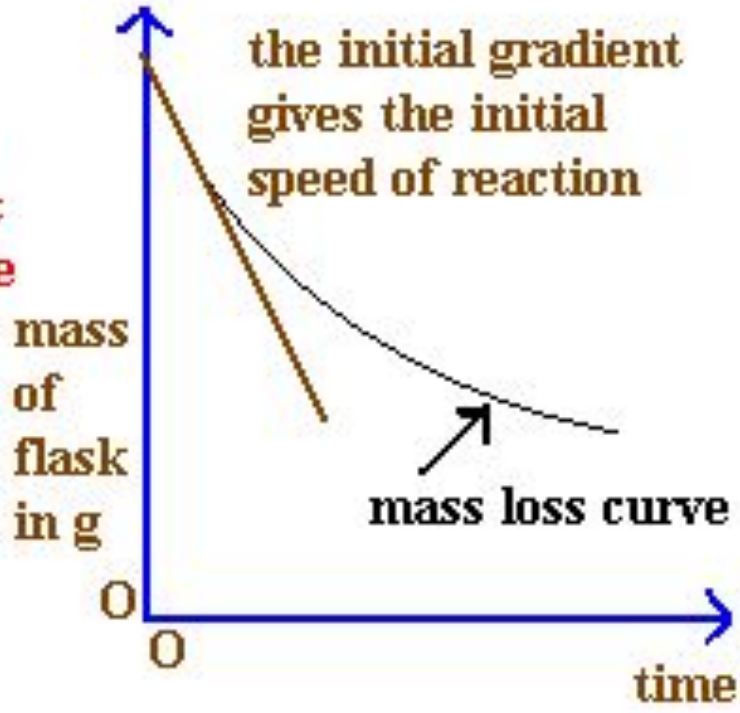

Method of gas collection
using a gas syringe system
gas syringe
(c) Doc Brown
A graph of
typical results
is
shown below
rubber tubing
connection
rubber
bung
stand and clamp
gas
reactants
conical flask
stopwatch/timer
volume
of
gas
formed
measuring the initial rate
of reaction eg cm3/min.
reaction
slowing down
reaction
stopped
fastest at the start
0
0
time

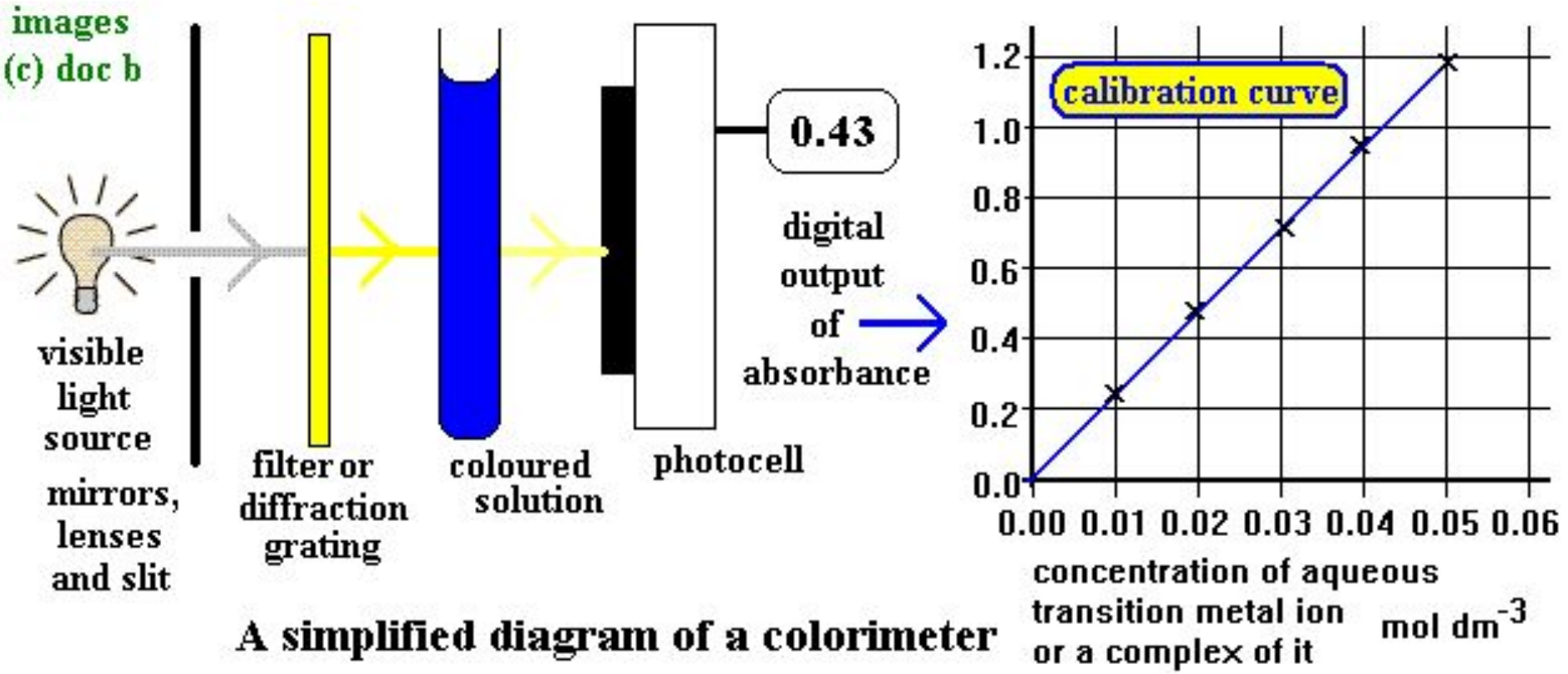
(c)
doc b



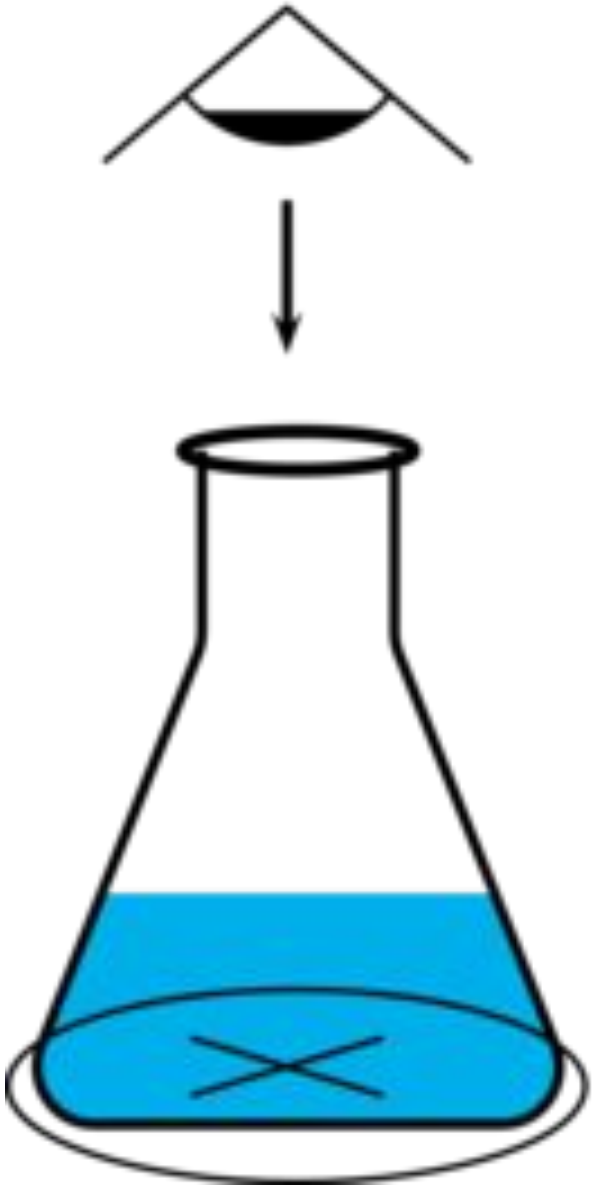
MASS LOSS METHOD

typical results are shown below





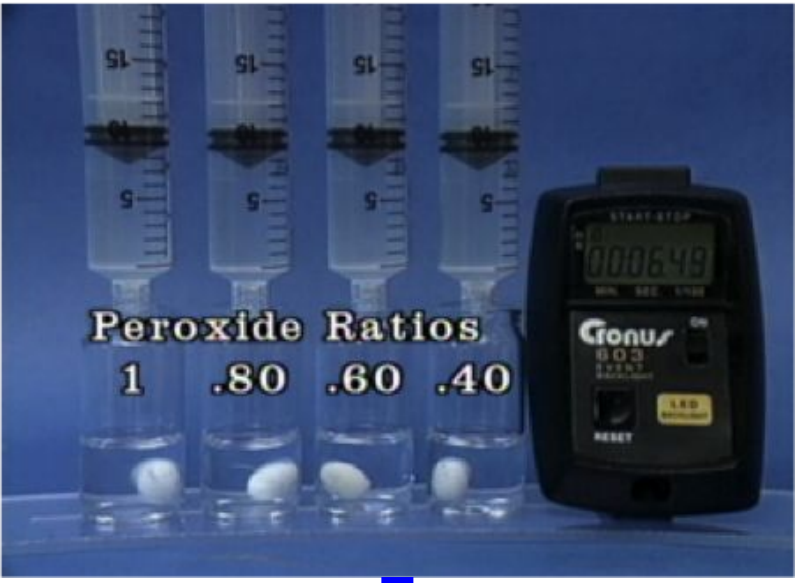
A simplified diagram of a colorimeter

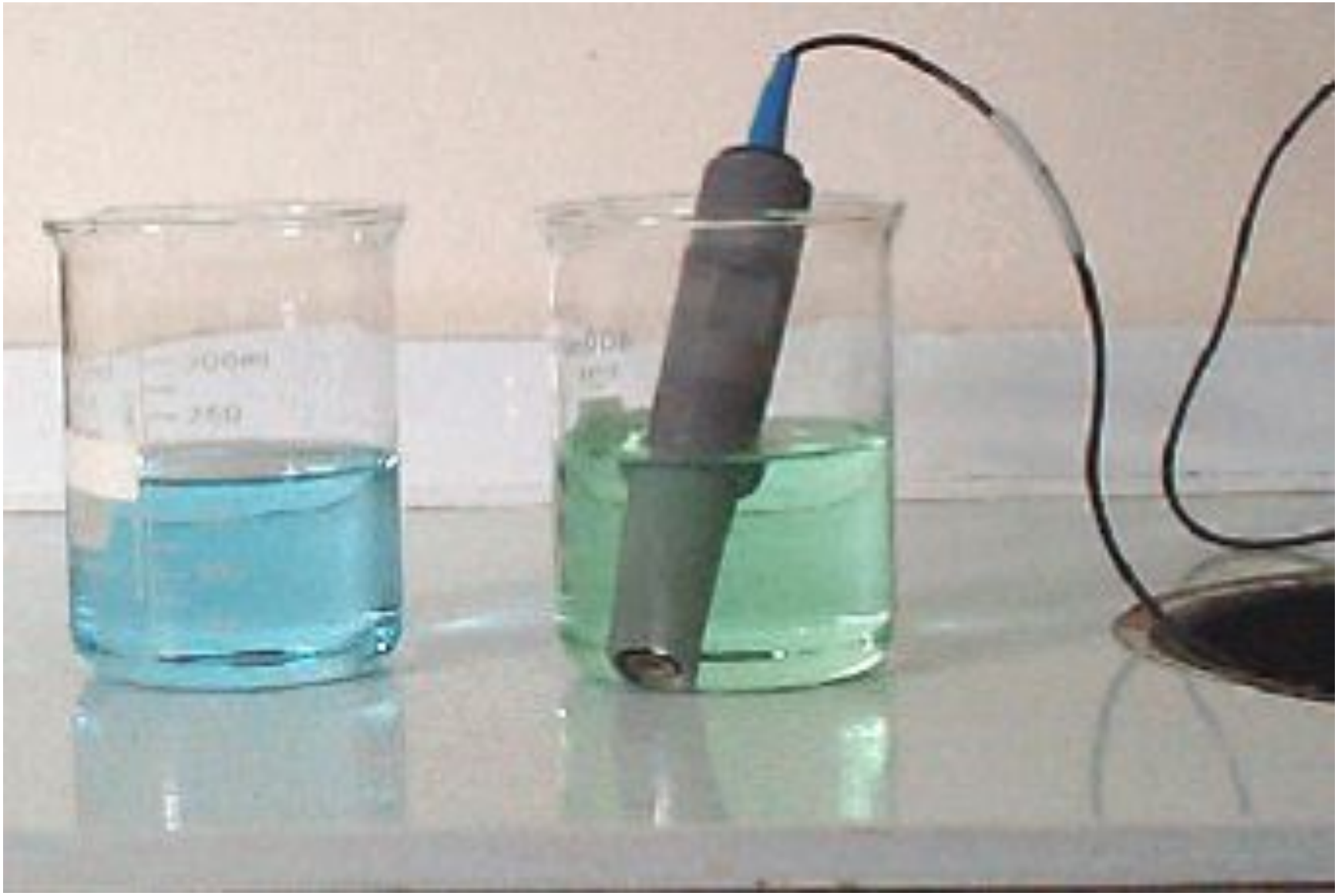


view from the top

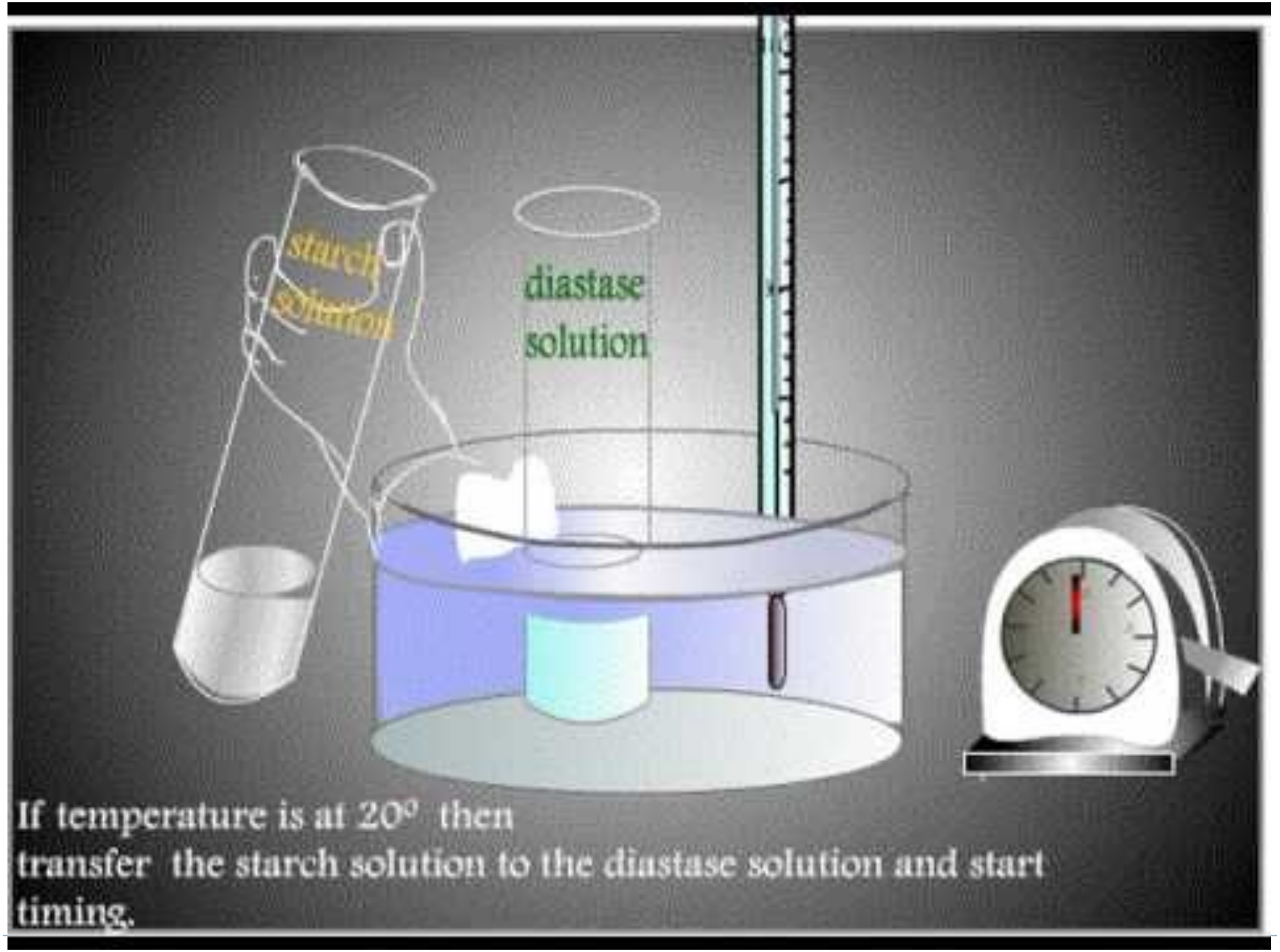
without precipitate

with precipitate


Peroxide Ratios
1 .80 .60 .40



Conductivity
Probe
Vernier CONDUCTIVITY


starch solution
diastase solution
If temperature is at 20° then
transfer the starch solution to the diastase solution and start timing.

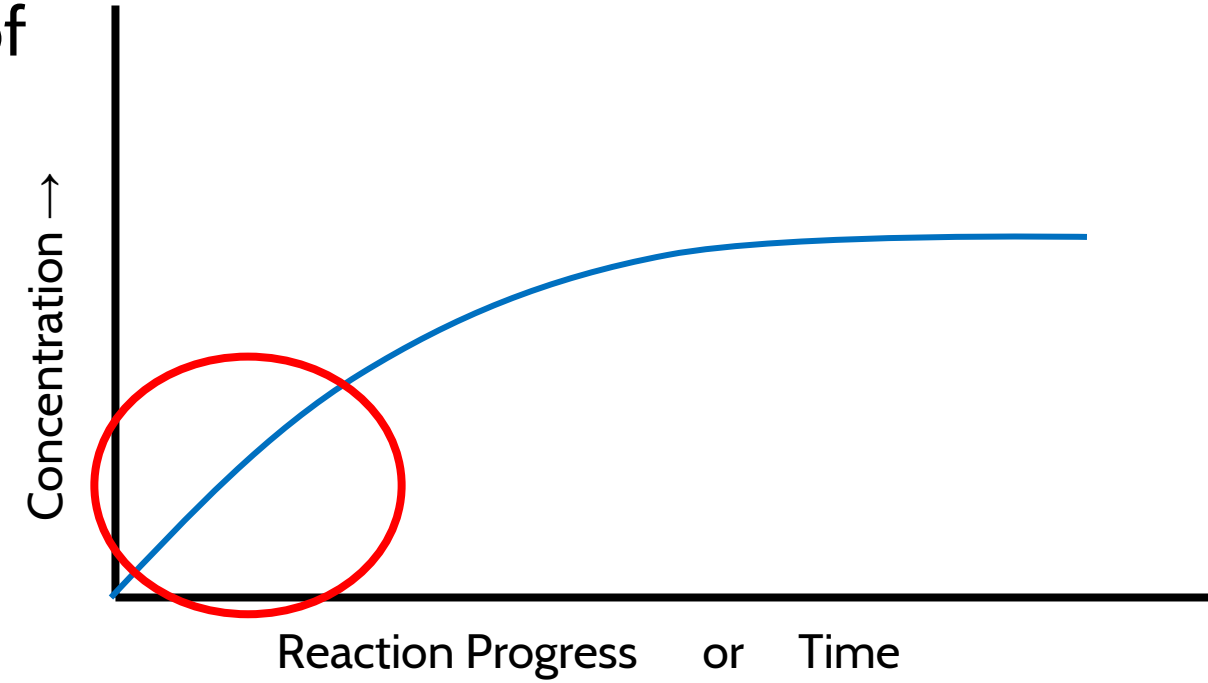
Analyzing Reaction Rate Graphs

Initial rates are fastest

-Graph steepest

-Lower concentration

-Lower frequency of collision



Main

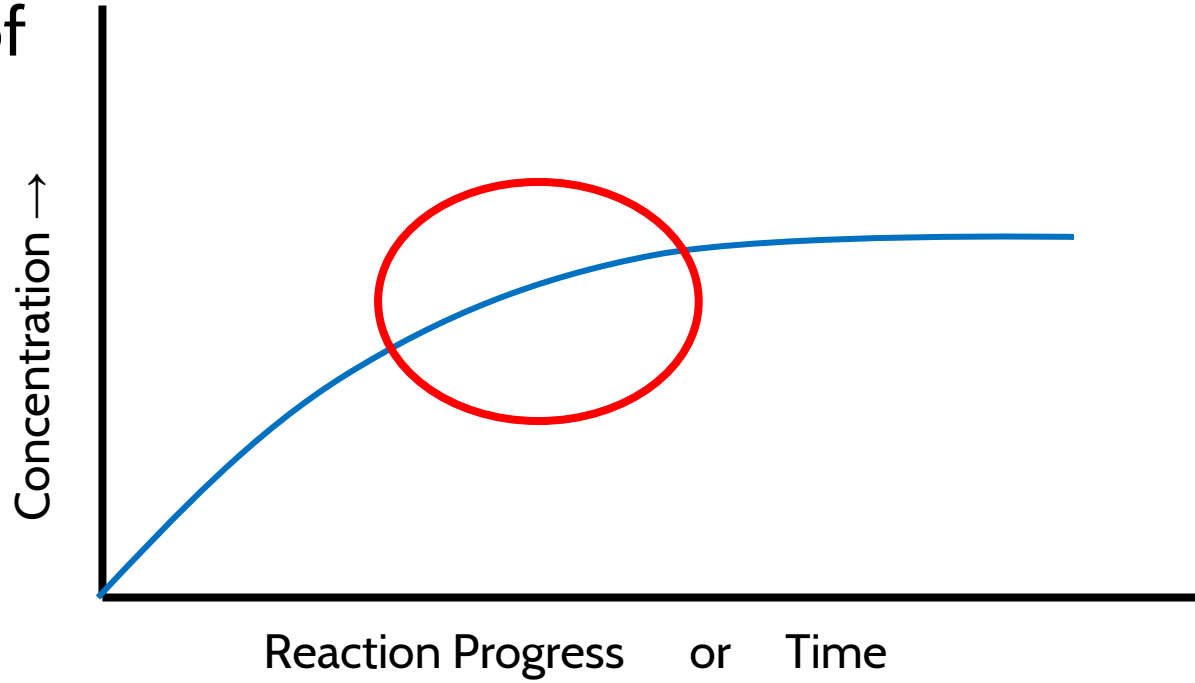
Analyzing Reaction Rate Graphs

Graph becomes less steep

-Rate decreases

-Higher concentration

-Higher frequency of collision

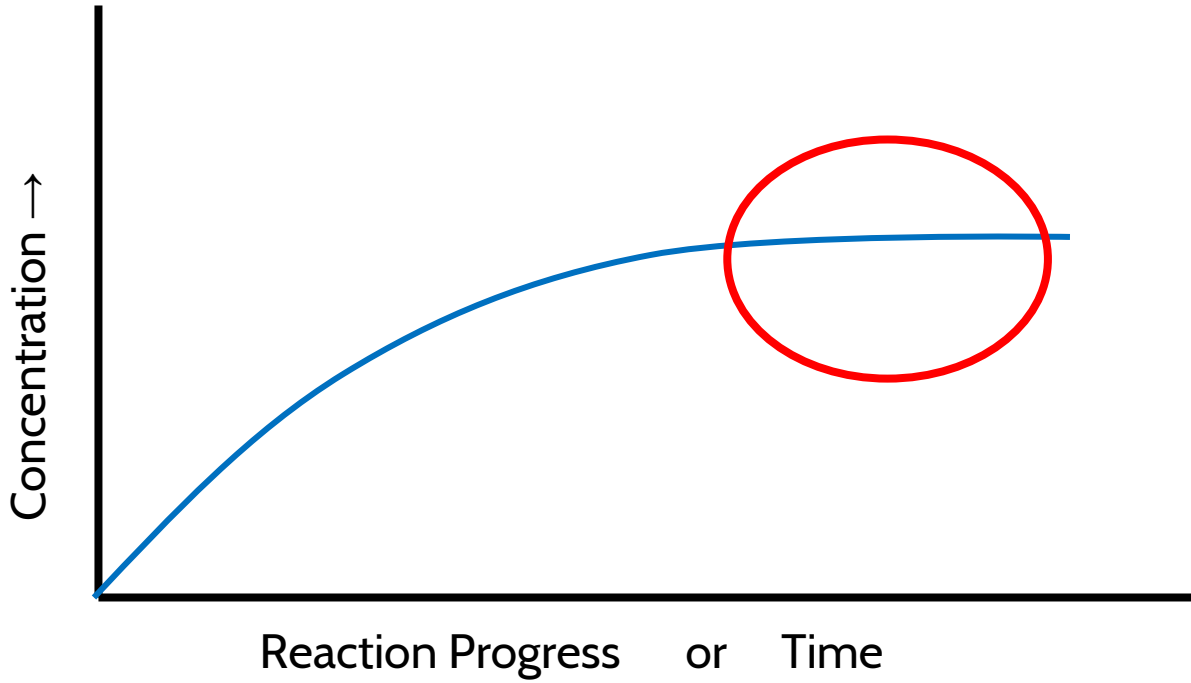


Main

Analyzing Reaction Rate Graphs

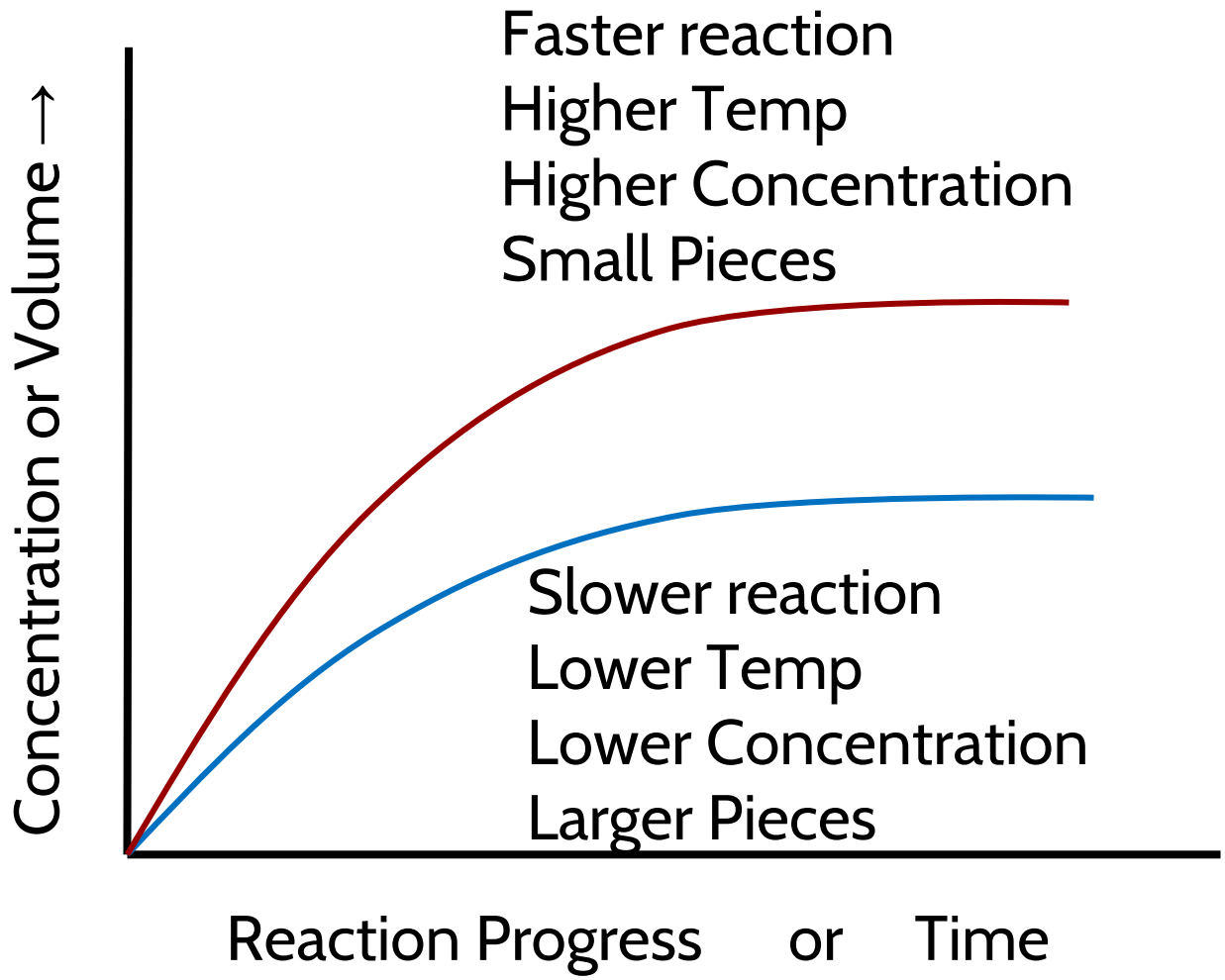
Graph levels off

Reactants are all used up and no more products are being formed



Main

Analyzing Reaction Rate Graphs



Main

Analyzing Reaction Rate Graphs

$CaCO_3(s) + 2HCl(aq) \longrightarrow CO_2(g) + H_2O(l) + CaCl_2(aq)$

Same initial concentration

$100cm^3/1000=0.1dm^3$

$(2.0mol\ dm^{-3})(0.1dm^3)$

$=0.20mol\ HCl$

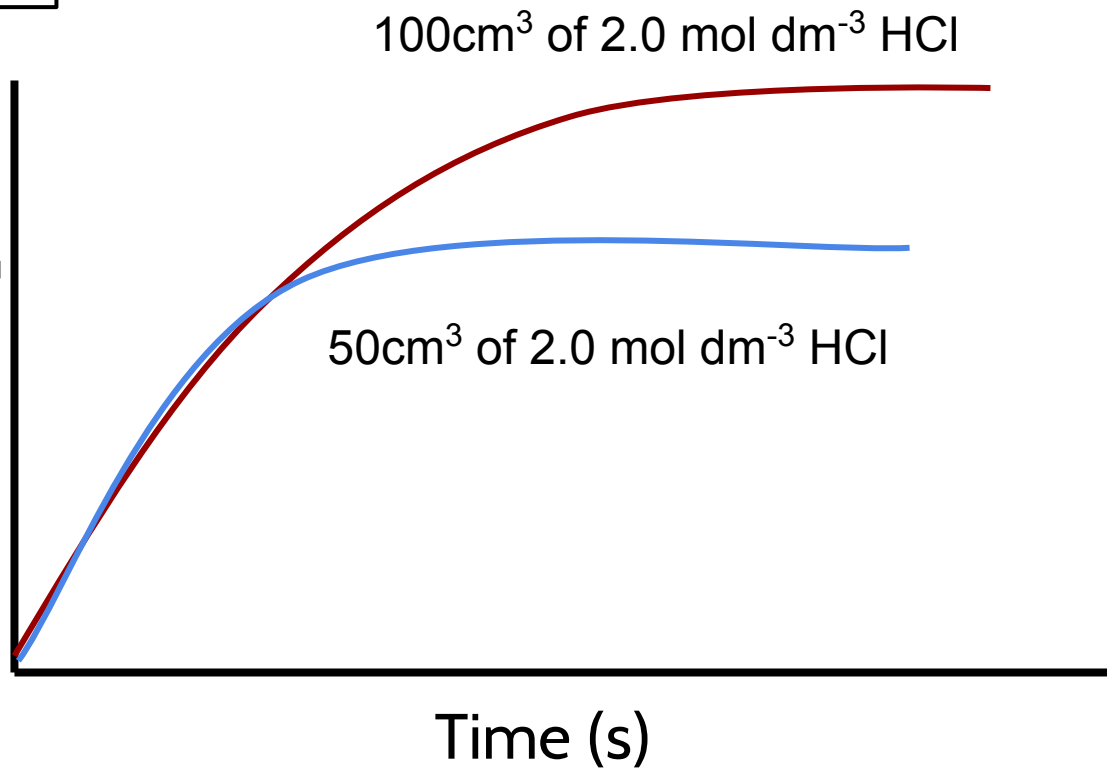
$=0.1mol\ CO_2$

$50cm^3/1000=0.05dm^3$

$(2.0mol\ dm^{-3})(0.05dm^3)$

$=0.10mol\ HCl$

$=0.05mol\ CO_2$

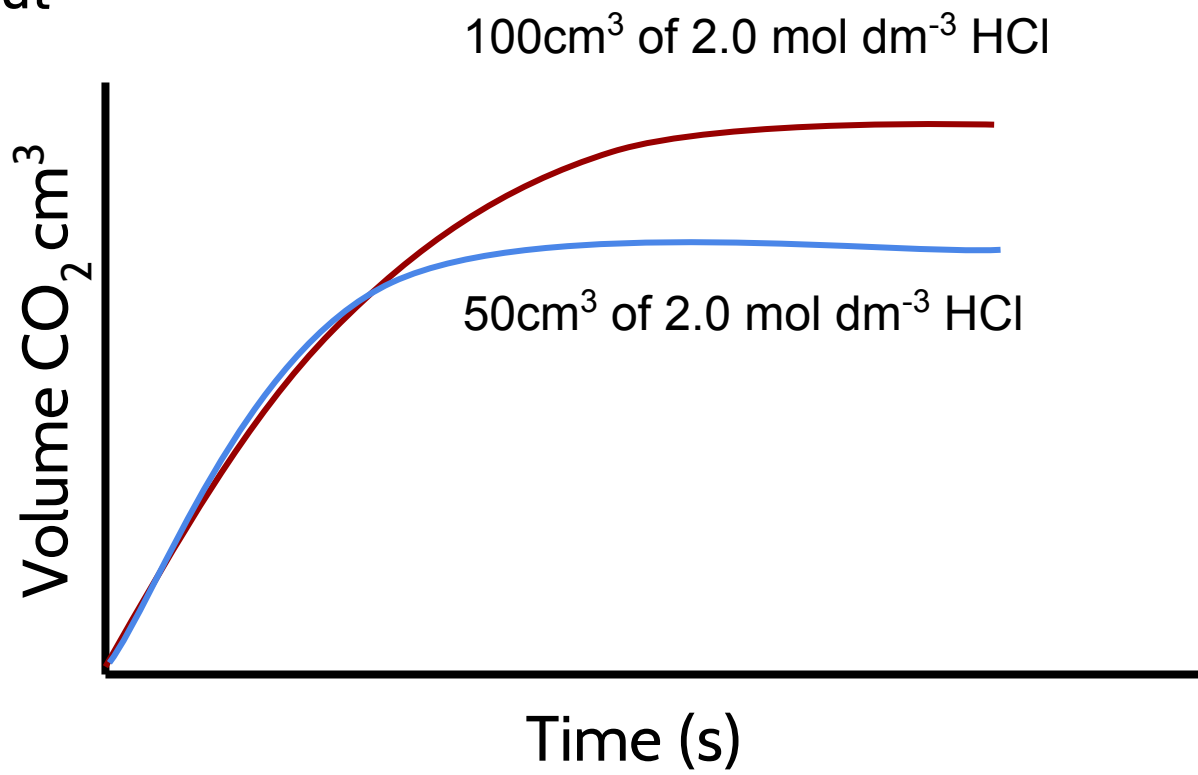


Main

Analyzing Reaction Rate Graphs

$$CaCO_3(s) + 2HCl(aq) \longrightarrow CO_2(g) + H_2O(l) + CaCl_2(aq)$$

Initial rate is the same but half as much gas is produced because concentration is the same



Main

Analyzing Reaction Rate Graphs

$CaCO_3(s) + 2HCl(aq) \longrightarrow CO_2(g) + H_2O(l) + CaCl_2(aq)$

Same initial volume

$100cm^3/1000=0.1dm^3$

$(2.0mol\ dm^{-3})(0.1dm^3)$

$=0.20mol\ HCl$

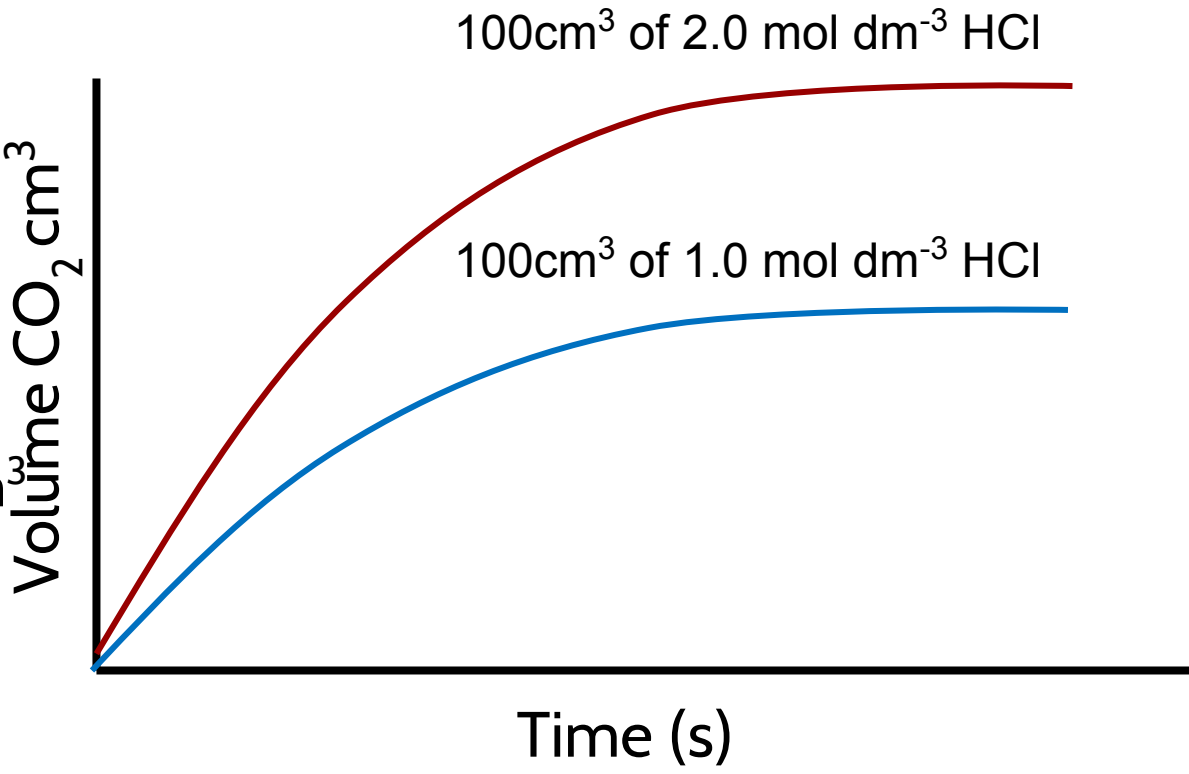
$=0.10mol\ CO_2$

$100cm^3/1000=0.05dm^3$

$(1.0mol\ dm^{-3})(0.1dm^3)$

$=0.10mol\ HCl$

$=0.05mol\ CO_2$

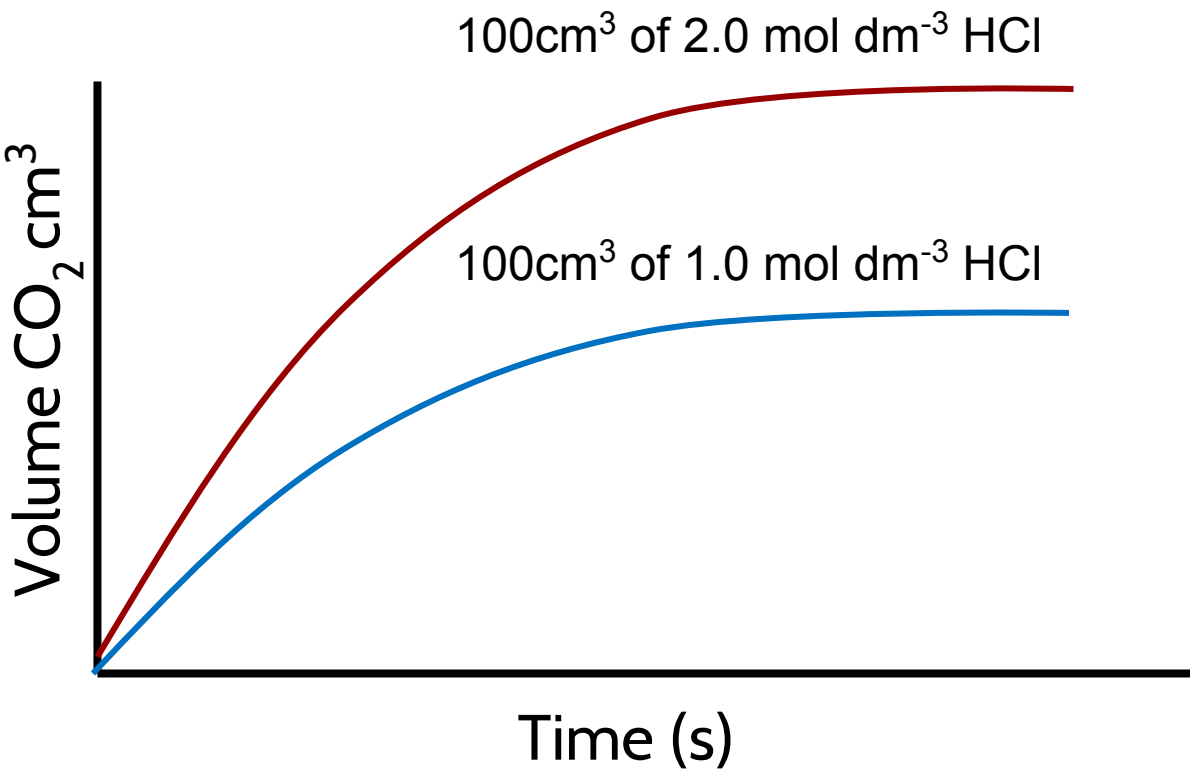


Main

Analyzing Reaction Rate Graphs

$$CaCO_3(s) + 2HCl(aq) \longrightarrow CO_2(g) + H_2O(l) + CaCl_2(aq)$$

Initial rate is lower and half as much gas is produced because concentration is different



Main

Analyzing Reaction Rate Graphs

$CaCO_3(s) + 2HCl(aq) \longrightarrow CO_2(g) + H_2O(l) + CaCl_2(aq)$

Different initial volume and concentration

$100cm^3/1000=0.1dm^3$

$(2.0mol\ dm^{-3})(0.1dm^3)$

$=0.20mol\ HCl$

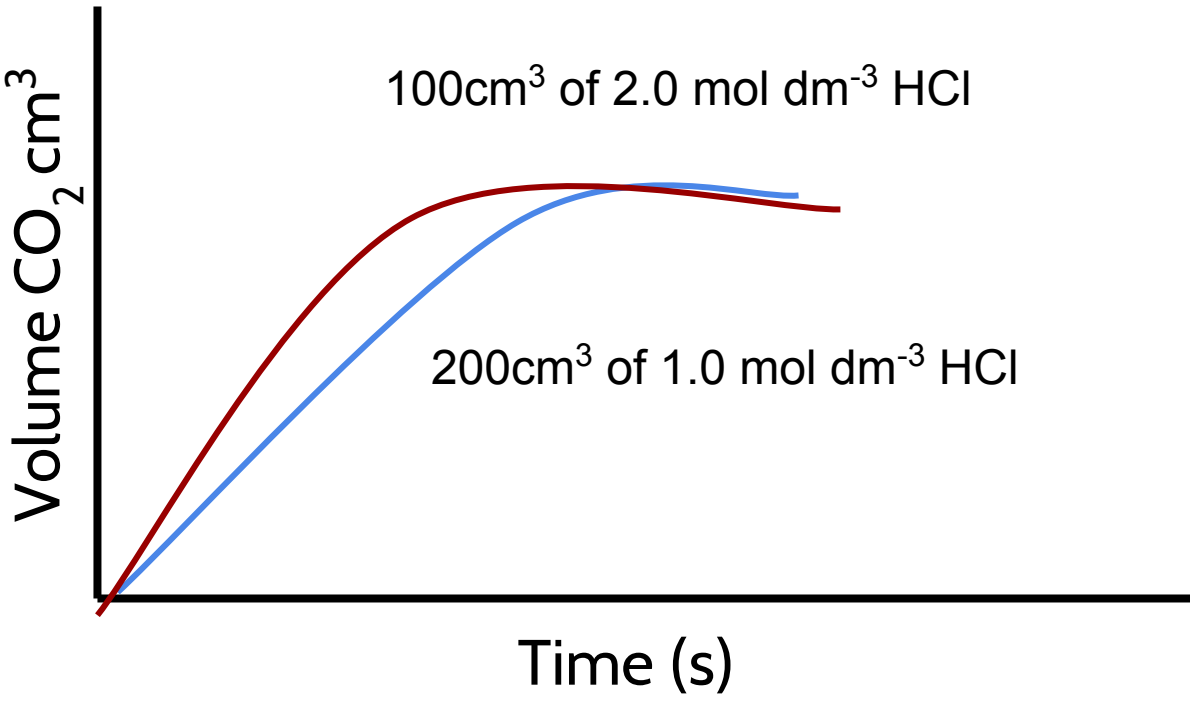
$=0.10mol\ CO_2$

$200cm^3/1000=0.2dm^3$

$(1.0mol\ dm^{-3})(0.2dm^3)$

$=0.20mol\ HCl$

$=0.1mol\ CO_2$

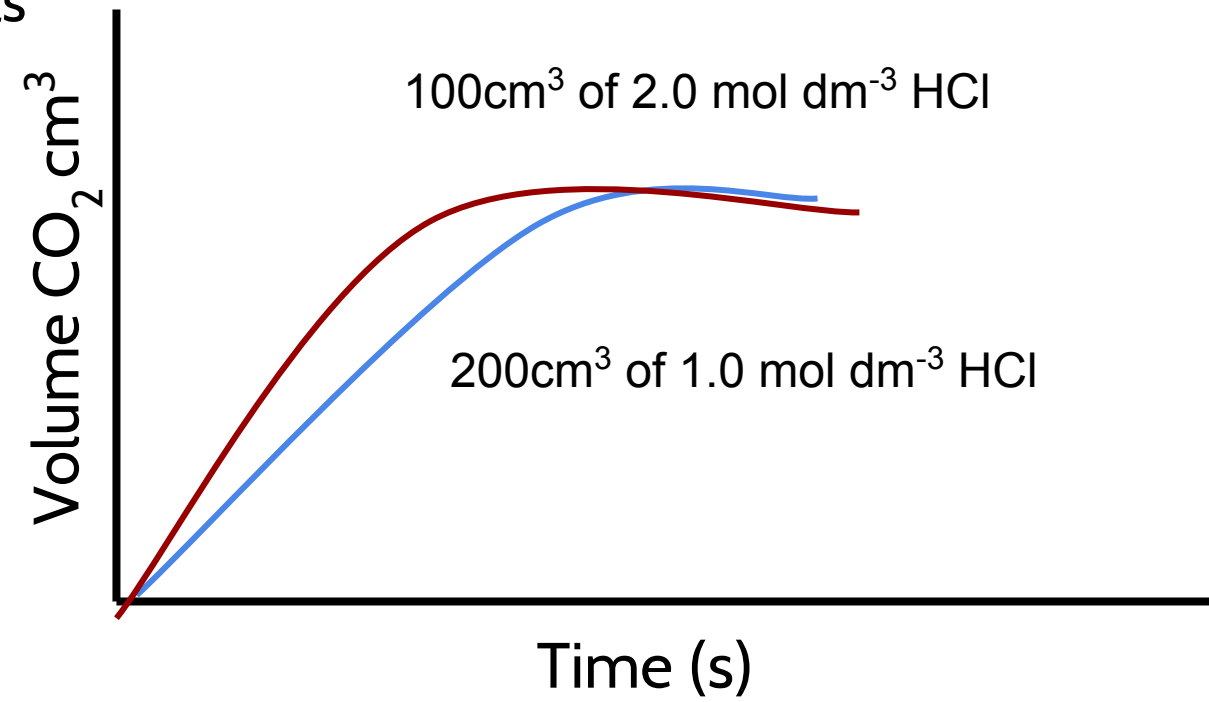


Main

Analyzing Reaction Rate Graphs

$CaCO_3(s) + 2HCl(aq) \longrightarrow CO_2(g) + H_2O(l) + CaCl_2(aq)$

Initial rate is lower and the same amount of gas Is produced



Main

Analysis of Reaction Rate Graphs

Analysis of Reaction Rate Graphs

Main

Analysis of Reaction Rate Graphs

Tangent lines represent the rate of the reaction

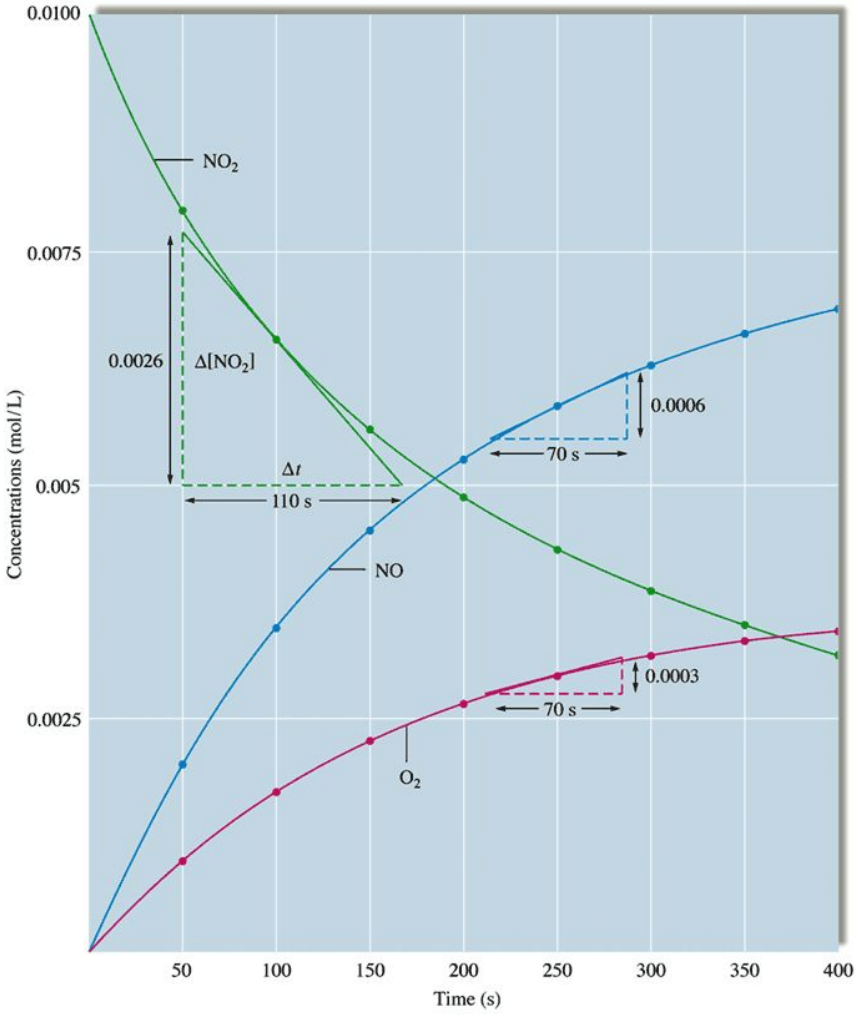
-Referred to as a gradient

Lower gradient

-lower rate

Steeper gradient

-higher rate



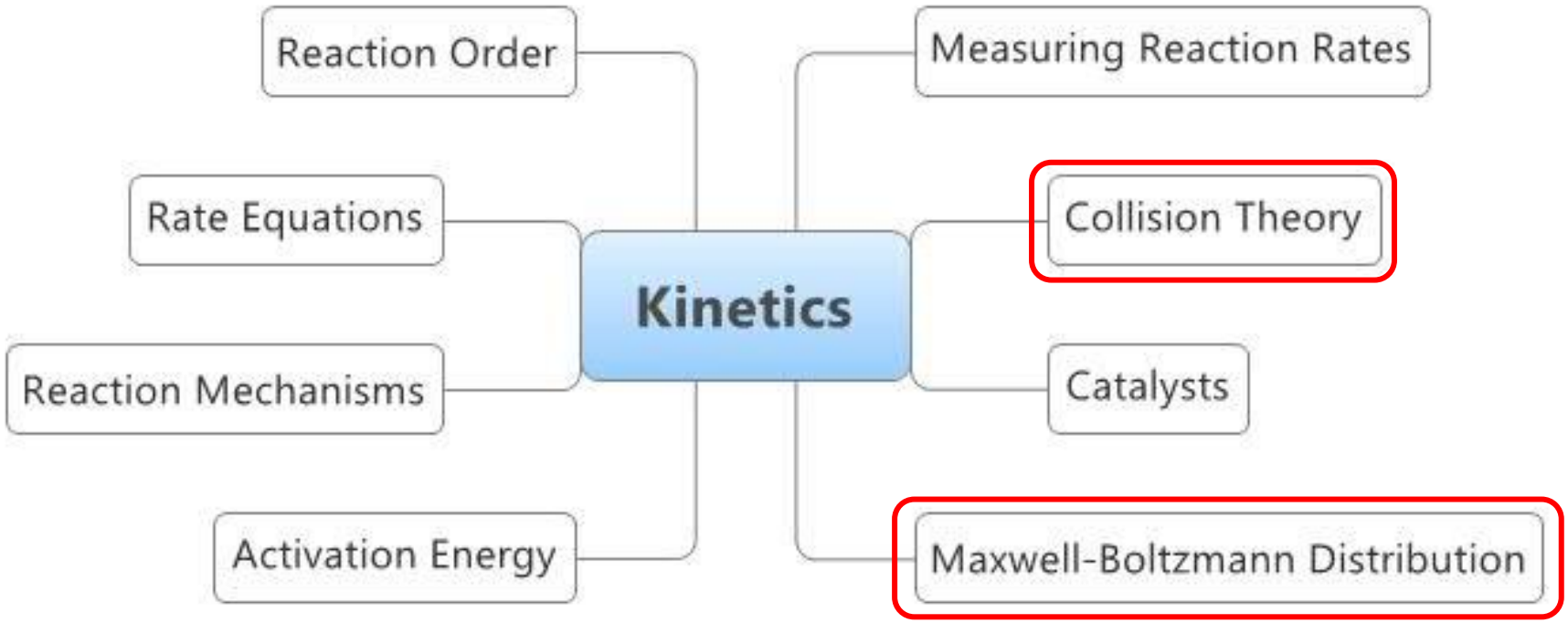
Main

Lesson 2

6.1 Collision Theory and Rates of Reactions

Main Menu

We Are Here



Main

Collision Theory

Two conditions must be fulfilled:

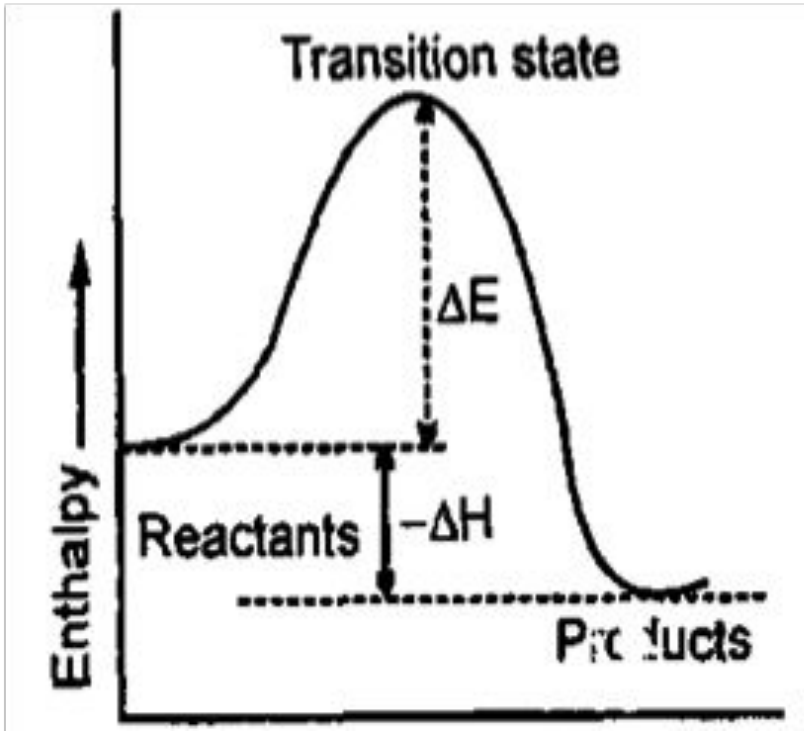
- A collision must involve more than a certain minimum amount of energy
  - Reactions occur as the result of two particles colliding with enough energy.
  - 'Enough energy' is better known as the activation energy
- Molecules must collide with the correct orientations
  - If molecules do not collide with the correct orientation they will not react

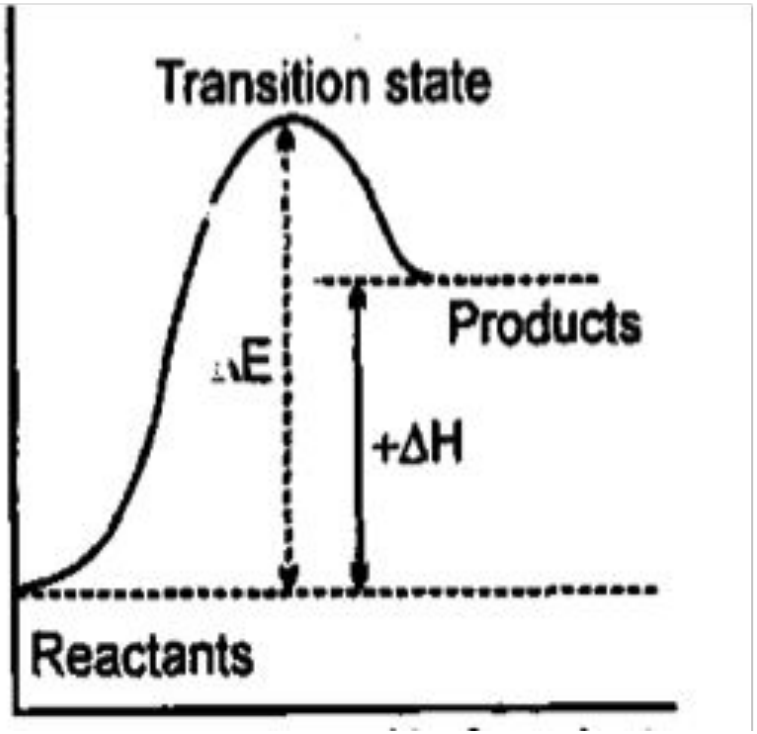
Collision Theory

- Anything that increases the number of collisions, or the proportion of collisions that have enough energy will increase the rate of reaction

- Not every collision with energy greater than the activation energy results in a reaction

Potential Energy Profile

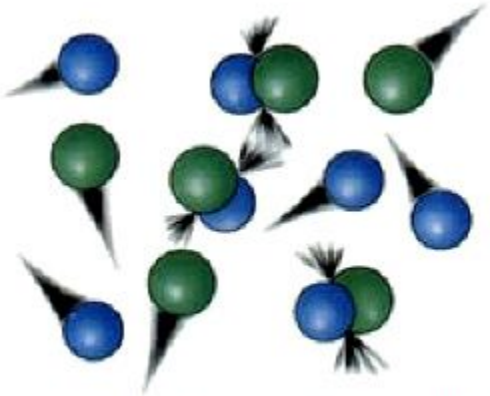




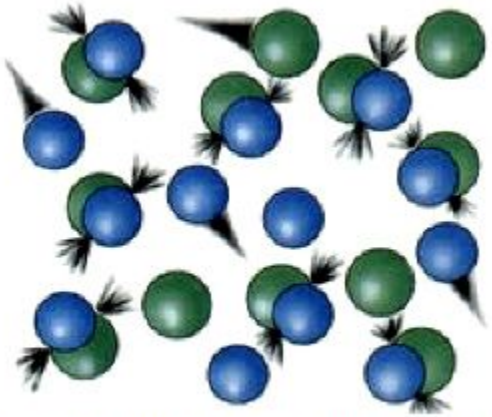
Main

Factors Affecting Reaction Rate

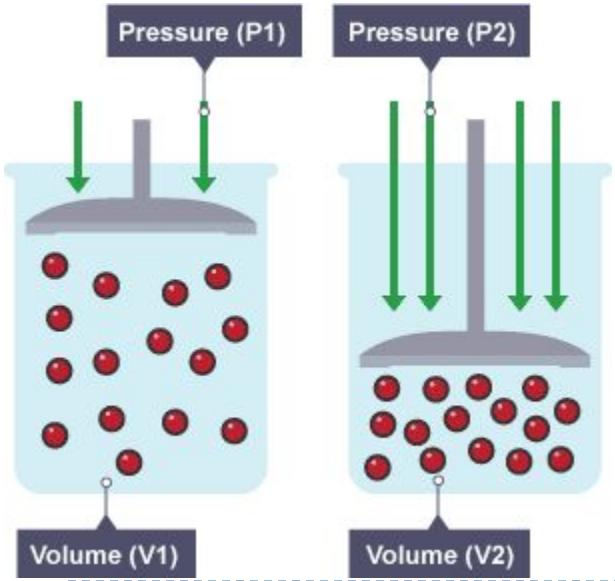
Concentration of reactants	As amount of particles increases, collision frequency increases
Pressure (reactions involving gases)	As pressure increases, collision frequency increases
Surface Area	More finely divided surface, more chance of particles to collide
Temperature	As the temperature increases, the rate of the reaction increases exponentially
Catalysis	Increases the rate of the reaction without being used up in the reaction; lowers activation energy

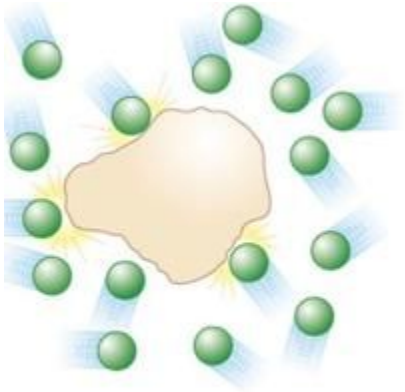


Low concentration = Few collisions

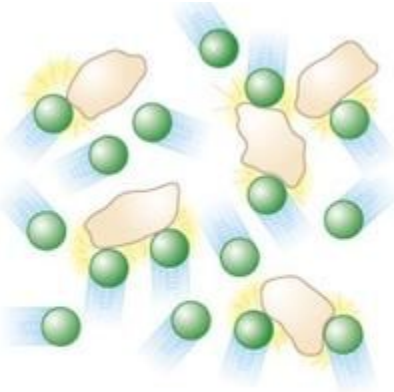


High concentration = More collisions

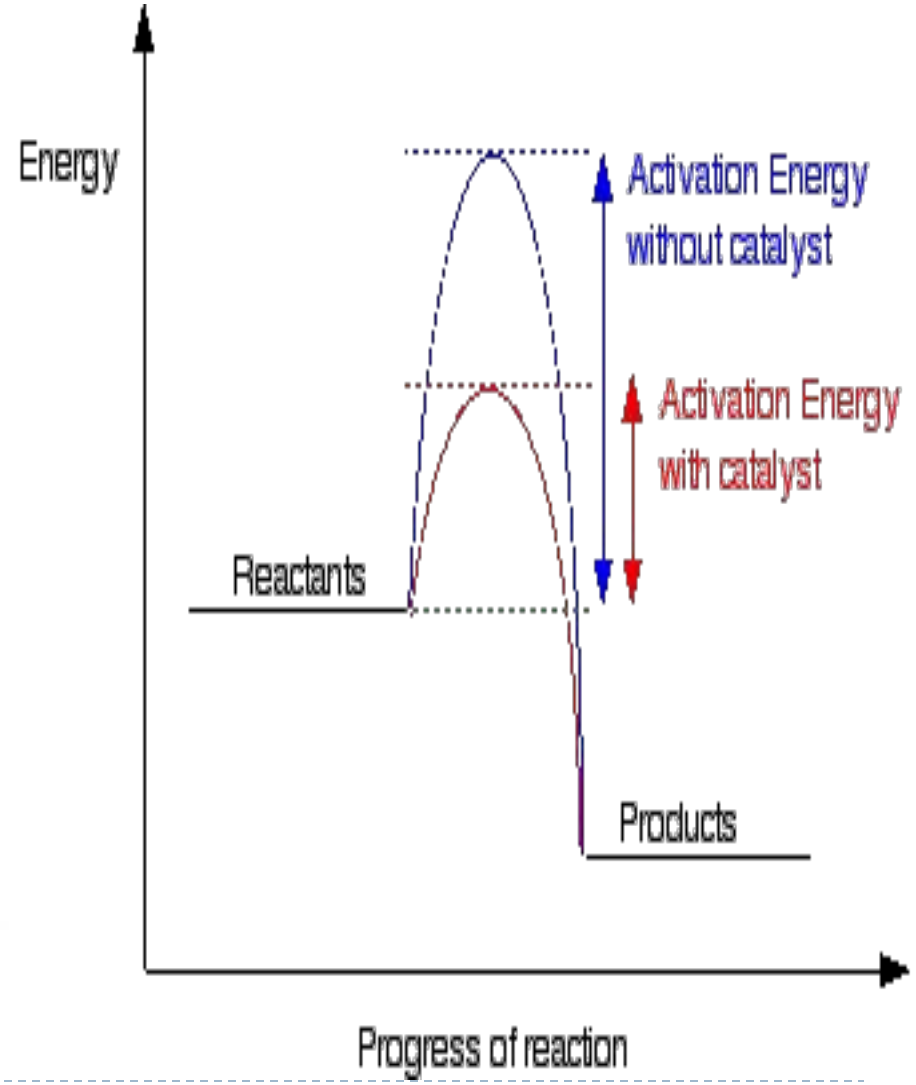


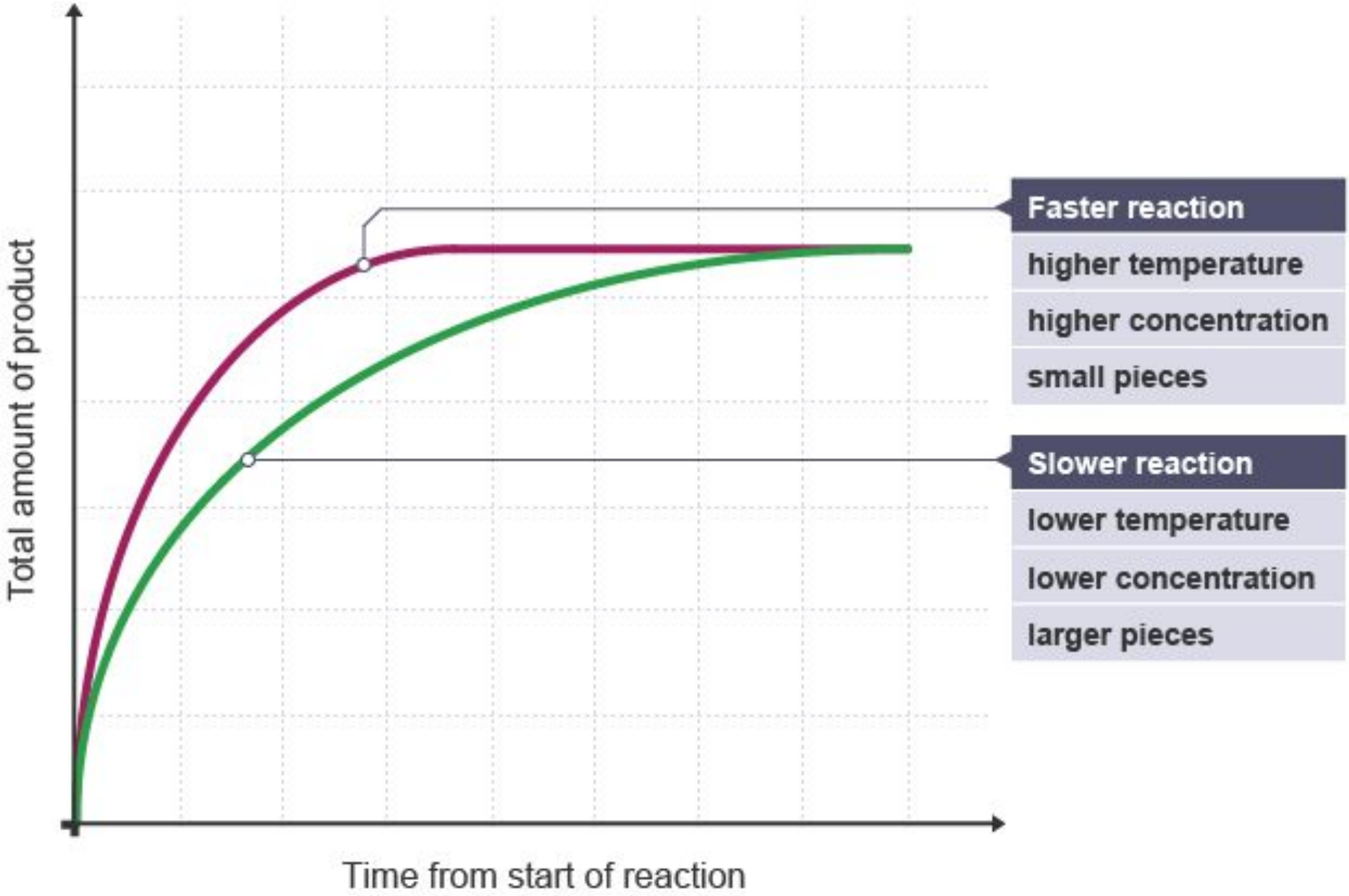


one big lump (slow reaction)



several small lumps (fast reaction)


Energy
Activation Energy without catalyst
Activation Energy with catalyst
Reactants
Products
Progress of reaction


Total amount of product
Time from start of reaction
Faster reaction
higher temperature
higher concentration
small pieces
Slower reaction
lower temperature
lower concentration
larger pieces

Relationship Between Temp and Energy

- At the same temperature lighter particles travel faster than heavier ones

- The main reason that the rate of reaction increases with temperature is an increase in the number of particles with energy greater than the activation energy

Main

Maxwell Boltzmann

- Two scientists, James Maxwell and Ludwig Boltzmann, proposed an equation that could be used to predict the speeds of ideal gas particles (atoms or molecules) at any temperature.

- Their equation is based on statistics and thermodynamic relationships. It is used by chemists and physicists to predict properties of gases such as pressure and diffusion rates, and it can be used to predict rates of reactions involving gases.

Main

Maxwell Boltzmann

- When a sample of matter is heated, the particles speed up. But what does that mean?
  - Are all the particles in a sample moving at the same speed?
  - Do they all speed up equally?
  - Does mass affect particle speed?

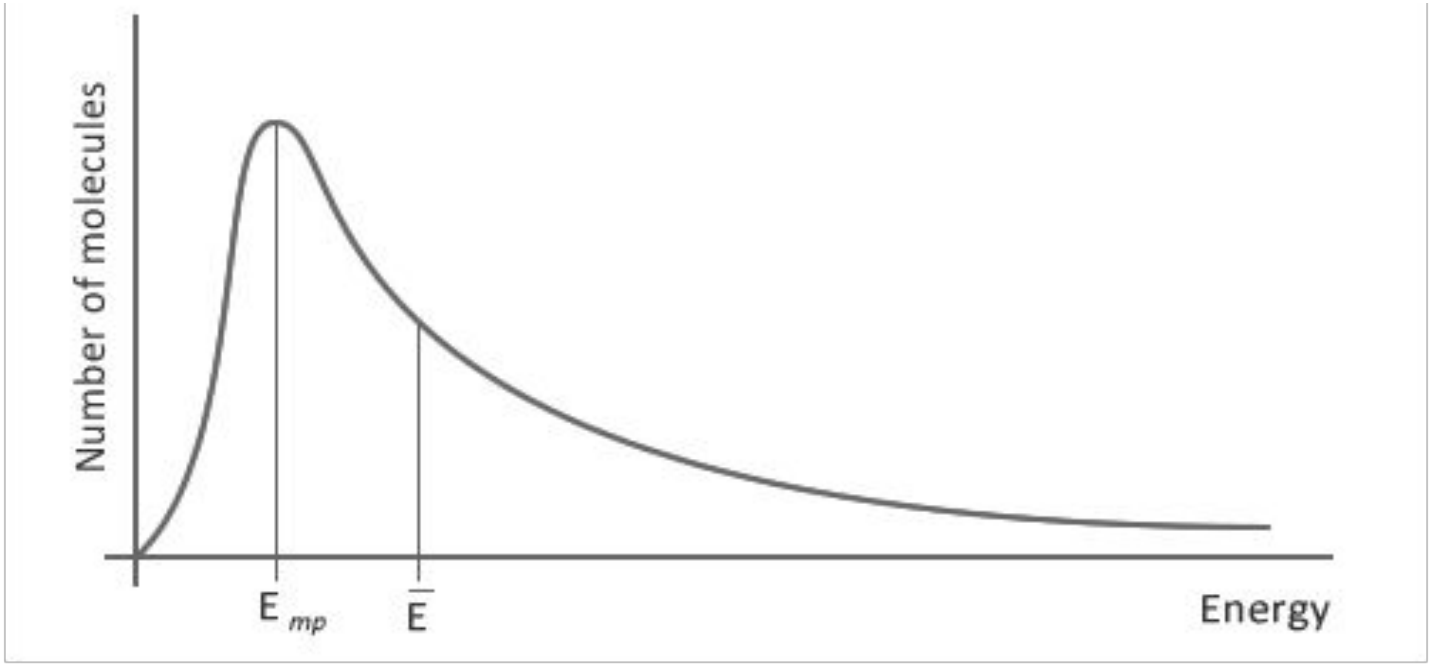
Maxwell-Boltzmann Distribution

- It is not symmetrical
- No molecules have zero kinetic energy
- At higher energy the line does not reach the energy axis
- The area under the curve represents the total number of particles and will not change as the temperature changes

Main

The Maxwell-Boltzmann Distribution

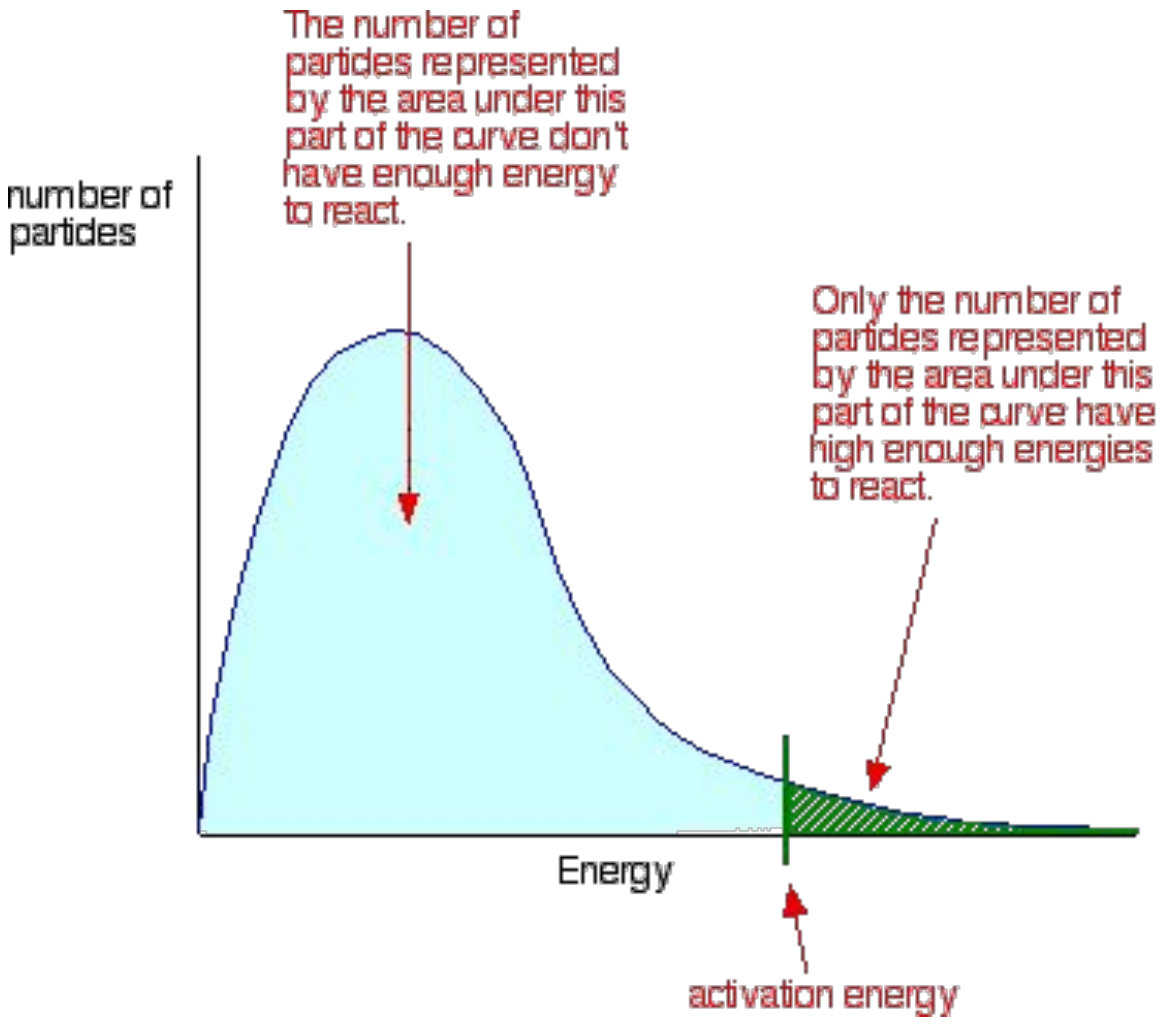
- Describes how energy is distributed in a collection of particles:



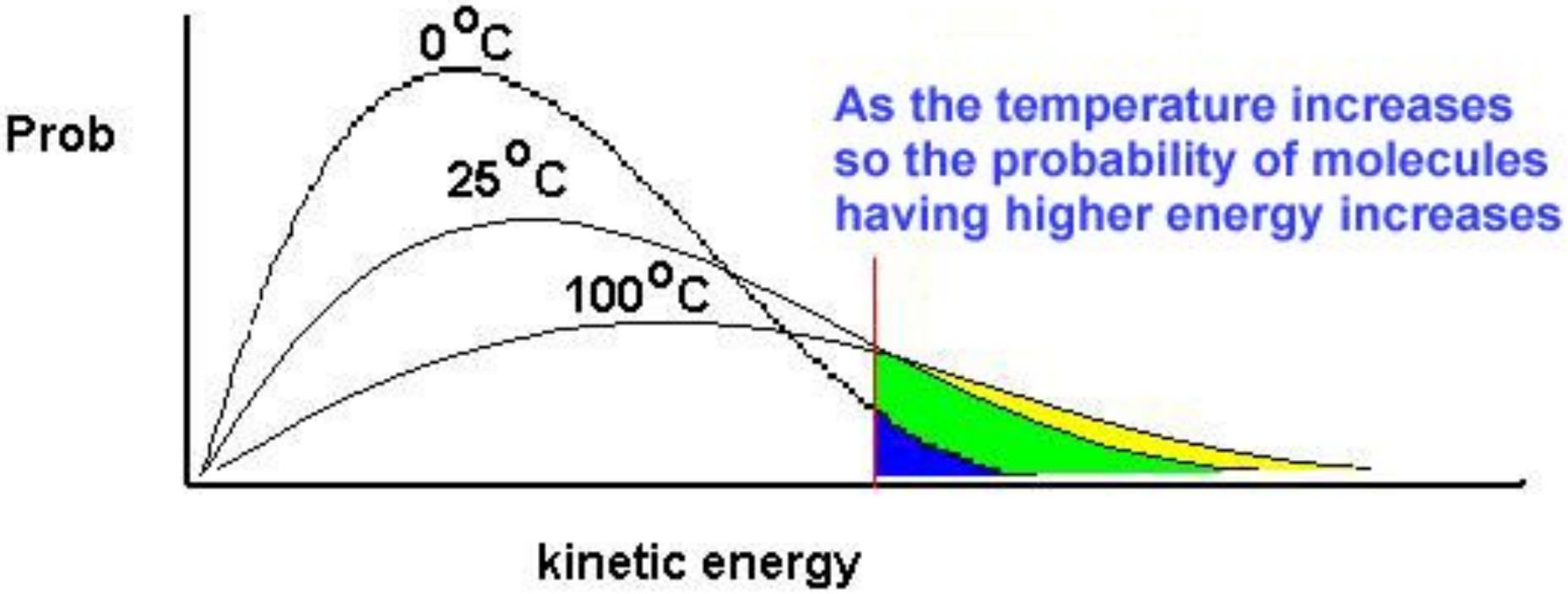
- x-axis: Energy of particles
- y-axis: Number of particles with a given energy
- E_{mp}: most-populated energy level
- **Ē**: the average energy, i.e the temperature

Main

Maxwell-Boltzmann Distribution



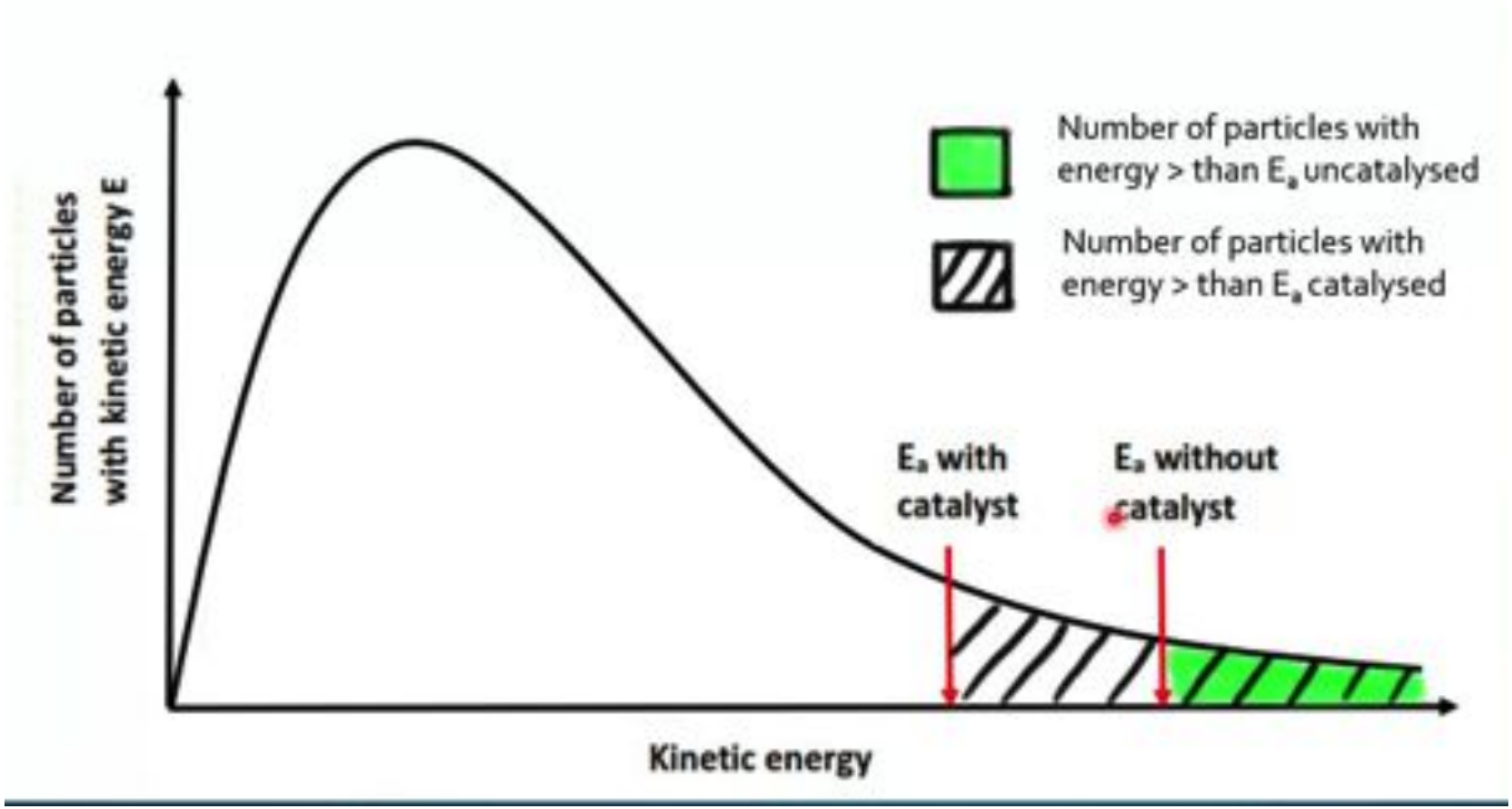
Maxwell-Boltzmann Distribution



At higher temp, the activation energy is lowered.

Main

Maxwell-Boltzmann Distribution Catalyst



Catalytic Converters

A **catalytic converter** is an emissions control device that converts toxic gases and pollutants in exhaust gas to less toxic pollutants by catalyzing a redox reaction (an oxidation and a reduction reaction).

How does this apply to Maxwell Boltzmann?

Main

Occman Razor

The principle of Occam's razor is used as a guide to developing a theory—although we cannot directly see reactions taking place at the molecular level, we can theorize based on the current atomic models.

How can we use this application in the process of collision theory and kinetics?

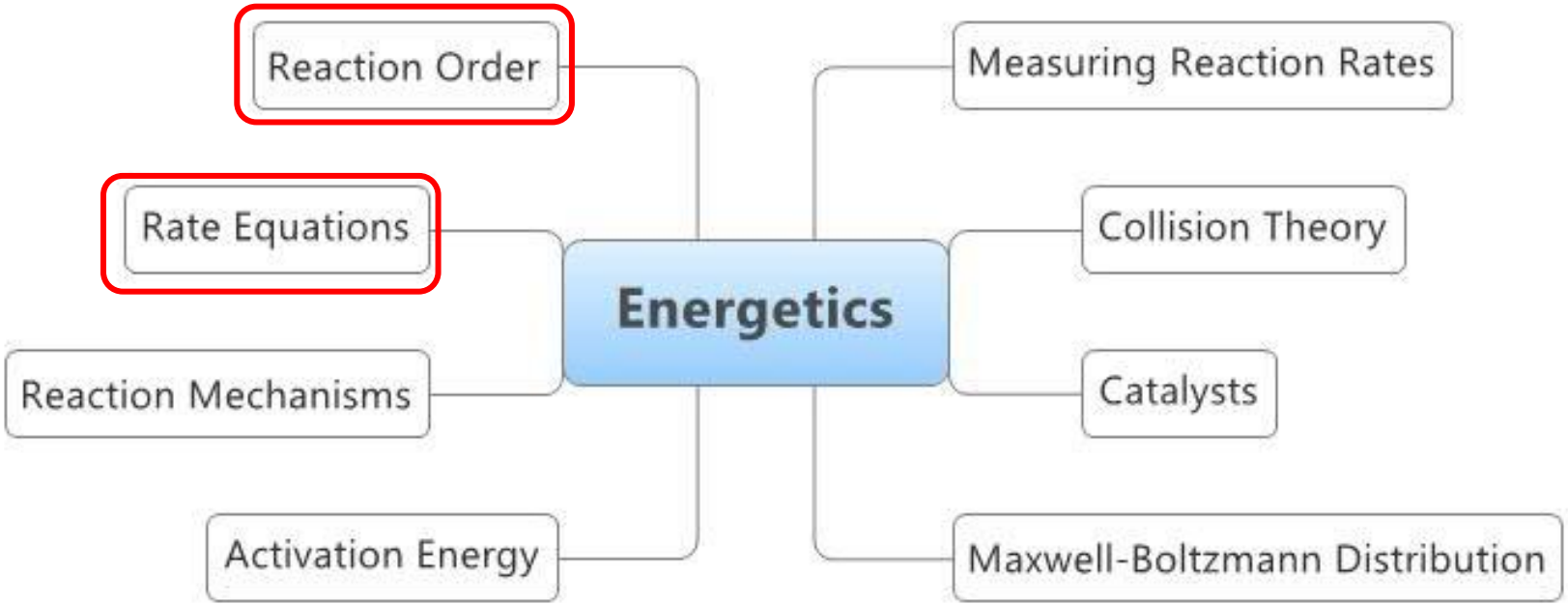
Main

Lesson 3

16.1 Reaction Mechanism and Reaction Expression

Main Menu

We Are Here



Main

What is a rate equation?

- A rate equation allows us to calculate the rate we would expect for any concentration of reactants.

- For example in the reaction:

$$A + B \rightarrow C$$

- The rate equation is:

$$Rate = k[A]^x[B]^y$$

- Where:
  - [A] and [B] are the concentrations of each reactant
  - x and y are the order of reaction with respect to each reactant
  - k is the 'rate constant'

Main

Order of a Reaction

- The rate equation is an experimentally determined equation that relates the rate of the reaction to the concentration of the substances in the reaction mixture
  - Assuming temperature and pressure are fixed
- The order of a reaction can be either integer or fractional in nature. The order of a reaction can describe, with respect to a reactant, the number of particles taking part in the rate-determining step
- The overall rate reaction is the sum of the exponents
  - Rate= $k[W]^m[X]^n$
  - m+n= overall order

Main

Temperature and the Rate Constant

- The rate constant k is essentially a measure of how readily a reaction will take place:
  - Higher k → faster reaction
  - Lower k → slower reaction

- k is dependent on temperature
  - As temperature increases, so does k
  - As temperature decreases, so does k

What is reaction order?

0^{th} Order (0°)

Changing the concentration does not affect the rate

Doubling the concentration of a reactant would have no effect on rate

1^{st} Order (1°)

$Rate \propto [R]$

Doubling the concentration of a reactant would double the rate, tripling it would triple the rate

2^{nd} Order (2°)

$Rate \propto [R]^2$

Doubling the concentration of a reactant would quadruple the rate, tripling it would increase rate nine-fold

Main

Units of Rate Reaction

Units of k are concentration$^{(1\text{-overall order})}$ time $^{-1}$

Overall Order	Units of k	Examples of units
0	Concentration time^{-1}	mol dm^{-3} s^{-1}
1	time^{-1}	s^{-1}
2	Concentration^{-1} time^{-1}	mol^{-1} dm^{3} s^{-1}
3	Concentration^{-2} time^{-1}	mol^{-2} dm^{6} s^{-1}

Main

Example

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

- The reaction is 0^{th} order w.r.t reactant A
  - Comparing Runs 2 and 3:
    - [A] doubles but [B] remains fixed
    - Rate unchanged
- The reaction is 1^{st} order w.r.t reactant B
  - Comparing Runs 1 and 2:
    - [B] doubles but [A] remains fixed
    - Rate doubles
- Overall the reaction is 1^{st} order

Main

Example

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

- The reaction is 0^{th} order w.r.t reactant A, and 1^{st} order w.r.t reactant B
- Therefore, the rate equation is:
  - Rate = k[B]
- The value of k is given by (using values for Experiment 1):

  k = Rate / [B]

  k = 1.25×10^{-2} / 1.00 = **1.25×10^{-2} s^{-1}**

Main

Example:

Experiment	Initial [NO] / mol dm^{-3}	Initial [H_2] / mol dm^{-3}	Initial rate / mol (N_2) dm^{-3} s^{-1}
1	0.100	0.100	2.53×10^{-6}
2	0.100	0.200	5.05×10^{-6}
3	0.200	0.100	1.01×10^{-5}
4	0.300	0.100	2.28×10^{-5}

- The reaction is 1st order w.r.t reactant H_2
  - Comparing Runs 1 and 2:
    - [H_2] doubles but [NO] remains fixed
    - Rate doubles
- The reaction is 2nd order w.r.t reactant NO
  - Comparing Runs 1 and 3:
    - [NO] doubles but [H_2] remains fixed
    - Rate quadruples
- Overall the reaction is 3rd order (1st order + 2nd order = 3rd order)

Main

Example:

Experiment	Initial [NO] / mol dm^{-3}	Initial [H_2] / mol dm^{-3}	Initial rate / mol (N_2) dm^{-3} s^{-1}
1	0.100	0.100	2.53×10^{-6}
2	0.100	0.200	5.05×10^{-6}
3	0.200	0.100	1.01×10^{-5}
4	0.300	0.100	2.28×10^{-5}

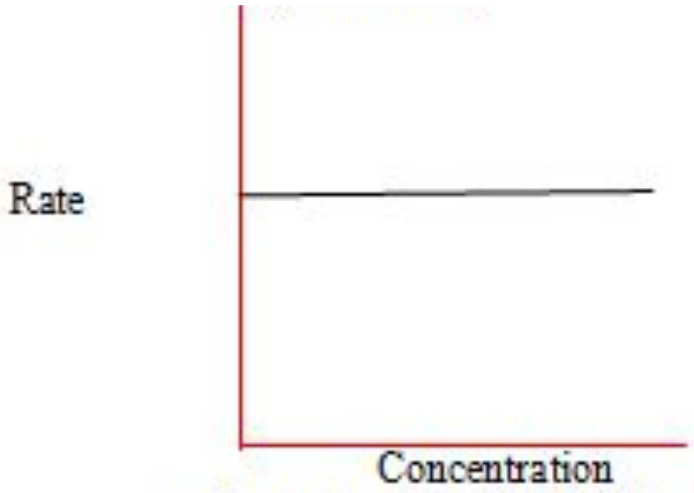
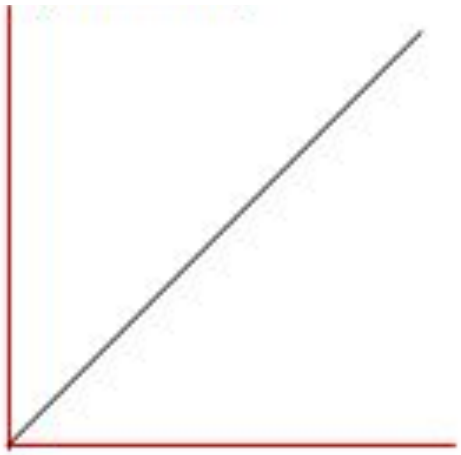
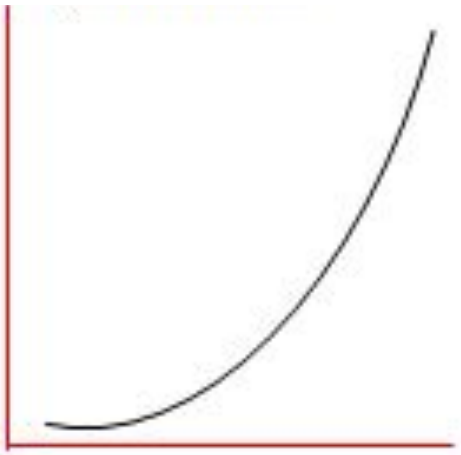
- The reaction is 1st order w.r.t [H_2], and second order w.r.t [NO]
- Therefore, the rate equation is:
  - Rate = $k[H_2][NO]^2$
- The value of k is given by (using values for Experiment 2):

  k = Rate / $[H_2][NO]^2$

  $k = 5.05\times10^{-6} / (0.200\times0.100^2)$ = **2.53×10^{-3} mol^{-2} dm^6 s^{-1}**

Main

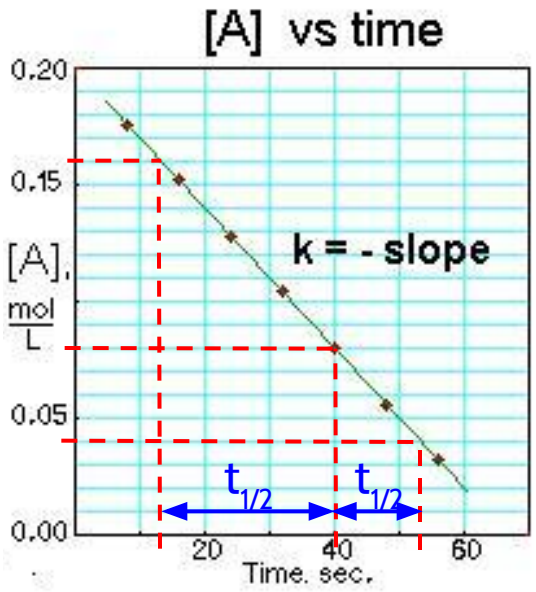
Rate-Concentration Graphs

0th Order	1st Order	2nd Order
		
▸ No effect ▸ Gradient 0	▸ Direct proportion ▸ Gradient positive and constant	▸ Squared relationship ▸ Gradient positive and increasing

Main

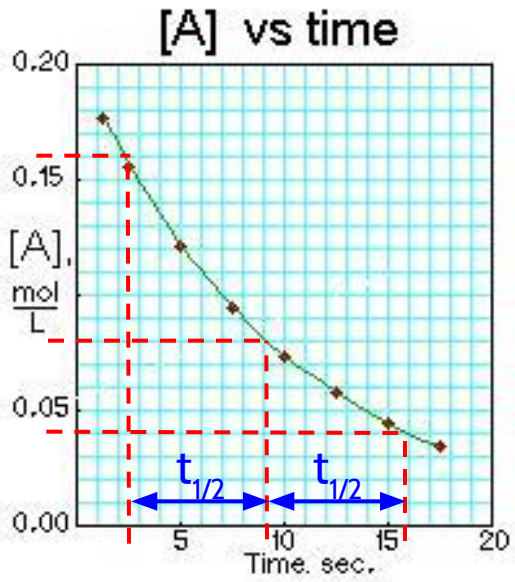
Concentration-Time Graphs

0th Order



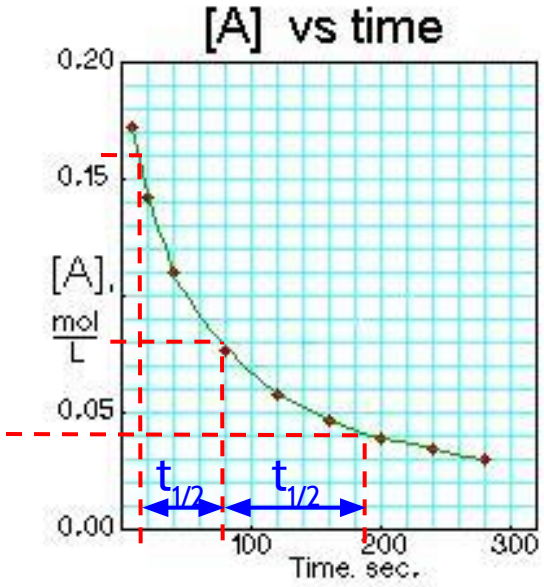
Half-life decreases

1st Order



Half-life constant

2nd Order



Half-life increases

Main

Lesson 4

16.1 Reaction Mechanism and Reaction Expression

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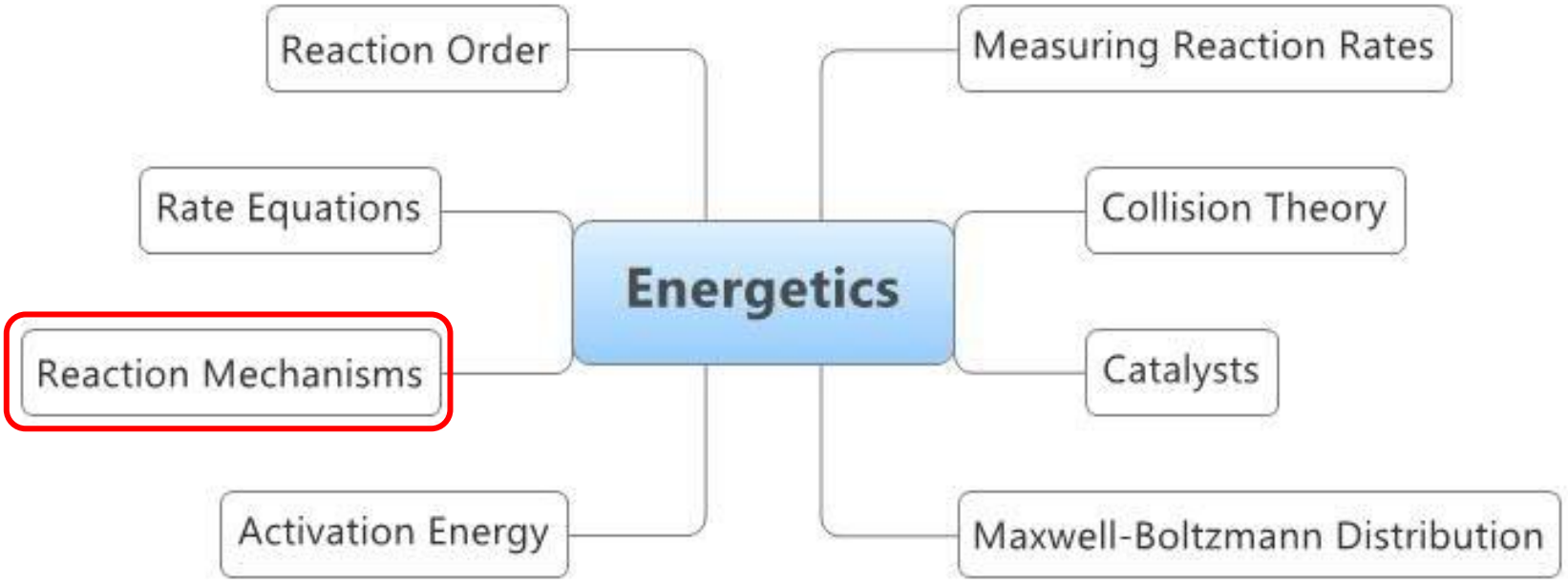


Main

Reflecting on the silly ping-pong balls thing

- What were the main factors that influenced how fast the balls could be passed around?
- Was each step in the reaction the same speed?
- Picture a million ping-pong balls being passed around the circle, which person would have the biggest impact on how long it took to pass them all around.
- How much can the people present after the slow one influence the rate?

Main

Eating…

- How do you eat a pizza?
- One mouthful at a time!
- Chemical reactions are similar.

Main

A note on molecularity…

- **Molecularity** describes the number of particles involved in a single step:

- **Unimolecular:** one molecule involved:

$$A \rightarrow B + C$$

- **Bimolecular:** two molecules involved

$$A + A \rightarrow C$$

$$A + B \rightarrow C$$

- **Termolecular:** three molecules involved (extremely rare, you will not encounter these at IB level).

Mechanisms of Reactions

- A reaction mechanism consists of a series of steps that make up a more complex reaction. Each simple step involves a maximum of two molecules colliding

- The slowest step is the **rate-determining step.**

- Each elementary step has its own rate constant, k, and its own activation energy

Mechanisms of Reactions

Step 1: $NO_2(g) + NO_2(g) \rightarrow NO(g) + NO_3(g)$ (slow)

This step is bimolecular

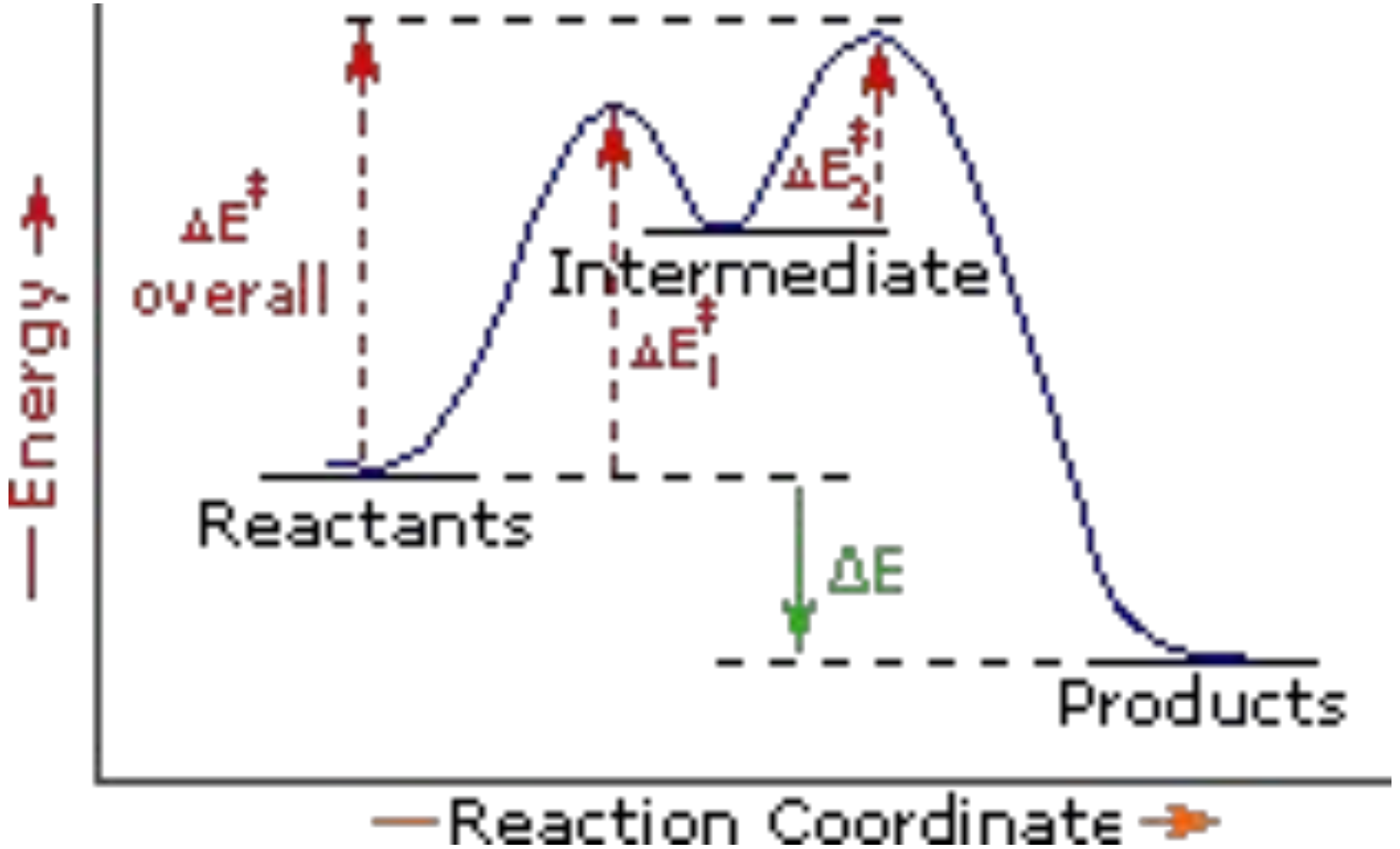
Step 2: $NO_3(g) + CO(g) \rightarrow NO_2(g) + CO_2(g)$ (fast)

This step is bimolecular

Overall Reaction: $NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$

NO_3 is described as the reaction intermediate

Potential Energy Profile



Mechanisms and Rates
Example 1

- Step 1: $NO_2(g) + NO_2(g) \rightarrow NO(g) + NO_3(g)$ (slow)
- Step 2: $NO_3(g) + CO(g) \rightarrow NO_2(g) + CO_2(g)$ (fast)
- Overall Reaction: $NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$

- If you think about it....
  - Changing the concentration of CO will not affect the rate
    - Because it is involved in a fast step after the RDS, and so the only thing relevant to this step is how quickly the NO_3 can be made, and this is made by a step which is very slow.
  - Changing the concentration of NO_2 will affect the rate
    - Due to it being involved in the slow step
    - Since it appears twice in the slow step, changing it's concentration will have double the impact

Deducing Rate Equation for Reaction Mechanism

1. Decide on which step is the RDS. The rate of the overall reaction mechanism is equal to the rate of the slow step.
2. Deduce the rate equation from step 1

- In effect, the reaction mechanism is essentially a hypothesis of the sequence of events that has led to the overall reaction converting the reactants into products.
- There could be a number of possible reaction mechanisms that equate with the experimental rate equation

Main

Reaction Mechanism

Step 1: $NO_2(g) + NO_2(g) \rightarrow NO(g) + NO_3(g)$ (slow)

Step 2: $NO_3(g) + CO(g) \rightarrow NO_2(g) + CO_2(g)$ (fast)

Overall Reaction: $NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$

- For temperatures less than 498K, the experimental rate equation for the reaction:
  - $rate=k[NO_2]^2$
- For temperatures greater than 498K, the experimental rate can be found as:
  - $rate=k[NO_2][CO]$

Single Step: $NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$ (slow)

This is consistent with experimentally determined rate equation

Main

Lesson 5

16.2 Activation Energy

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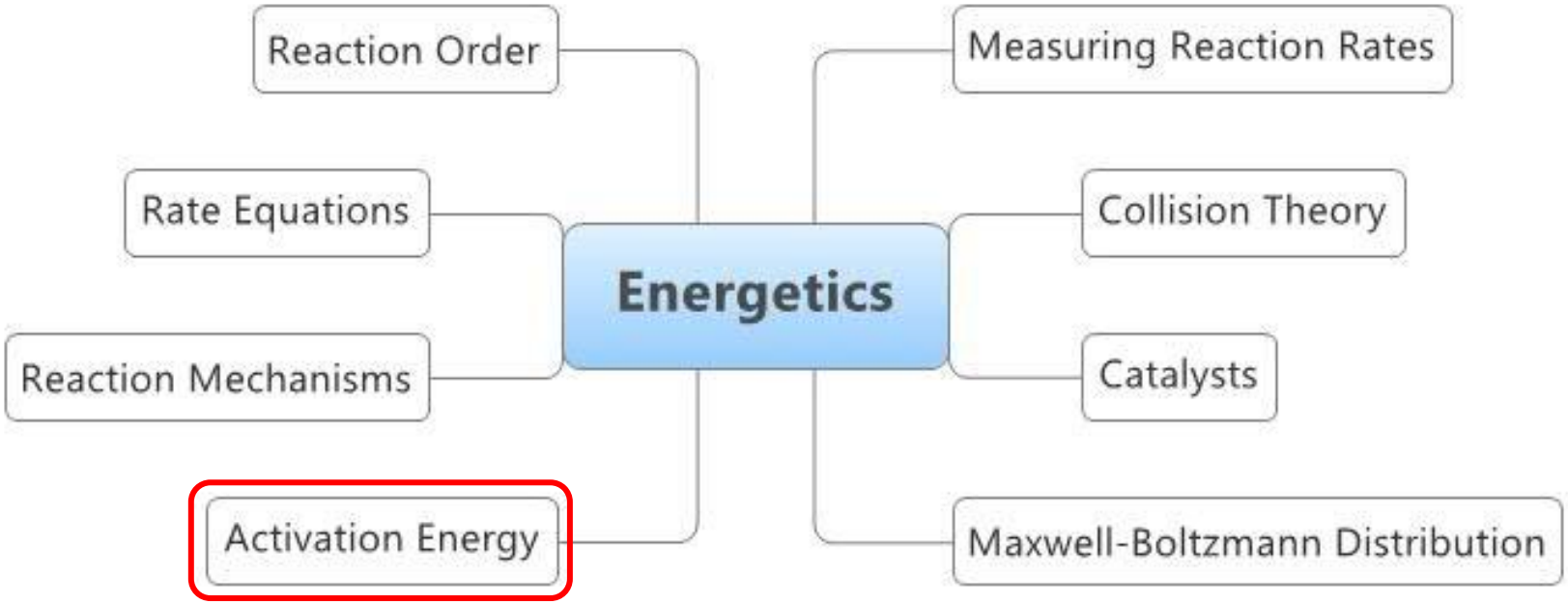


Main

Activation Energy

- Activation energy is the minimum energy two colliding particles need in order to react

- You can think of it as:
  - The energy required to begin breaking bonds
  - The energy that particles need to overcome the mutual repulsion of their electron shells.

The Arrhenius Equation

- The Arrhenius Equation tells us how k is related to a variety of factors:

$$k = A\, e^{\frac{-E_a}{RT}}$$

Where:

- k is the rate constant
- E_a is the activation energy
- T is the temperature measured in Kelvins
- R is the gas constant, 8.314 J mol^{-1} K^{-1}.
- e is Euler's number
- A is the 'frequency factor'

Main

Rearranging Arrhenius

$$k = A\, e^{\frac{-E_a}{RT}}$$

- If we take logs of both sides, we can re-express the Arrhenius equation as follows:

$$\ln k = \ln A - \frac{E_a}{RT}$$

- This may not look like it, but is actually an equation in the form y = mx + c

$$\ln k = \frac{-E_a}{R} . \frac{1}{T} + \ln A$$

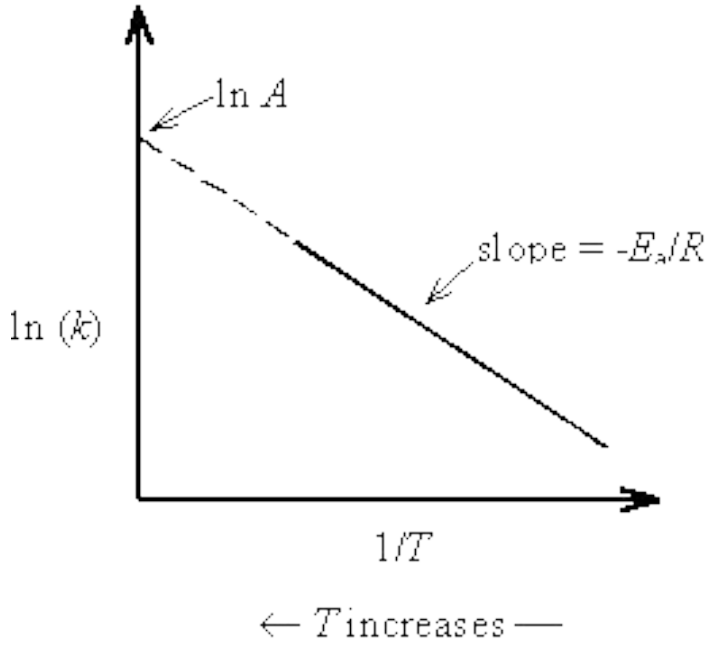
Where:

- 'y' is ln k
- 'm' is $-E_a/R$
- 'x' is 1/T
- 'c' is ln A

Main

To determine E_a Experimentally: (Assuming we know the rate equation)

- Measure the rate of reaction at various temperatures.
  - Keeping all concentrations the same
- Calculate the rate constant, k, at each temperature.
- Plot a graph of ln k (y-axis) vs 1/T (x-axis)
- The gradient of this graph is equal to '$-E_a/R$', this can be rearranged to calculate E_a.



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