30:00

Unit 5

- 11 topics
- 7-9% of exam
- Tentative test date: December 6th

Watch the following clip and think of what questions you have about what's happening

5.1 Reaction Rates

ENDURING UNDERSTANDING:	
TRA-3	Some reactions happen quickly, while others happen more slowly and depend on reactant concentrations and temperature.
LEARNING OBJECTIVE:	
TRA-3.A	Explain the relationship between the rate of a chemical reaction and experimental parameters.

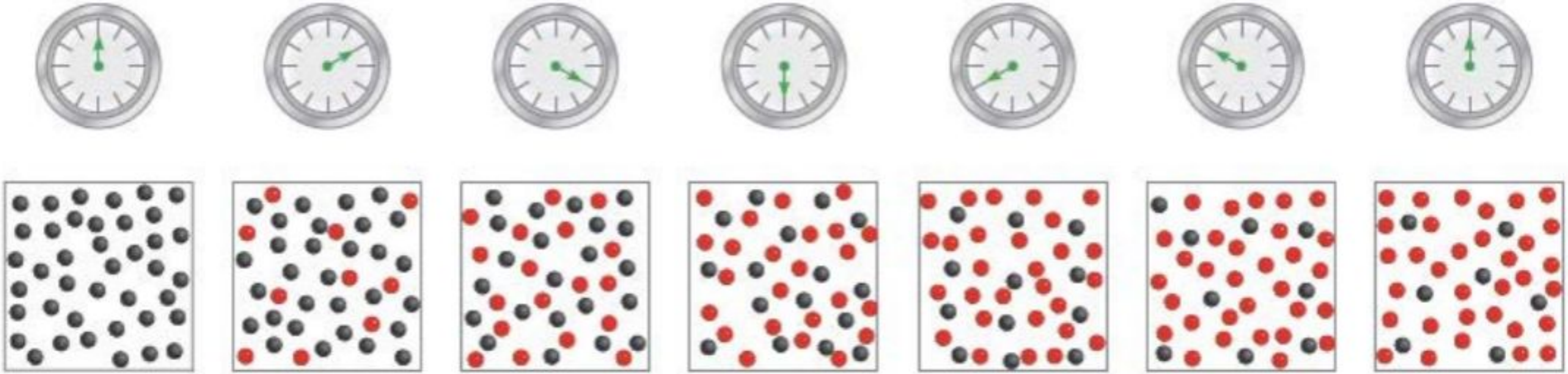
CHEMICAL KINETICS

Chemical reactions involve the conversion of reactants with a particular set of properties into products with a whole new set of properties.

$$\text{reactants} \longrightarrow \text{products}$$

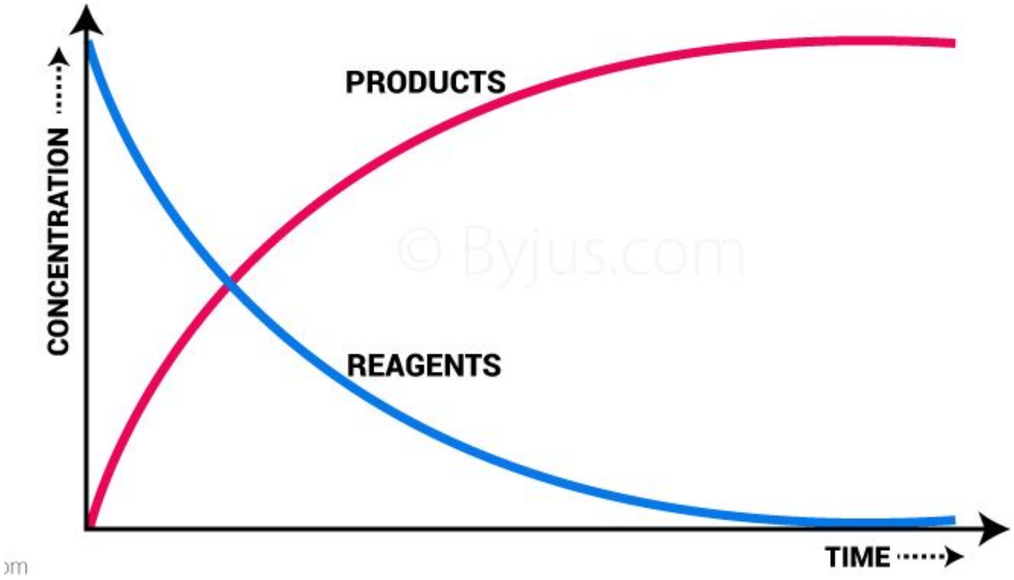
Chemical kinetics is the investigation of the ***rate** at which these reactions occur* and the ***factors** that affect them.*

$$\text{A} \longrightarrow \text{B}$$



REACTION RATES

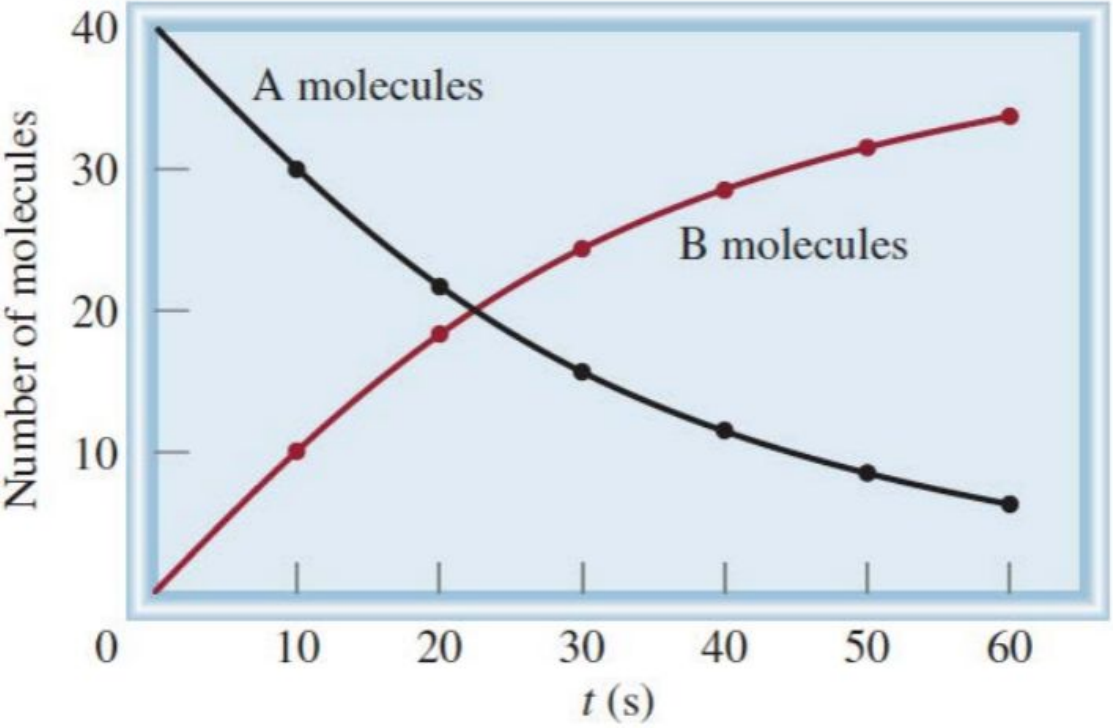
Experimentally, for most reactions, the rate is greatest at the beginning of the reaction and decreases as the reaction continues. Because the rate changes as a reaction proceeds, reaction rates are generally expressed as averages over a particular time period.



© Byjus.com

RATE IS POSITIVE

Since Δ[A] will be a negative value (as amount of A is decreasing) we include a negative sign to ensure Rate is always a positive value.



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

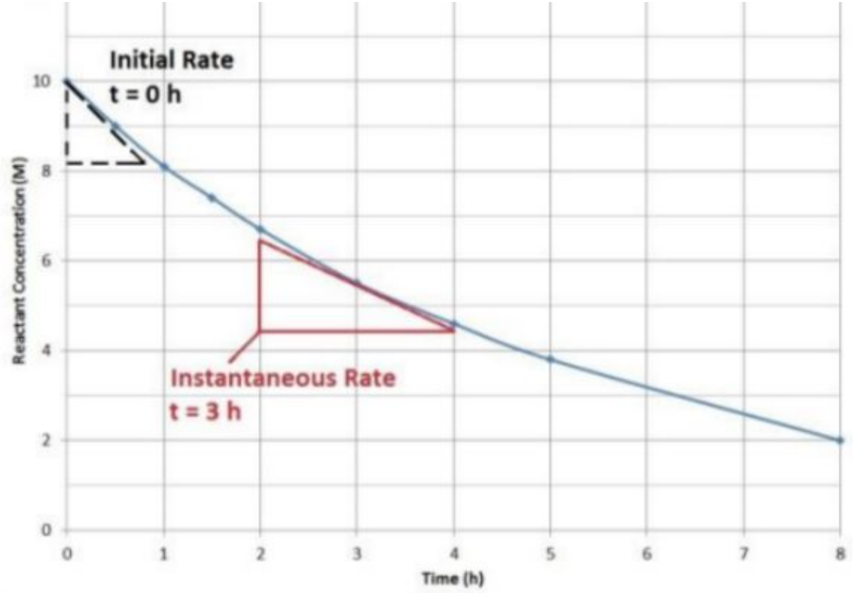
AVERAGE REACTION RATE

$$\text{average reaction rate} = \frac{\text{change in a measurable quantity of a chemical species}}{\text{change in time}}$$

Average rate of reaction is found by taking the difference in molarity over the difference in time.

If you take very small time intervals you can get the **instantaneous reaction rate.**

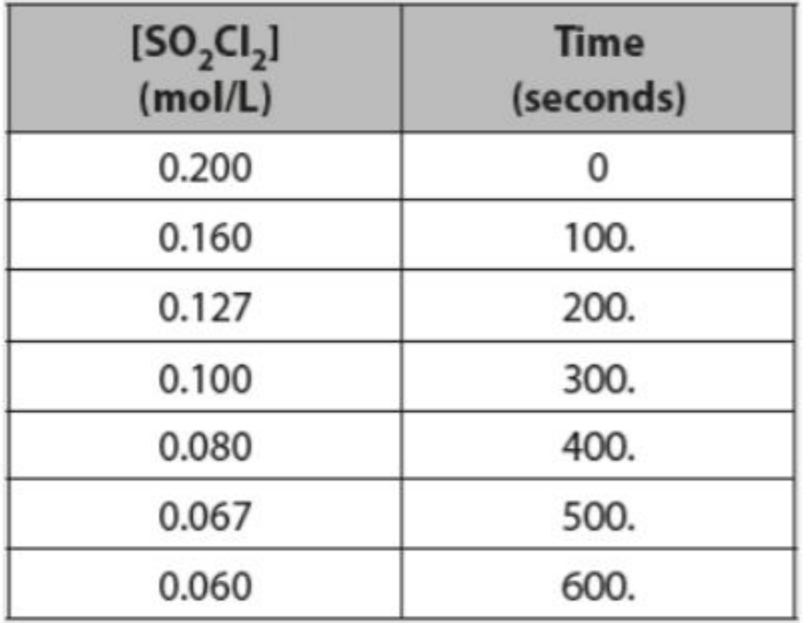
The **initial rate** is the rate for the first interval on the graph.



EXAMPLE:

Thionyl chloride decomposes according to the reaction:

$$SO_2Cl_{2(solvent)} \longrightarrow SO_{2(g)} + Cl_{2(g)}$$



$[SO_2Cl_2]$ (mol/L)	Time (seconds)
0.200	0
0.160	100.
0.127	200.
0.100	300.
0.080	400.
0.067	500.
0.060	600.

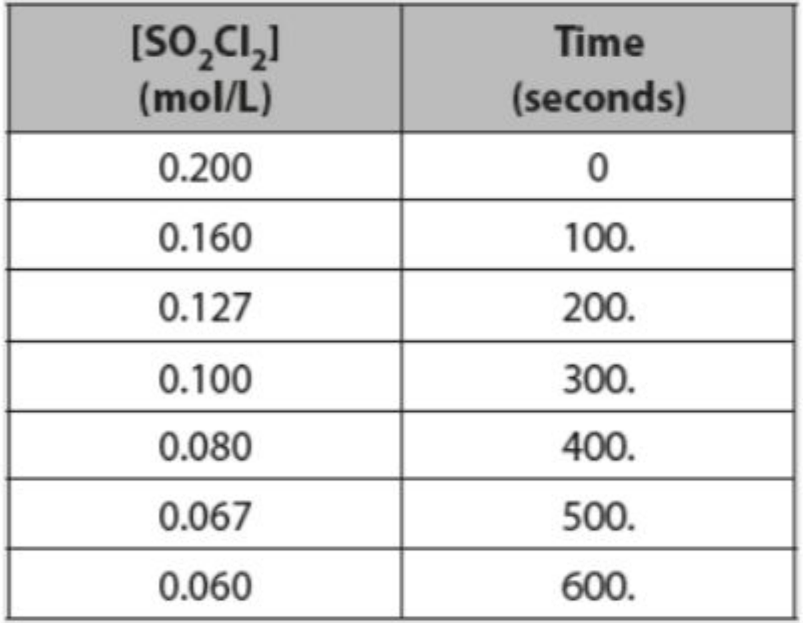
Calculate the average reaction rate using:

average rate = $-\Delta[SO_2Cl_2]/\Delta t$

EXAMPLE:

Thionyl chloride decomposes according to the reaction:

$$SO_2Cl_{2(solvent)} \longrightarrow SO_{2(g)} + Cl_{2(g)}$$



$[SO_2Cl_2]$ (mol/L)	Time (seconds)
0.200	0
0.160	100.
0.127	200.
0.100	300.
0.080	400.
0.067	500.
0.060	600.

Given the stoichiometric equation for the reaction, rate could also be calculated relative to SO_2(g) or Cl_2(g).

average rate = $\Delta[SO_2]/\Delta t$ =

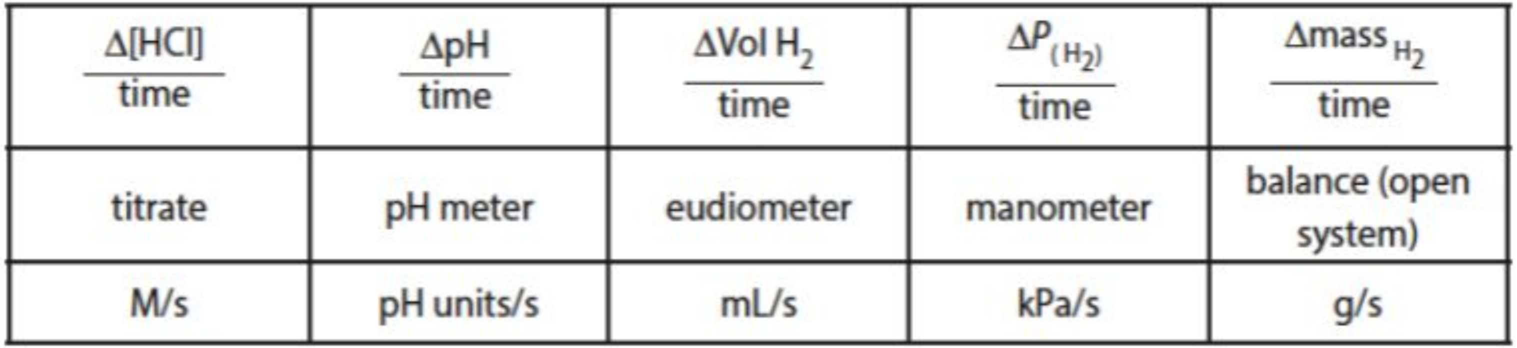
average rate = $\Delta[Cl_2]/\Delta t$ =

For this reaction, given the equimolar relationships, all the calculated reaction rates have the same values.

UNITS

Units can vary depending on the measurements being made.

$$Fe_{(s)} + 2\,HCl_{(aq)} \longrightarrow FeCl_{2\,(aq)} + H_{2\,(g)}$$



$\frac{\Delta[HCl]}{time}$	$\frac{\Delta pH}{time}$	$\frac{\Delta Vol\ H_2}{time}$	$\frac{\Delta P_{(H_2)}}{time}$	$\frac{\Delta mass_{H_2}}{time}$
titrate	pH meter	eudiometer	manometer	balance (open system)
M/s	pH units/s	mL/s	kPa/s	g/s

COEFFICIENTS

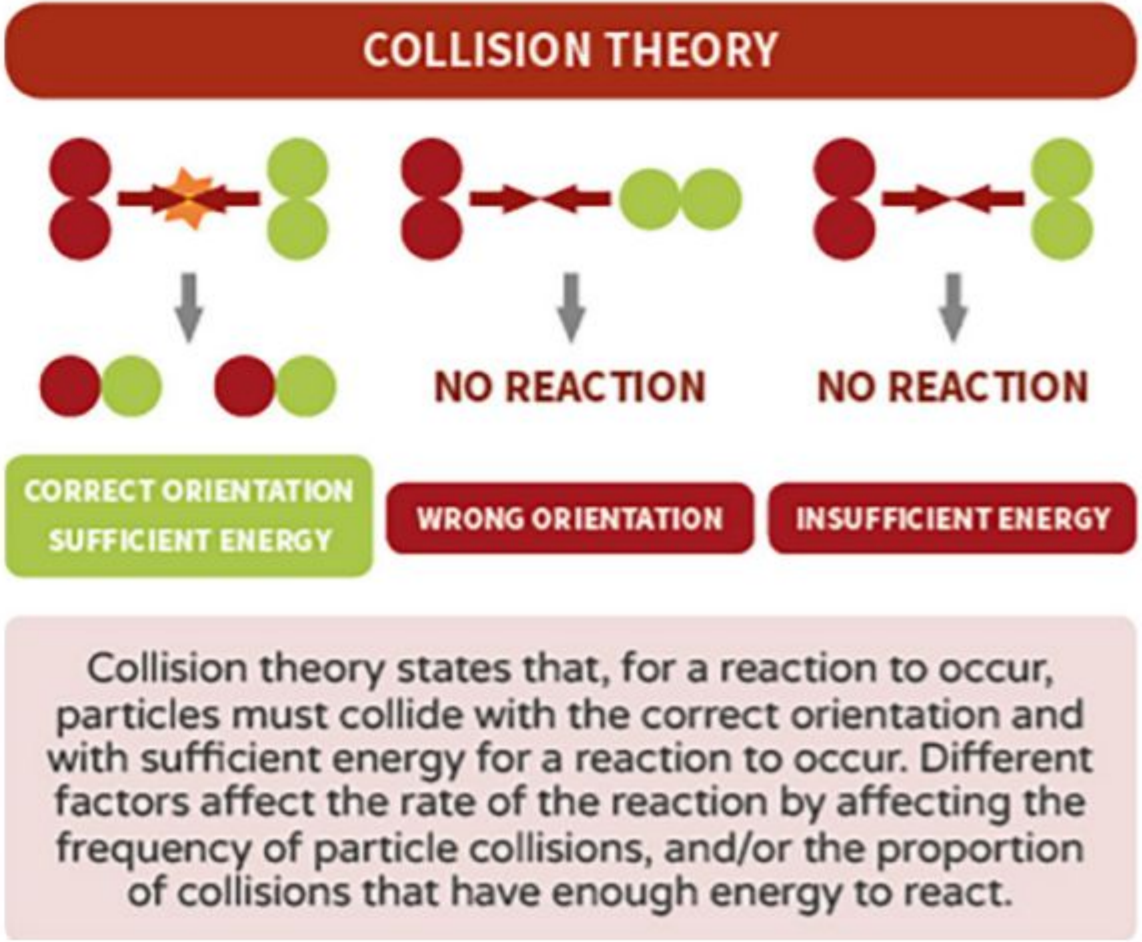
In general, for a reaction, $aA + bB \rightarrow cC + dD$

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

Consider the reaction: $4NO_{2(g)} + O_{2(g)} \longrightarrow 2N_2O_{5(g)}$

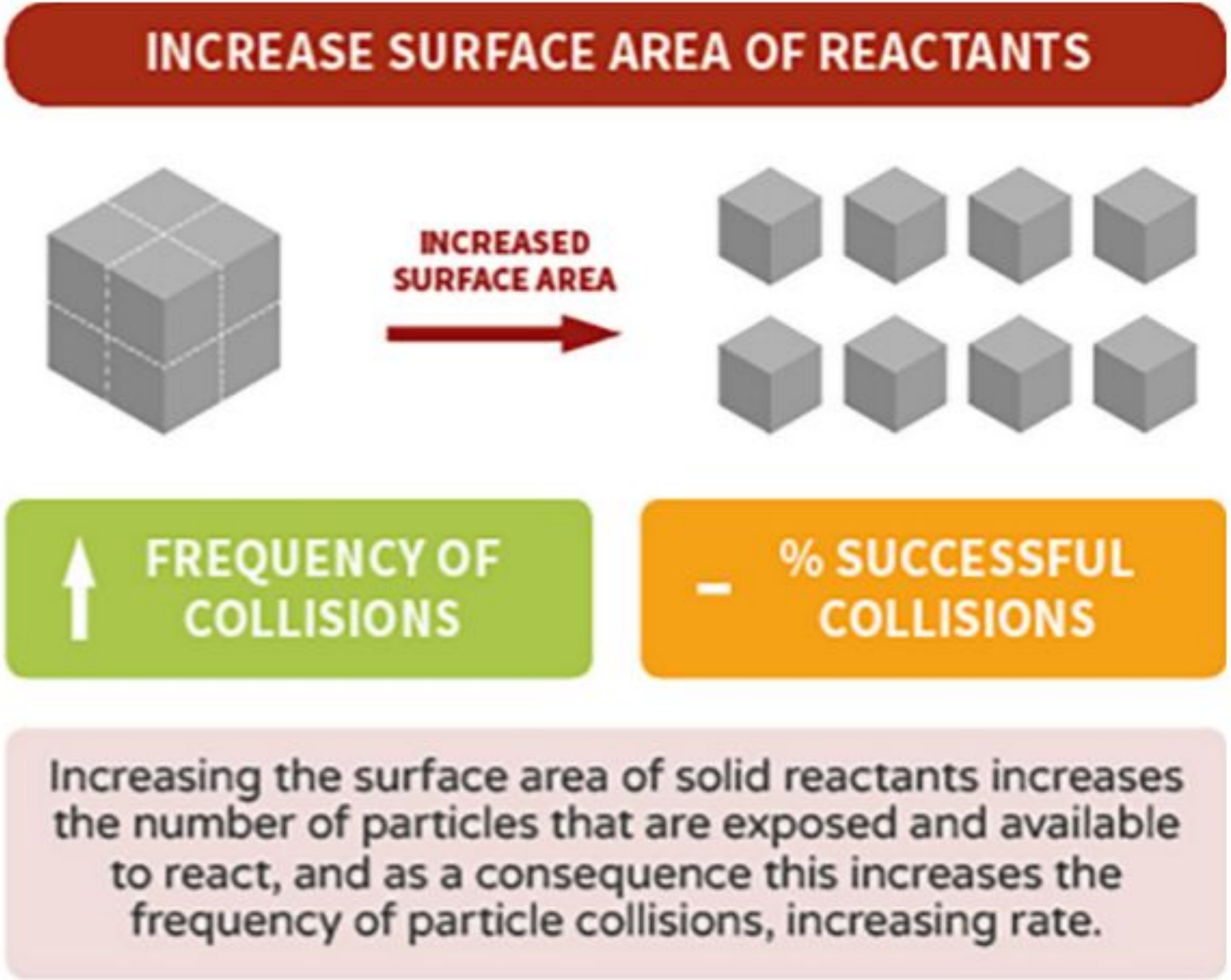
Suppose that, at a particular moment during the reaction, molecular oxygen is reacting at the rate of 0.024 M/s. ***a)*** At what rate is N_2O_5 being formed? ***b)*** At what rate is NO_2 reacting?

Collision Theory



Collision theory states that, for a reaction to occur, particles must collide with the correct orientation and with sufficient energy for a reaction to occur. Different factors affect the rate of the reaction by affecting the frequency of particle collisions, and/or the proportion of collisions that have enough energy to react.

SURFACE AREA



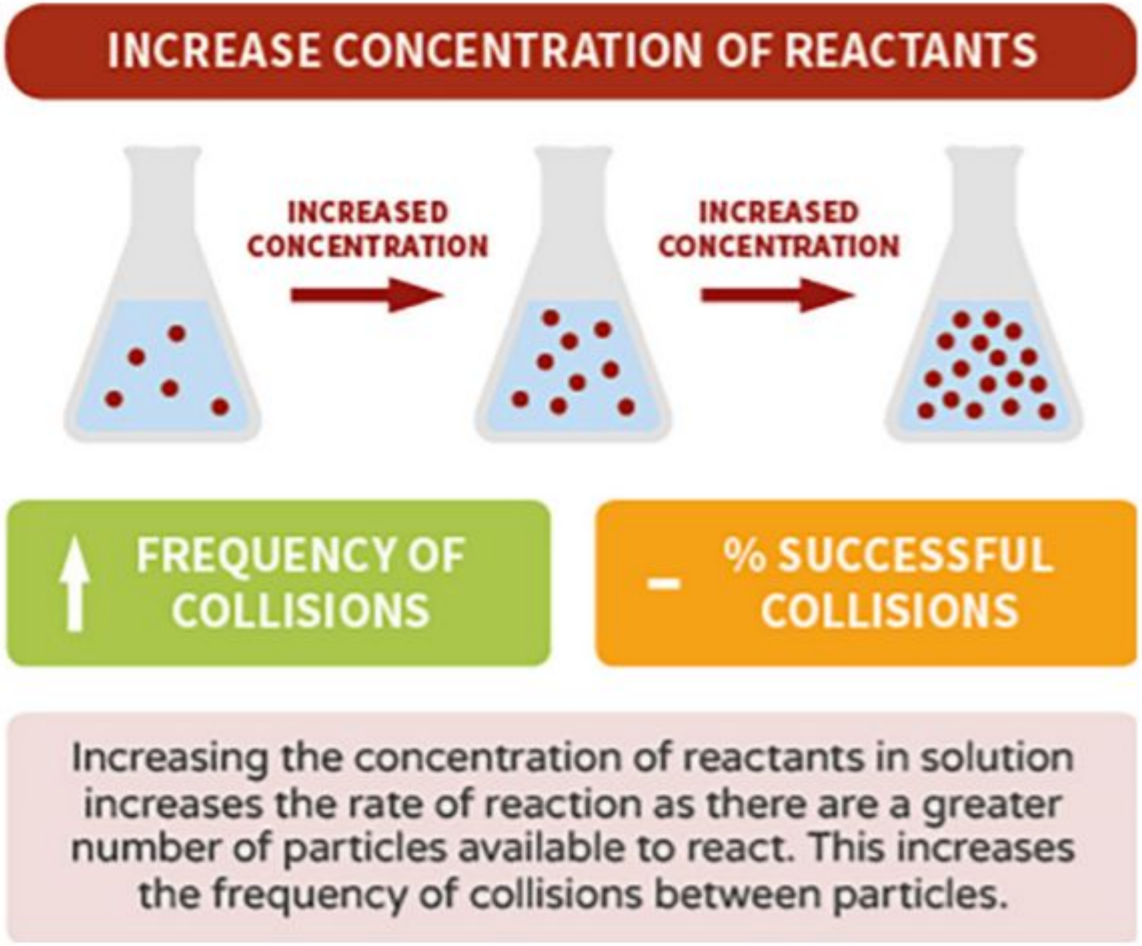
INCREASE SURFACE AREA OF REACTANTS

↑ FREQUENCY OF COLLISIONS

– % SUCCESSFUL COLLISIONS

Increasing the surface area of solid reactants increases the number of particles that are exposed and available to react, and as a consequence this increases the frequency of particle collisions, increasing rate.

Reactant Concentrations



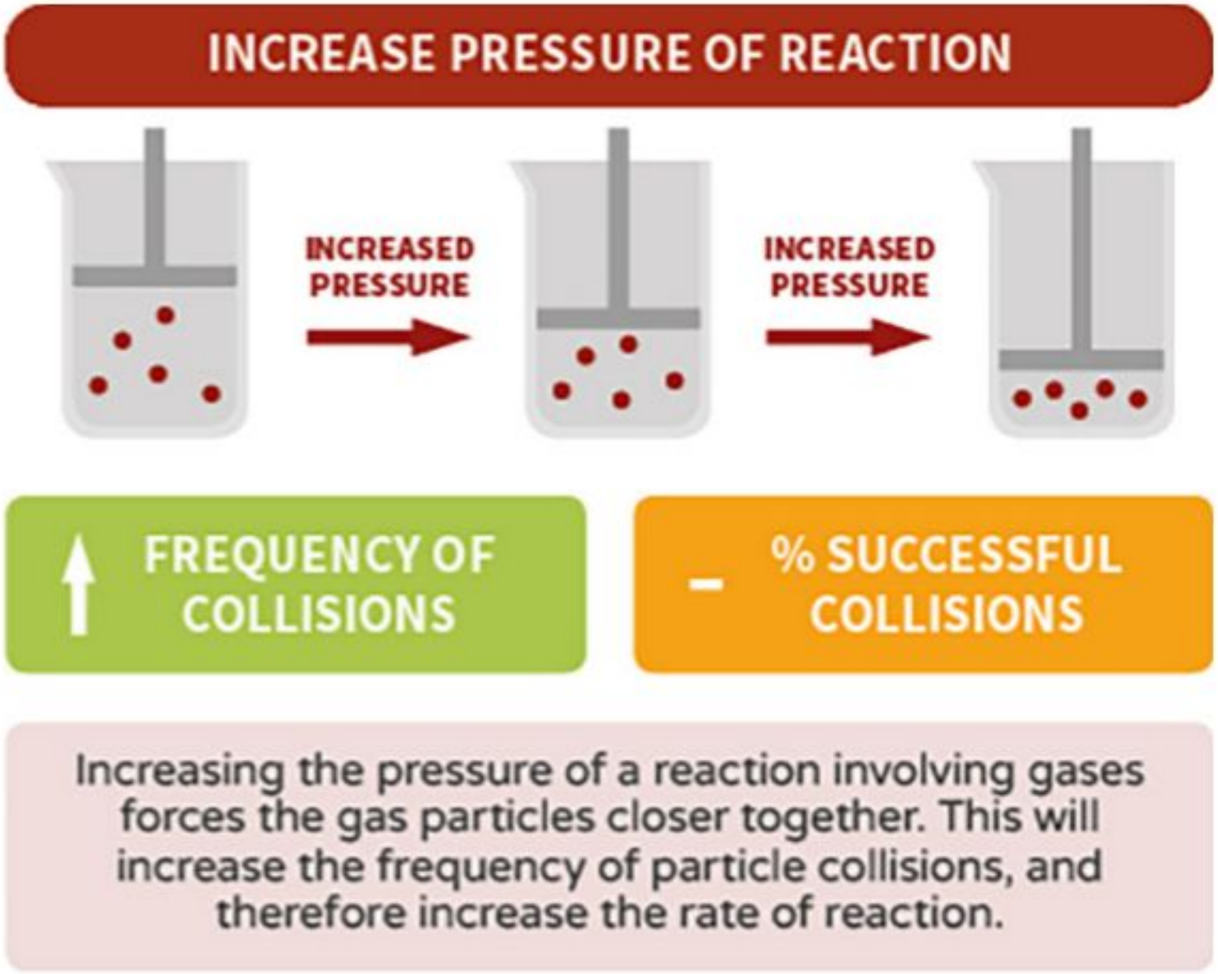
INCREASE CONCENTRATION OF REACTANTS

↑ FREQUENCY OF COLLISIONS

– % SUCCESSFUL COLLISIONS

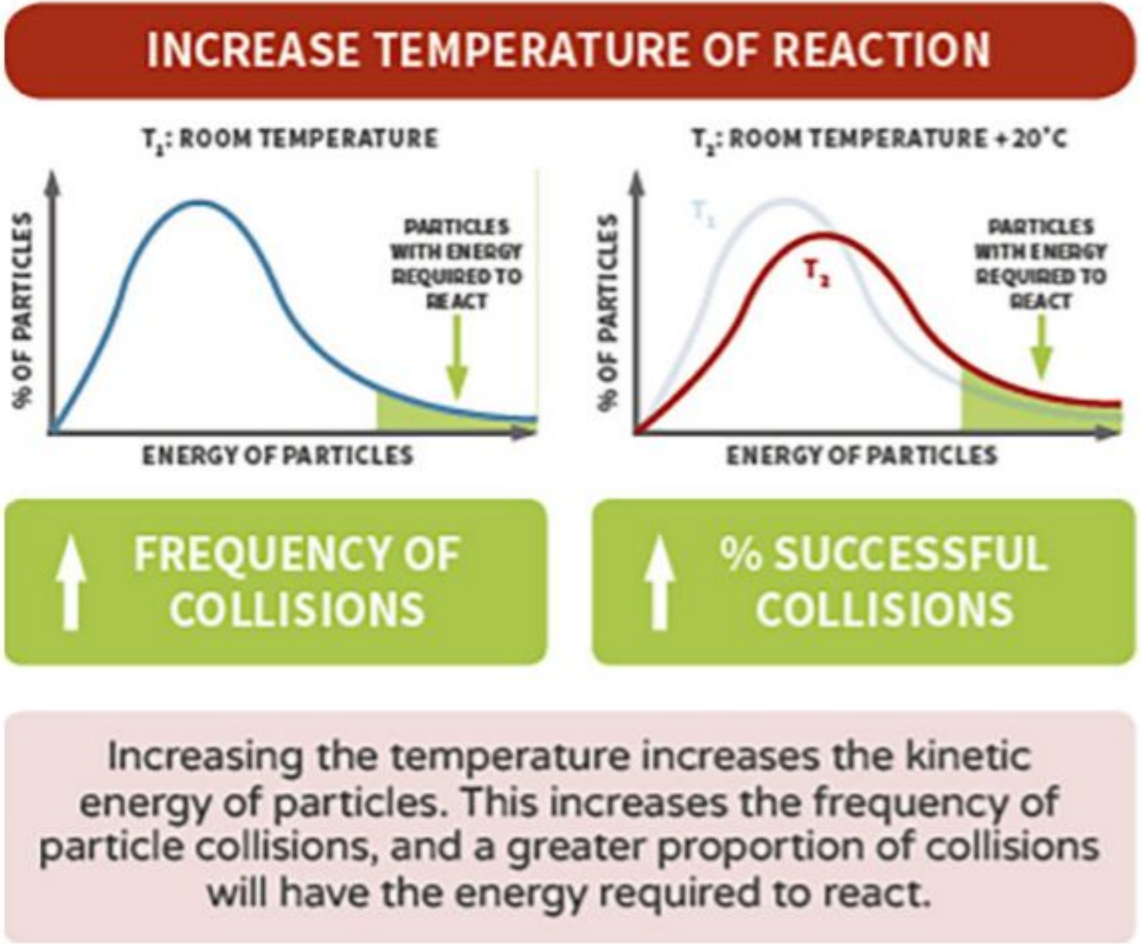
Increasing the concentration of reactants in solution increases the rate of reaction as there are a greater number of particles available to react. This increases the frequency of collisions between particles.

PRESSURE



Increasing the pressure of a reaction involving gases forces the gas particles closer together. This will increase the frequency of particle collisions, and therefore increase the rate of reaction.

Temperature



INCREASE TEMPERATURE OF REACTION

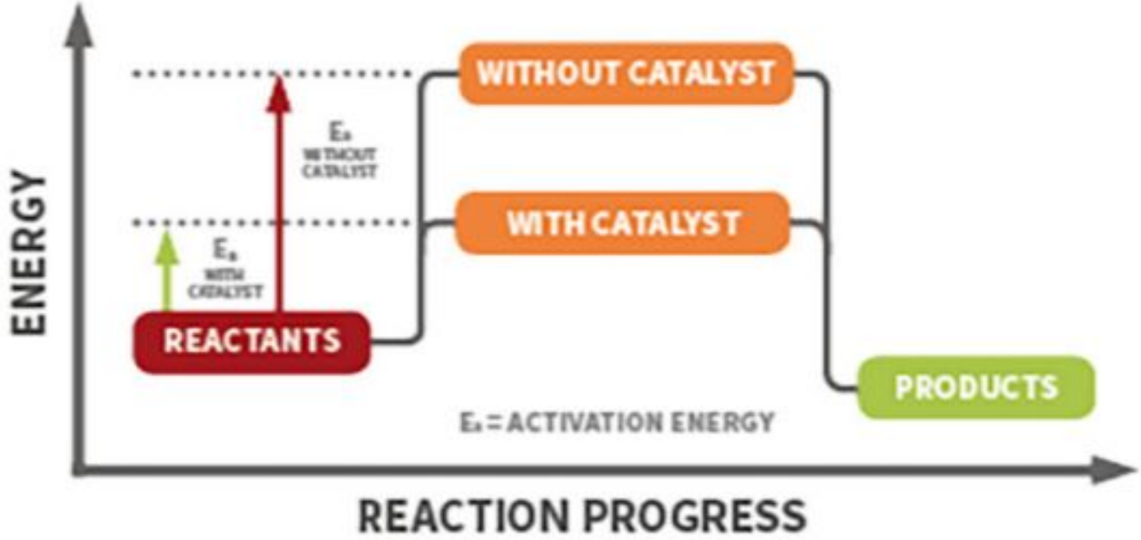
↑ **FREQUENCY OF COLLISIONS**

↑ **% SUCCESSFUL COLLISIONS**

Increasing the temperature increases the kinetic energy of particles. This increases the frequency of particle collisions, and a greater proportion of collisions will have the energy required to react.

Catalysts

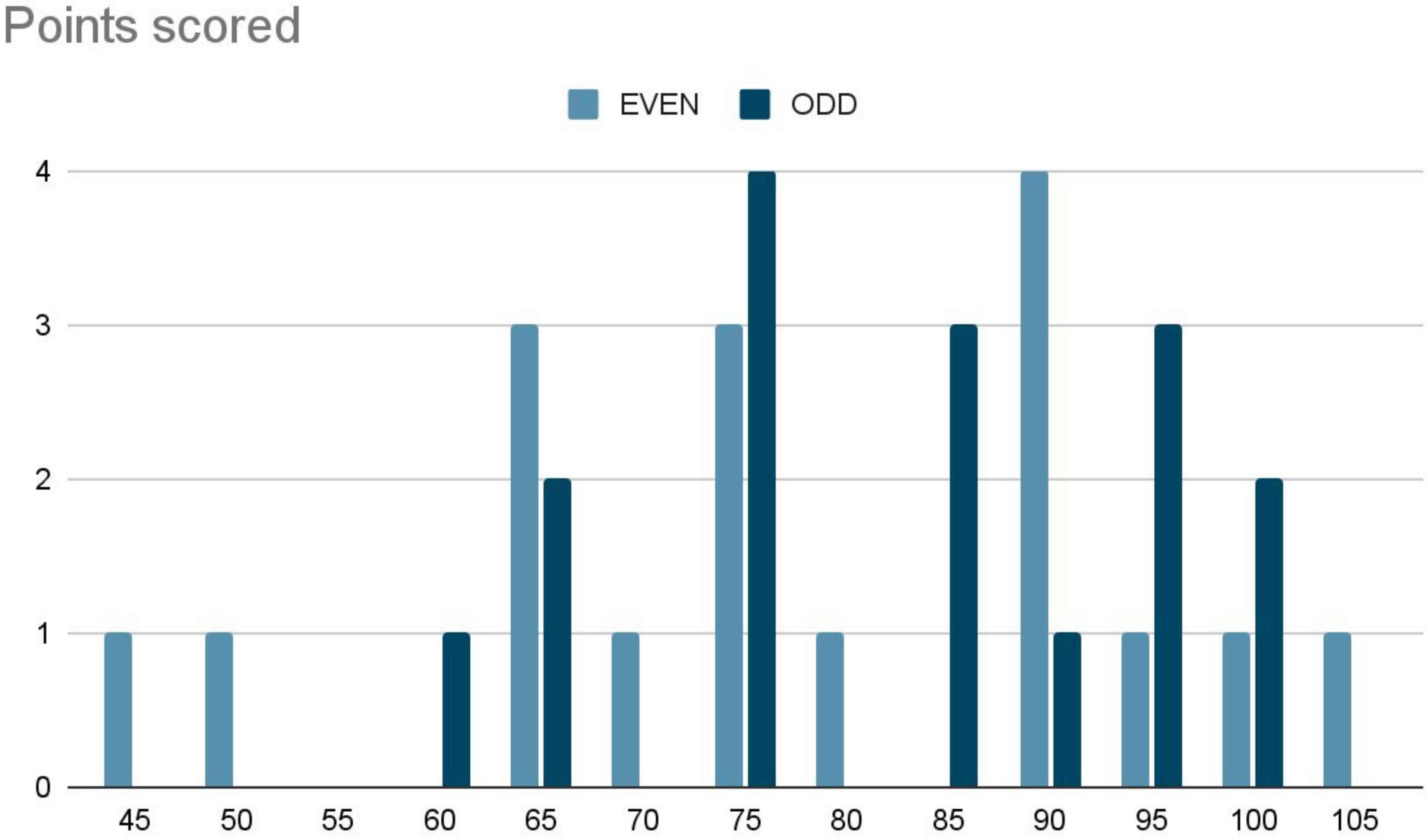
USE A CATALYST IN THE REACTION

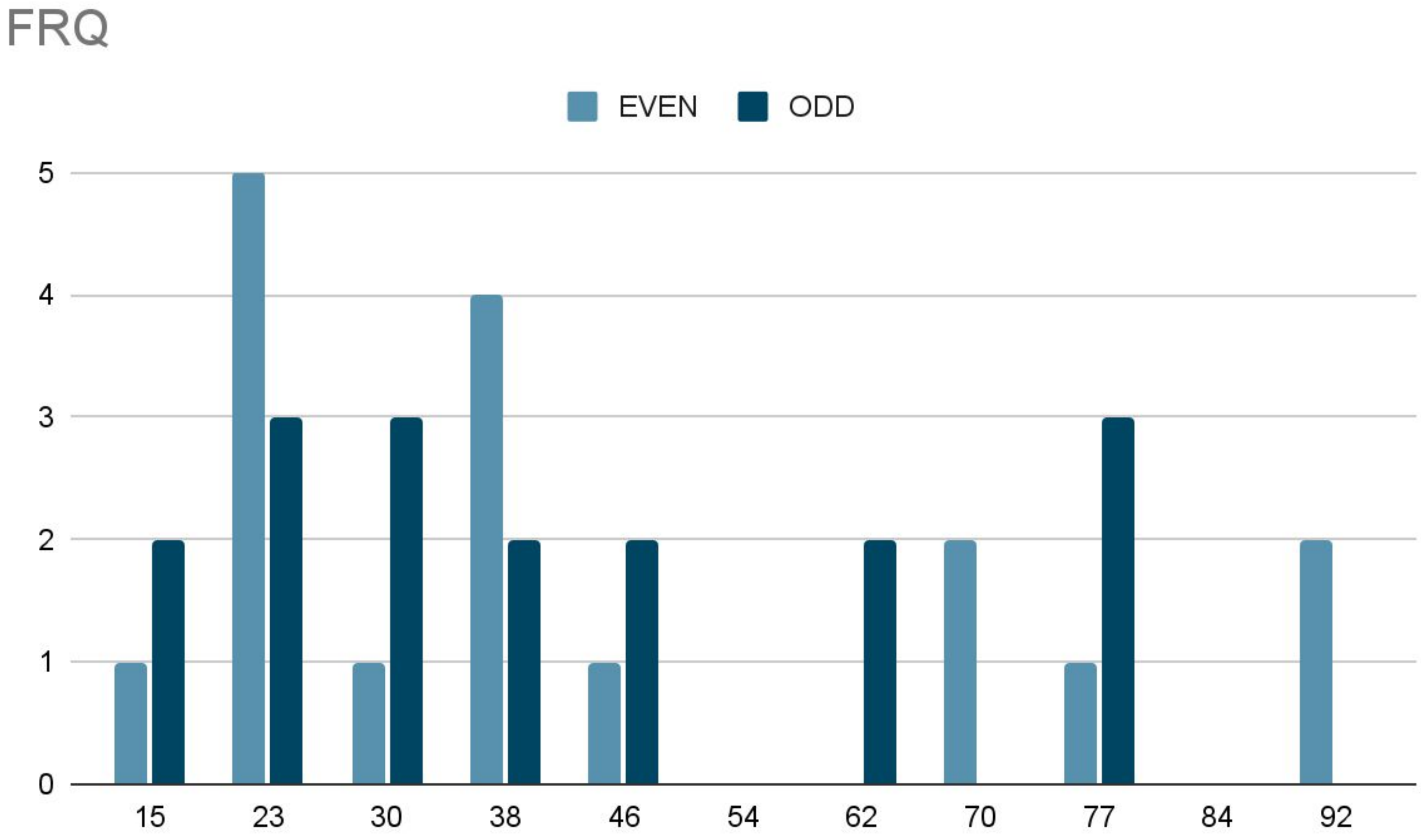


A catalyst provides an alternative route for the reaction, with a lower activation energy. This means that particle collisions need less energy in order for a reaction to occur, increasing the rate of the reaction.

Agenda

- Goal Setting Bellwork
- Test Review
- Finish 5.1-5.2


Points scored
EVEN
ODD
4
3
2
1
0
45
50
55
60
65
70
75
80
85
90
95
100
105


FRQ
EVEN
ODD
5
4
3
2
1
0
15
23
30
38
46
54
62
70
77
84
92

TEST

MCQ: 20

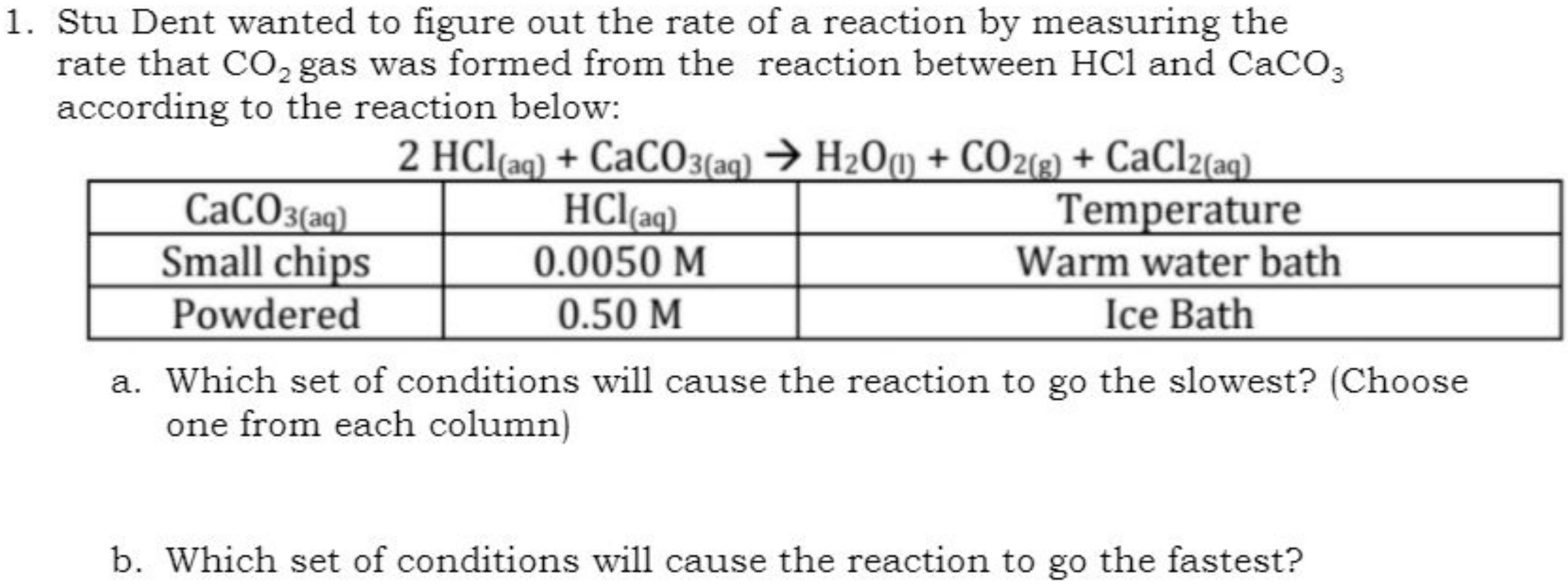
FRQ: 1c, 2b

Test Review and Reflection

REACTION ANALOGY

Work With your Partner to Finish the Hungry Hungry Hippo Packet

TOGETHER



1. Stu Dent wanted to figure out the rate of a reaction by measuring the rate that CO_2 gas was formed from the reaction between HCl and $CaCO_3$ according to the reaction below:

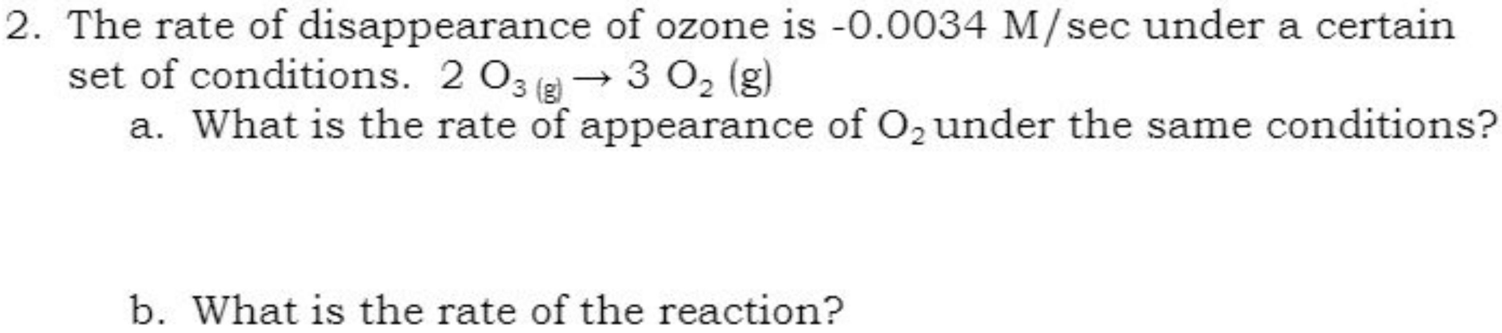
$$2\,HCl_{(aq)} + CaCO_{3(aq)} \rightarrow H_2O_{(l)} + CO_{2(g)} + CaCl_{2(aq)}$$

$CaCO_{3(aq)}$	$HCl_{(aq)}$	Temperature
Small chips	0.0050 M	Warm water bath
Powdered	0.50 M	Ice Bath

   a. Which set of conditions will cause the reaction to go the slowest? (Choose one from each column)

   b. Which set of conditions will cause the reaction to go the fastest?

YOU DO, WE REVIEW



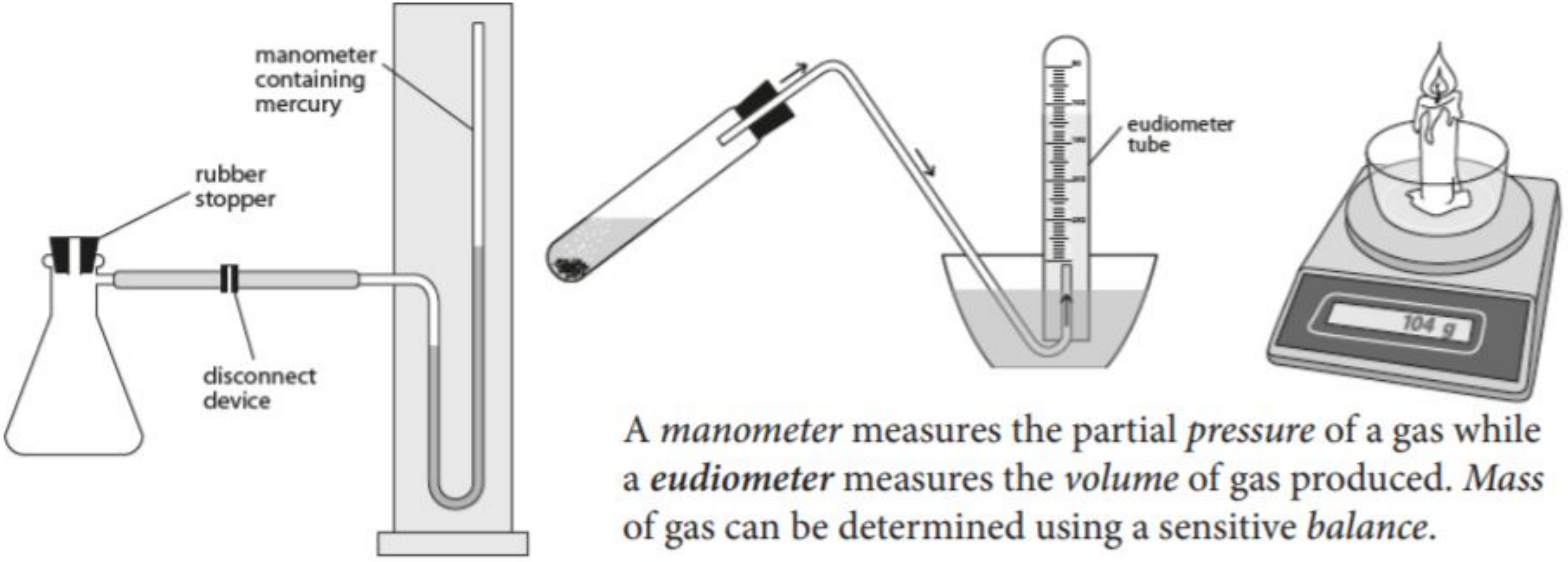
2. The rate of disappearance of ozone is -0.0034 M/sec under a certain set of conditions. $2\ O_{3\,(g)} \rightarrow 3\ O_2\ (g)$
   a. What is the rate of appearance of O_2 under the same conditions?

   b. What is the rate of the reaction?

EXPERIMENTAL METHODS

Rate laws can **only** be deduced from experimental data.

Experimental methods usually involve measuring chemicals which are gases.



A *manometer* measures the partial *pressure* of a gas while a ***eudiometer*** measures the *volume* of gas produced. *Mass* of gas can be determined using a sensitive *balance*.

5.2 Intro to Rate Laws

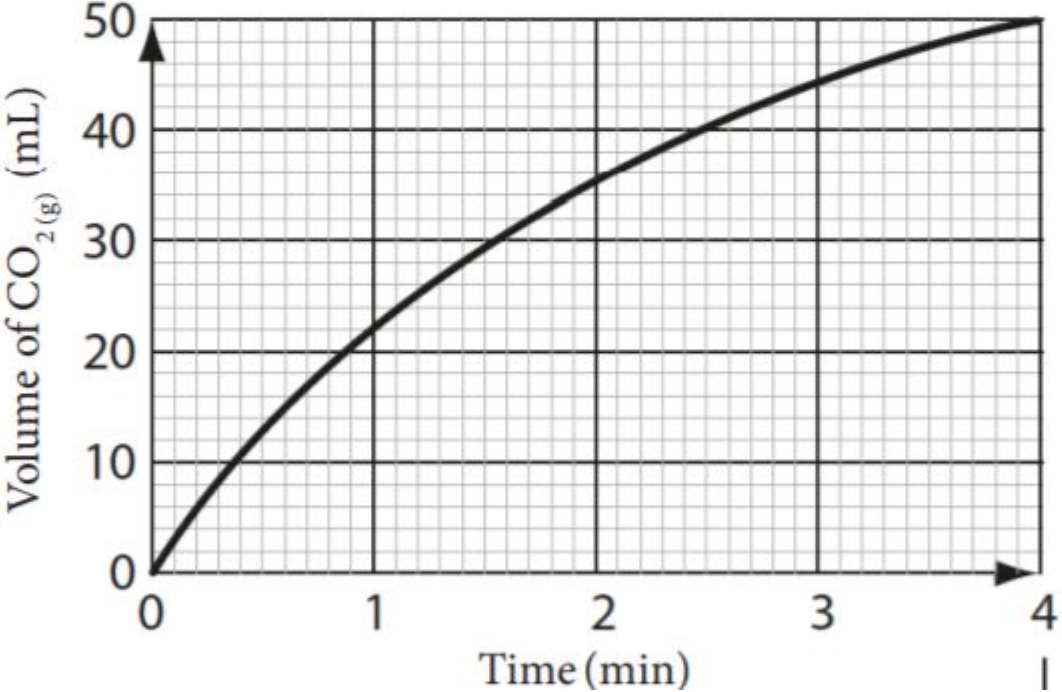
ENDURING UNDERSTANDING:

TRA-3	Some reactions happen quickly, while others happen more slowly and depend on reactant concentrations and temperature.

LEARNING OBJECTIVE:

TRA-3.B	Represent experimental data with a consistent rate law expression.

REACTION RATES



Average Reaction Rates can be calculated from a table of results, but normally require '*relatively large*' time ranges.

Graphs allow *Instantaneous Rates* to be determined for *specific times.*

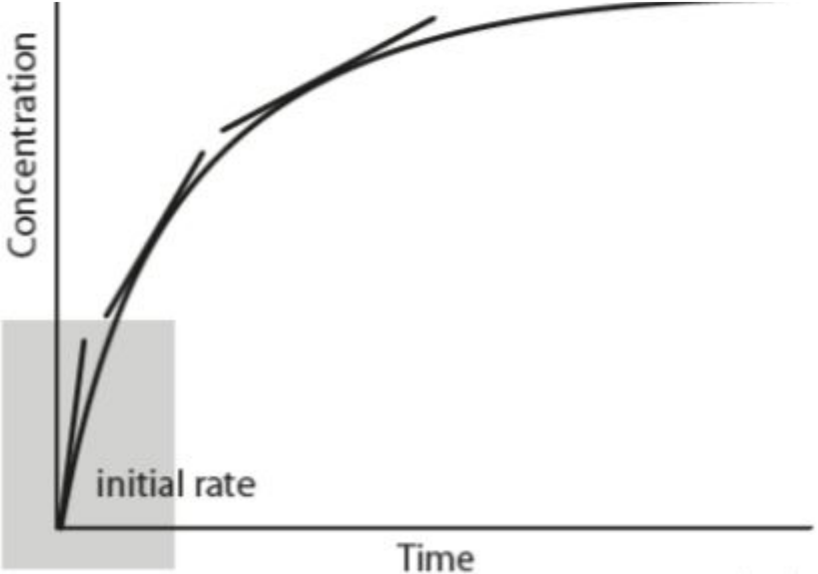
Most useful of all are ***Initial Rates*** - as close to *time = 0* as possible.

INITIAL RATES

The slope of a *tangent line* drawn to the curve at the beginning of a reaction is greater than that of any other tangent.

This slope gives the ***Initial Rate*** of a reaction.

Only at this point can we ***know the concentrations of reacting chemicals*** - *same as the starting concentrations.*



DETERMINING REACTION ORDERS

For all chemical reactions: **Rate ∝ [reactant]**

But rate order says HOW the rate is proportional to the reactant concentration, so: **Rate ∝ $[\text{reactant}]^n$**

Reaction Order	**Rate is proportional to:**	**If we double [reactant]:**
Zeroeth	$[\text{reactant}]^0$	Rate stays the same
First	$[\text{reactant}]^1$	Rate doubles
Second	$[\text{reactant}]^2$	Rate quadruples
Third	$[\text{reactant}]^3$	Rate octuples

EACH REACTANT GETS ITS OWN RATE ORDER

Rate = k [reactant 1]^n [reactant 2]^m

where k = rate constant

n = order with respect to reactant 1

m = order wrt reactant 2

An equation linking concentrations of reactants to the Rate of the reaction are called the **Rate Law.**

Examples

$2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$ Rate = $k[N_2O_5]$

$H_2(g) + I_2(g) \rightarrow 2\ HI(g)$ Rate = $k[H_2][I_2]$

$2NO(g) + 2H_2(g) \rightarrow 2N_2(g) + 2H_2O(g)$ Rate = $k[NO]^2[H_2]$

*Although the exponents in a rate law are sometimes the same as the coefficients in the balanced equation, this is not necessarily the case. **For any reaction, the rate law must be determined experimentally.**

In most rate laws, reaction orders are 0, 1, or 2. However, we also occasionally encounter rate laws in which the reaction order is fractional or even negative. These are rare and outside the scope of the AP exam.

Overall Reaction Order

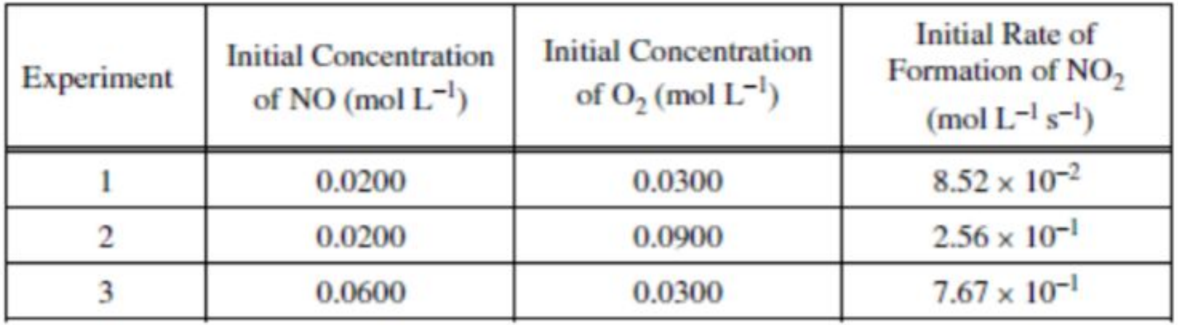
There is also an **overall order** to a reaction (n + m)

Rate = $k[H_2][I_2]$ would be first order wrt H_2, first order wrt I_2, but second order overall.

Rate = $k[NO]^2[H_2]$ is second order wrt NO, first order wrt H_2, but third order overall.

Work Through together!

$$2NO_{(g)} + O_{2\,(g)} \longrightarrow 2NO_{2\,(g)}$$



Experiment	Initial Concentration of NO (mol L^{-1})	Initial Concentration of O_2 (mol L^{-1})	Initial Rate of Formation of NO_2 (mol L^{-1} s^{-1})
1	0.0200	0.0300	8.52×10^{-2}
2	0.0200	0.0900	2.56×10^{-1}
3	0.0600	0.0300	7.67×10^{-1}

a. Determine the order of the reaction with respect to each of the reactants.

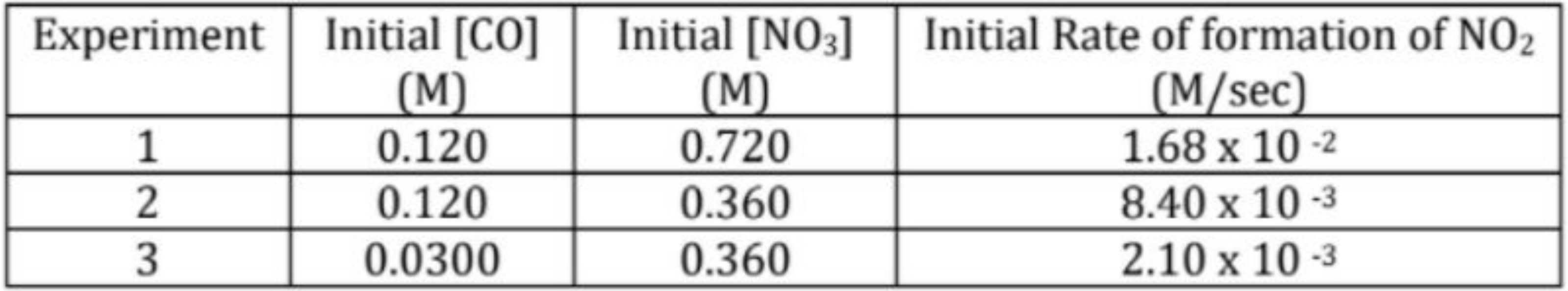
b. Write the expression for the rate law for the reaction as determined from the experimental data.

c. Determine the value of the rate constant for the reaction, clearly indicating the units.

TOGETHER

1. Consider the reaction: $CO_{(g)} + NO_{3(g)} \rightarrow NO_{2(g)} + CO_{2(g)}$

Several experiments were conducted and the data is shown below:



Experiment	Initial [CO] (M)	Initial [NO_3] (M)	Initial Rate of formation of NO_2 (M/sec)
1	0.120	0.720	1.68×10^{-2}
2	0.120	0.360	8.40×10^{-3}
3	0.0300	0.360	2.10×10^{-3}

a. What is the reaction order with respect to CO?

b. What is the reaction order with respect to NO_3?

c. What is the overall reaction order?

d. What is the rate law for this reaction?

e. What is the value of k with units?

You Do, We Review

SCAN ME

2. Consider the reaction: $2NOCl_{(g)} \rightarrow 2NO_{(g)} + Cl_{2(g)}$

The rate law shows that it is a bimolecular reaction: Rate = $k[NOCl]^2$

When the initial concentration of NOCl is 0.391M, the rate is 9.32×10^{-3} M/sec.

a. Find the value for k with units.

b. What will the rate of reaction be when the concentration of NOCl is 0.634M, if the reaction takes place at the same temperature?

Agenda

- Bellwork
- Stoichiometry review
- 5.3
- Relay race
- 5.4

5.3 Concentration Changes Over Time

ENDURING UNDERSTANDING:

TRA-3	Some reactions happen quickly, while others happen more slowly and depend on reactant concentrations and temperature.

LEARNING OBJECTIVE:

TRA-3.C	Identify the rate law expression of a chemical reaction using data that show how the concentrations of reaction species change over time.

First order Reactions

A first-order reaction is one of the most common reactions, radioactive decay, for example, is first order.

- A → product
- rate = $- \Delta[A]/\Delta t$
- rate = $k[A]$
- Combining the two above (setting rate = rate)
  $- \Delta[A]/\Delta t = k[A]$

First order Reactions

Using calculus, we can produce an integrated rate law expression which can be a useful tool when analyzing these reactions.

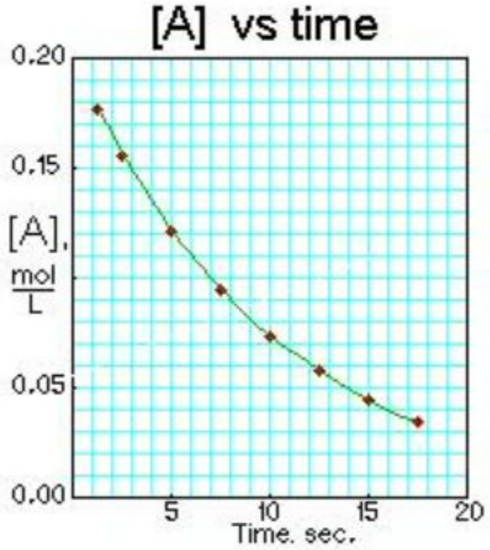
AP Formula Sheet gives you: $\ln[A]_t - \ln[A]_0 = -kt$

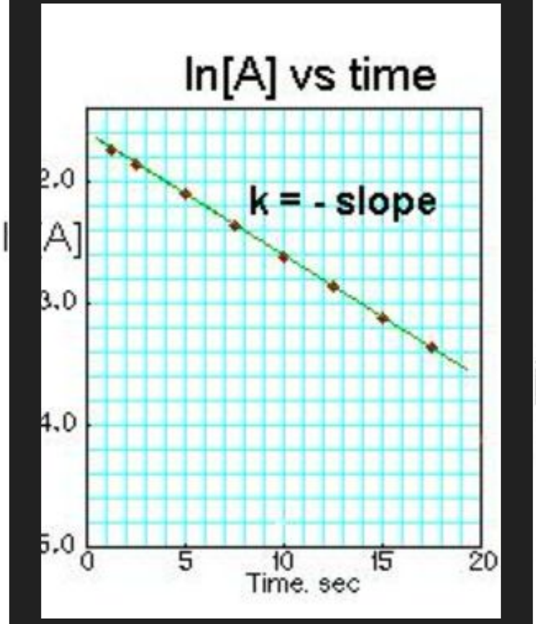
This can be rearranged to: $\ln[A]_t = -kt + \ln[A]_0$

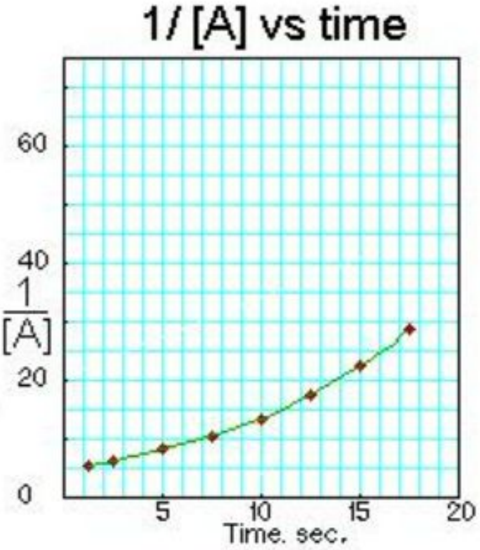
Which takes the form of y = mx + b!

First order Graphs

You are required to identify the following graphs as 1st order. How? For 1st order reactions the ln[A] vs time graph is ALWAYS linear.

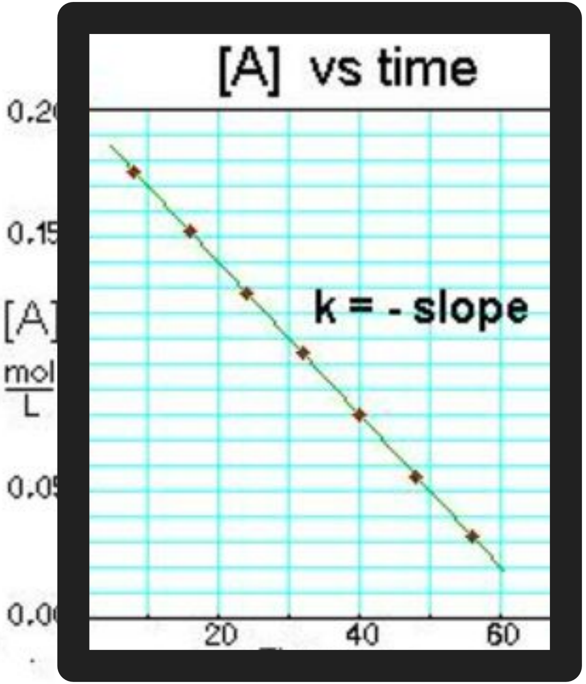




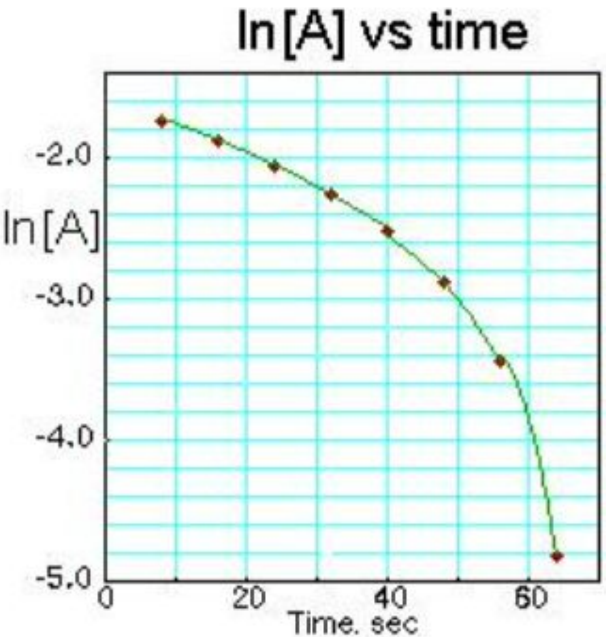


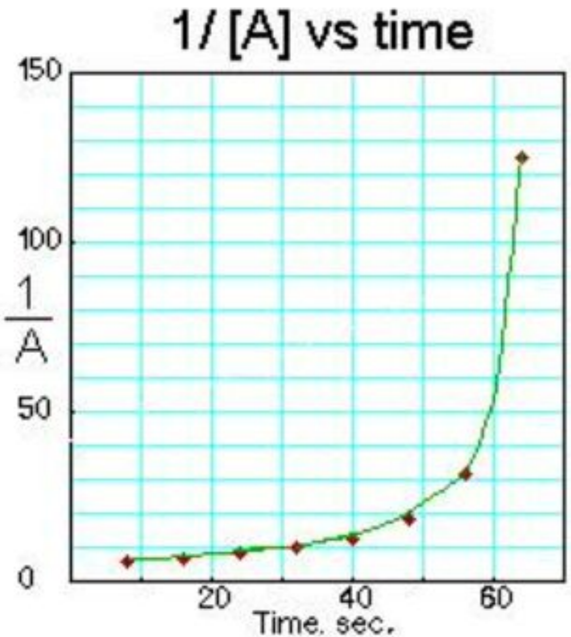
ZEROTH ORDER GRAPHS

The [A] vs time graph is ALWAYS linear for zero order reactions!


[A] vs time

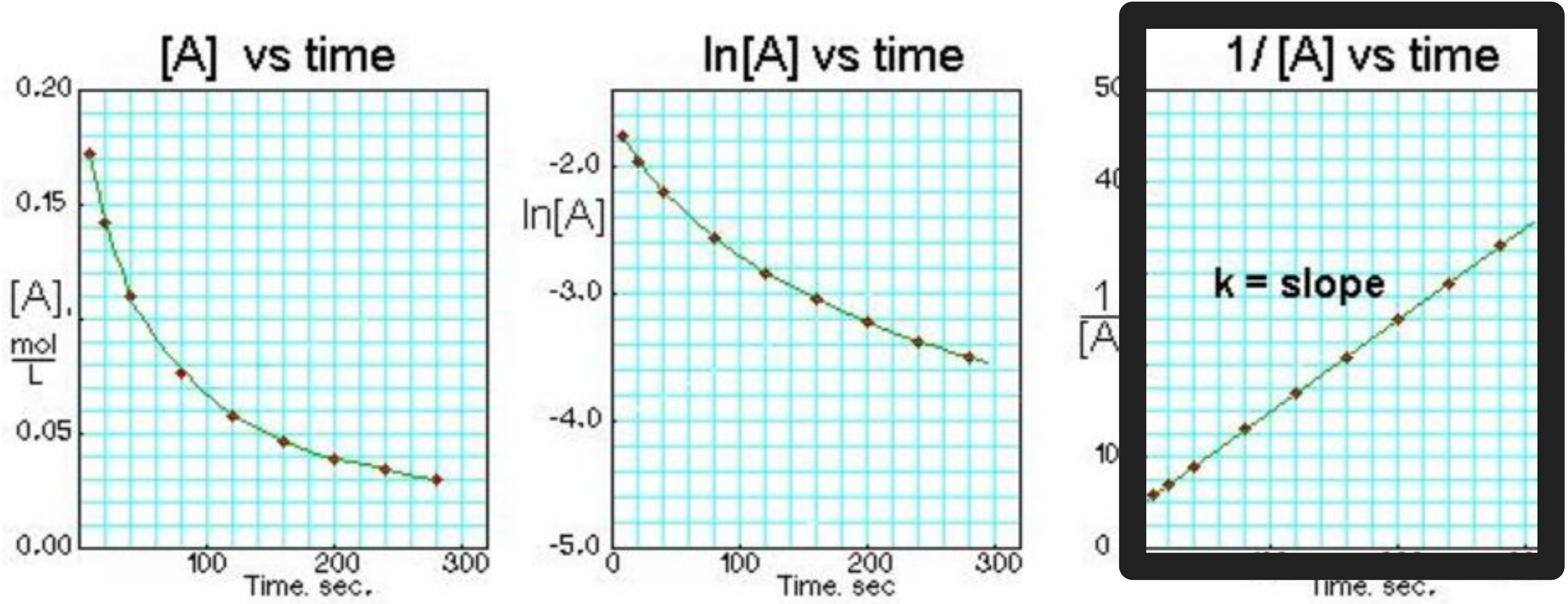
k = - slope


ln[A] vs time


1/ [A] vs time

SECOND ORDER GRAPHS

The 1/[A] vs time graph is ALWAYS linear for second order reactions!



[A] vs time

ln[A] vs time

1/ [A] vs time

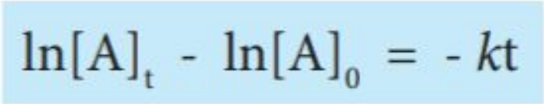
k = slope

INTEGRATED RATE LAW QUESTIONS

The other use for the integrated rate law can be to do calculations relating to:

- how long will it take for the concentration to change to/by ....?
- what will the concentration be after a certain time?

Use the AP Formula Sheet!



$$\ln[A]_t - \ln[A]_0 = -kt$$

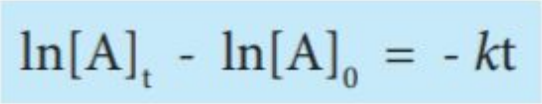
*note that $[A]_0$ does not need to be the initial [A] at the beginning of the experiment, $[A]_t$ and $[A]_0$ can be any two concentrations along the way.

INTEGRATED RATE LAW EXAMPLE

The conversion of cyclopropane (0.25 M) to propene in the gas phase is a first-order reaction with a rate constant of 6.7 x10^{-4} s^{-1} at 500°C.

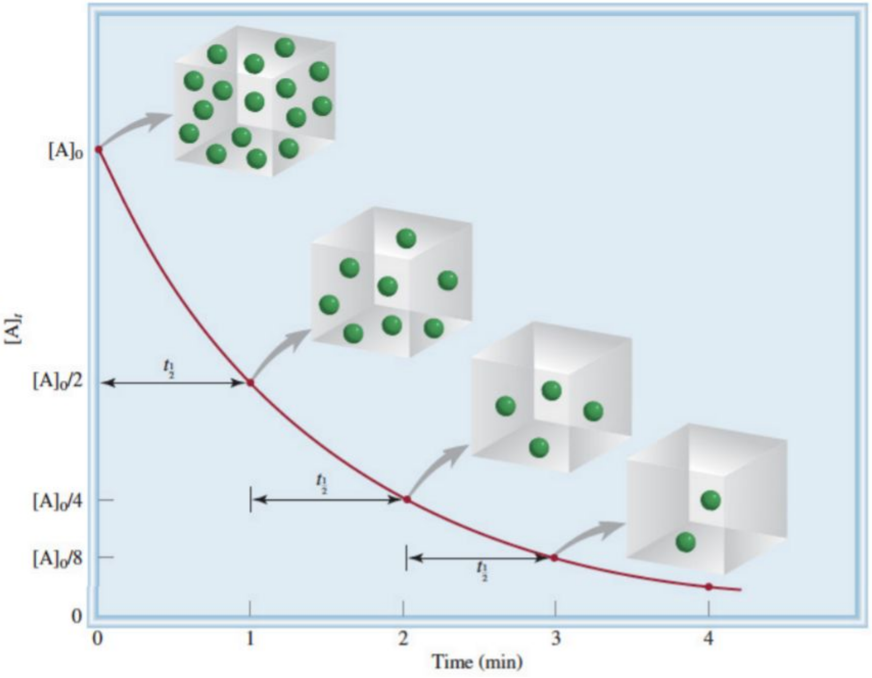
What would be the concentration of cyclopropane after 8.8 min?

*don’t forget to convert to seconds to match k’s units!



$$\ln[A]_t - \ln[A]_0 = -kt$$

First order Reactions - Half life



- The other way that a first-order reaction can be identified is the presence of a regular half life.
- Half-life, t½, is the time required for the concentration of a reactant to decrease to half of its initial concentration.
- In a first-order reaction, subsequent half-lives are always exactly the same time as the initial half-life allowing first-order reactions to be deduced simply by inspecting graph.

Half life and Rate constant

The shorter the half-life, the faster the reaction.

The higher the rate constant, the faster the reaction.

Can we link the two?

Start with the modified integrated rate law:

$$\ln[A_t / A_0] = -kt$$

at half-life $t = t_{½}$ and $[A_t] = ½\,[A_0]$ so

$$\ln[½\,A_0 / A_0] = -kt_{½}$$

$$\ln[½] = -kt_{½}$$

$$-0.693 = -kt_{½}$$

$$t_{½} = 0.693 / k$$

Equation is on the AP Formula sheet.

Used to calculate half life OR k.

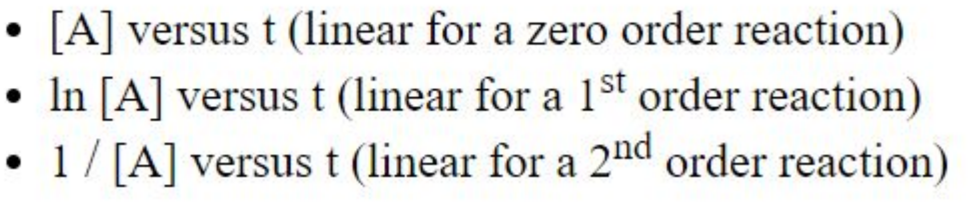
Half Life Example

The decomposition of ethane (C_2H_6) to methyl radicals is a first-order reaction with a rate constant of $5.36 \times 10^{-4}\ s^{-1}$ at 700°C.

Calculate the half-life of the reaction in minutes.

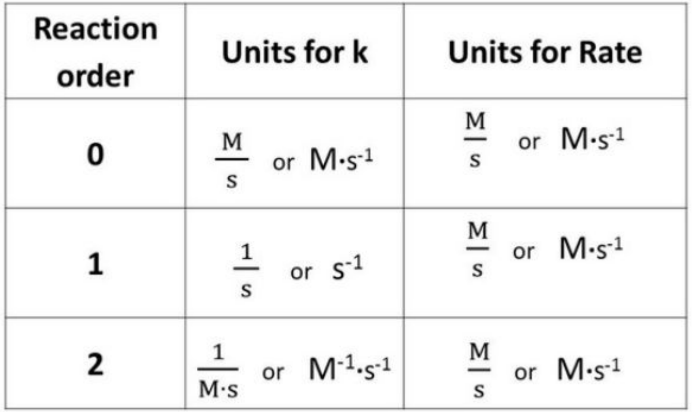
Summary (make flashcards of this slide)

Which graph is linear?



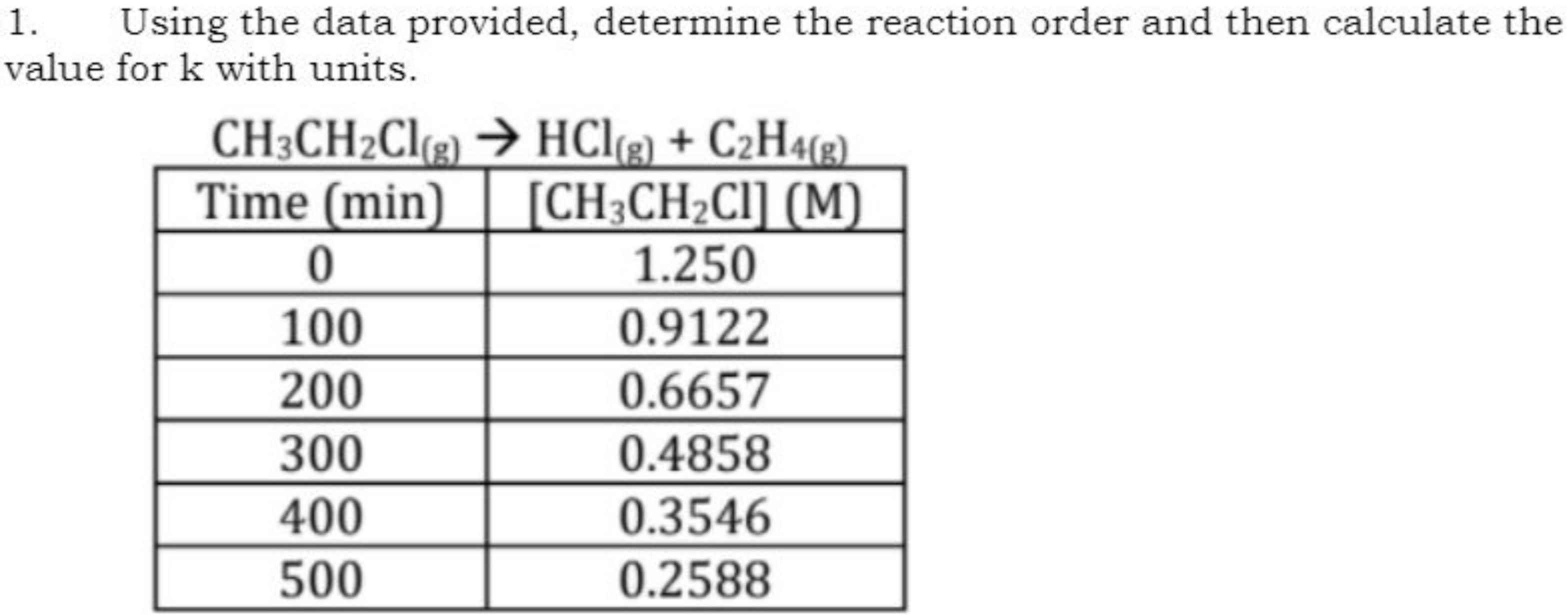
- [A] versus t (linear for a zero order reaction)
- ln [A] versus t (linear for a 1st order reaction)
- 1 / [A] versus t (linear for a 2nd order reaction)

What are the rate constant units?



Reaction order	Units for k	Units for Rate
0	$\frac{M}{s}$ or $M \cdot s^{-1}$	$\frac{M}{s}$ or $M \cdot s^{-1}$
1	$\frac{1}{s}$ or s^{-1}	$\frac{M}{s}$ or $M \cdot s^{-1}$
2	$\frac{1}{M \cdot s}$ or $M^{-1} \cdot s^{-1}$	$\frac{M}{s}$ or $M \cdot s^{-1}$

TOGETHER



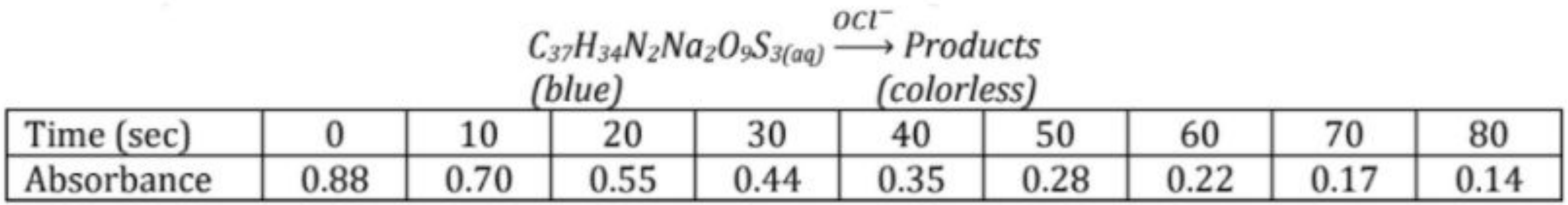
1. Using the data provided, determine the reaction order and then calculate the value for k with units.

$CH_3CH_2Cl_{(g)} \rightarrow HCl_{(g)} + C_2H_{4(g)}$

Time (min)	$[CH_3CH_2Cl]$ (M)
0	1.250
100	0.9122
200	0.6657
300	0.4858
400	0.3546
500	0.2588

YOU DO, WE REVIEW

2. The decomposition of blue dye using bleach was studied. The concentration of bleach was 1.13 M, while the concentration of the blue dye was 6.2 x 10^{-6} M. The reaction was monitored by measuring the absorbance at 630 nm.



$$\underset{\text{(blue)}}{C_{37}H_{34}N_2Na_2O_9S_{3(aq)}} \xrightarrow{OCl^-} \underset{\text{(colorless)}}{\text{Products}}$$

Time (sec)	0	10	20	30	40	50	60	70	80
Absorbance	0.88	0.70	0.55	0.44	0.35	0.28	0.22	0.17	0.14

Based on the information provided, what is the reaction order? Explain.

5.4 Elementary Reactions

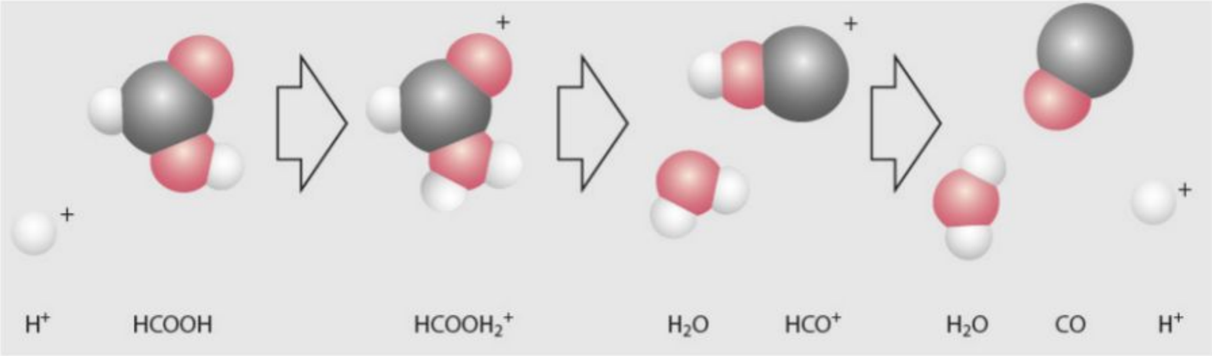
ENDURING UNDERSTANDING:	
TRA-4	There is a relationship between the speed of a reaction and the collision frequency of particle collisions.

LEARNING OBJECTIVE:	
TRA-4.A	Represent an elementary reaction as a rate law expression using stoichiometry.

ELEMENTARY REACTIONS

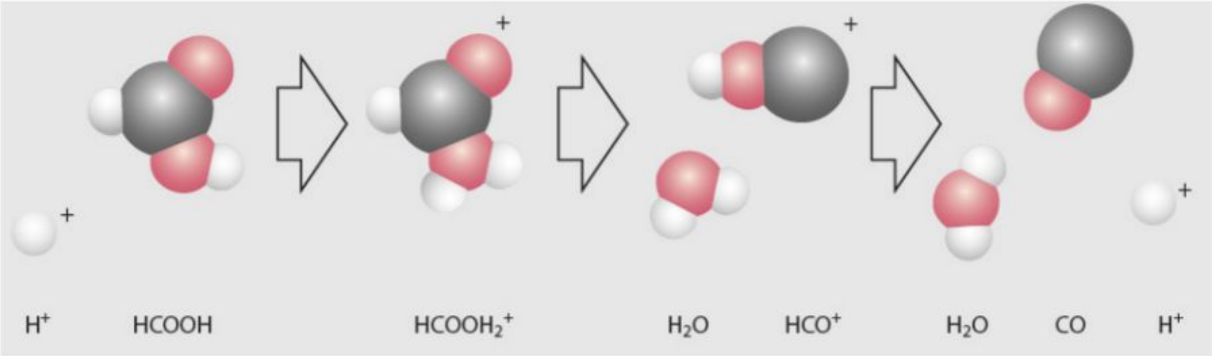
An overall balanced chemical equation does not tell us much about how a reaction actually takes place. In many cases, it merely represents the sum of several **elementary steps.**

Elementary reactions are a series of simple reactions that represent the progress of the overall reaction at the molecular level.



REACTION MECHANISMS

The term for the sequence of elementary steps that leads to product formation is **reaction mechanism.**

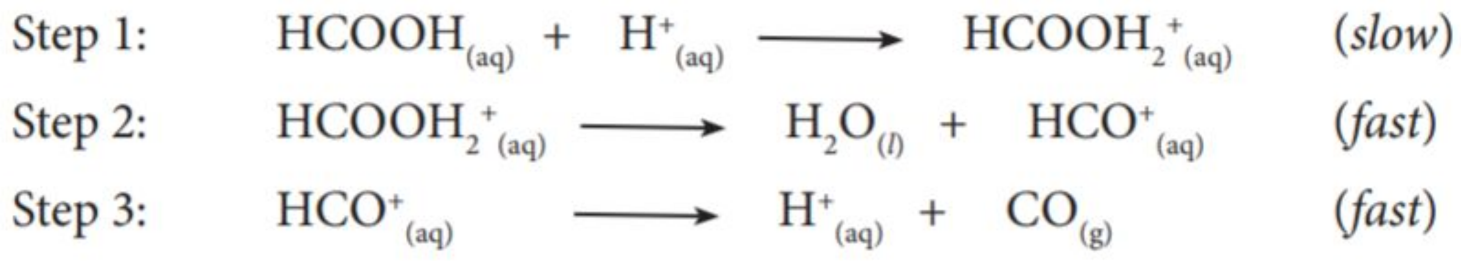


Step 1: $HCOOH_{(aq)} + H^+_{(aq)} \longrightarrow HCOOH_2^+{}_{(aq)}$ (*slow*)

Step 2: $HCOOH_2^+{}_{(aq)} \longrightarrow H_2O_{(l)} + HCO^+_{(aq)}$ (*fast*)

Step 3: $HCO^+_{(aq)} \longrightarrow H^+_{(aq)} + CO_{(g)}$ (*fast*)

REACTION MECHANISM PIECES



Step 1: $HCOOH_{(aq)} + H^{+}_{(aq)} \longrightarrow HCOOH_{2}^{+}{}_{(aq)}$ (*slow*)

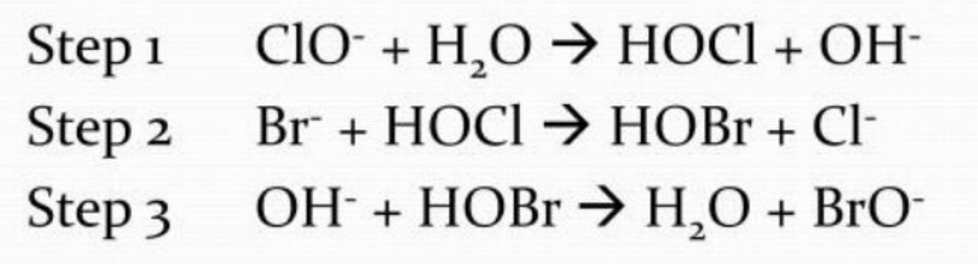
Step 2: $HCOOH_{2}^{+}{}_{(aq)} \longrightarrow H_{2}O_{(l)} + HCO^{+}_{(aq)}$ (*fast*)

Step 3: $HCO^{+}_{(aq)} \longrightarrow H^{+}_{(aq)} + CO_{(g)}$ (*fast*)

Overall reaction:

- $H^{+}_{(aq)}$ consumed in Step 1 is reformed in Step 3 - it is a **catalyst.**
- species such as $HCOOH_{2}^{+}$ and HCO^{+} that are not reactants or products (they are formed and then consumed) are **reaction intermediates.**

Example



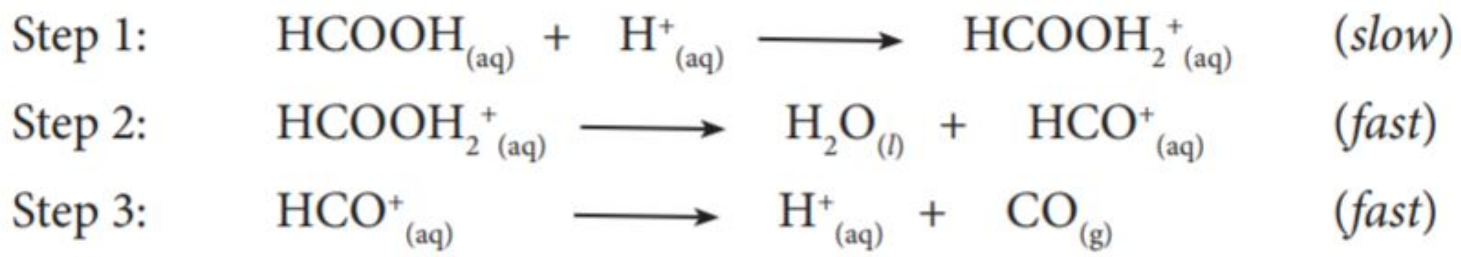
Step 1 $ClO^- + H_2O \rightarrow HOCl + OH^-$

Step 2 $Br^- + HOCl \rightarrow HOBr + Cl^-$

Step 3 $OH^- + HOBr \rightarrow H_2O + BrO^-$

1. What is the overall reaction?
2. Identify any catalysts.
3. Identify the intermediates.

RATE DETERMINING STEP



Step 1: $HCOOH_{(aq)} + H^+_{(aq)} \longrightarrow HCOOH_2^+{}_{(aq)}$ (*slow*)

Step 2: $HCOOH_2^+{}_{(aq)} \longrightarrow H_2O_{(l)} + HCO^+_{(aq)}$ (*fast*)

Step 3: $HCO^+_{(aq)} \longrightarrow H^+_{(aq)} + CO_{(g)}$ (*fast*)

Overall reaction:

- The slow step is the **rate determining step.**
- $H^+_{(aq)}$ does not appear in the overall equation, however it is part of the slow step so will be part of the Rate Law: **rate = k[HCOOH][H^+]**

RATE DETERMINING STEP

- If the first step is slow, then the overall rate for the reaction will be based on the stoichiometry of the first elementary reaction.

$$A + A \rightarrow B \text{ (slow)}$$
$$B + C \rightarrow D \text{ (fast)}$$
$$\text{Rate} = k\,[A]^2$$

- If a subsequent elementary reaction is slow, then you have to add all the reactants up to the slowest step and cancel any intermediates to determine the rate of reaction.

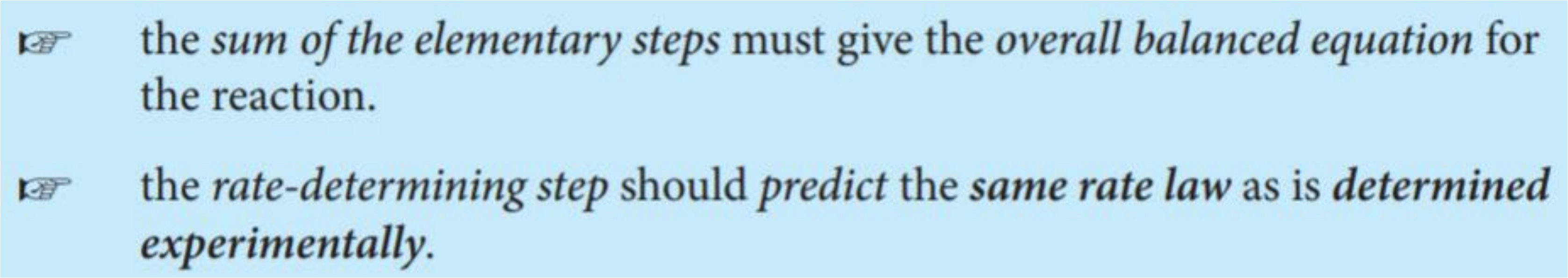
$$A + A \rightarrow B \text{ (fast)}$$
$$B + C \rightarrow D \text{ (slow)}$$
$$\text{Rate} = k\,[A]^2[C]$$

PROPOSING REACTION MECHANISMS

Studies of reaction mechanisms begin with the collection of data (rate measurements).

Next, the data is analysed to determine the rate constant and order of the reaction, and the rate law.

Finally, a plausible mechanism for the reaction can be suggested in terms of elementary steps. The elementary steps must satisfy two requirements:



☞ the *sum of the elementary steps* must give the *overall balanced equation* for the reaction.

☞ the *rate-determining step* should *predict* the ***same rate law*** as is ***determined experimentally***.

Example

The decomposition of hydrogen peroxide is catalysed by iodide ions.

The overall reaction is **$2H_2O_{2(aq)} \rightarrow 2H_2O_{(l)} + O_{2(g)}$**

By experiment, the rate law is found to be **rate = $k[H_2O_2][I^-]$**

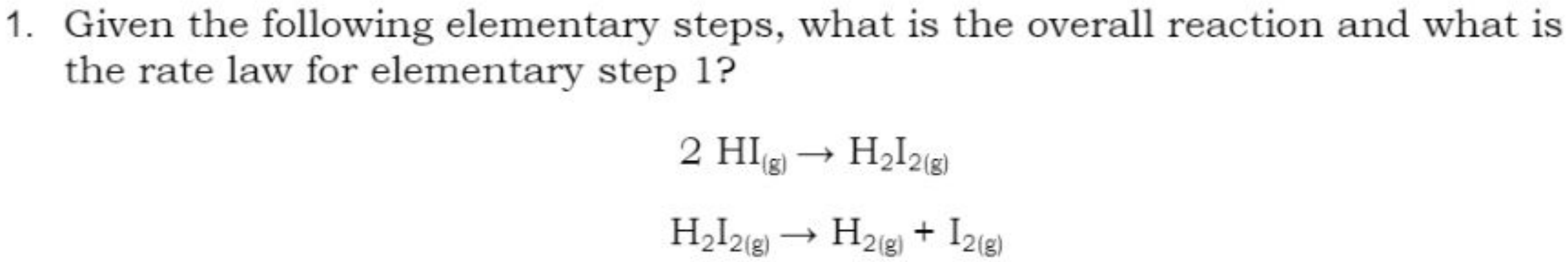
Proposed mechanism:

Step 1: $H_2O_{2(aq)} + I^-_{(aq)} \longrightarrow H_2O_{(l)} + IO^-_{(aq)}$

Step 2: $H_2O_{2(aq)} + IO^-_{(aq)} \longrightarrow H_2O_{(l)} + O_{2(g)} + I^-_{(aq)}$

What is the rate determining (slow) step?

Together

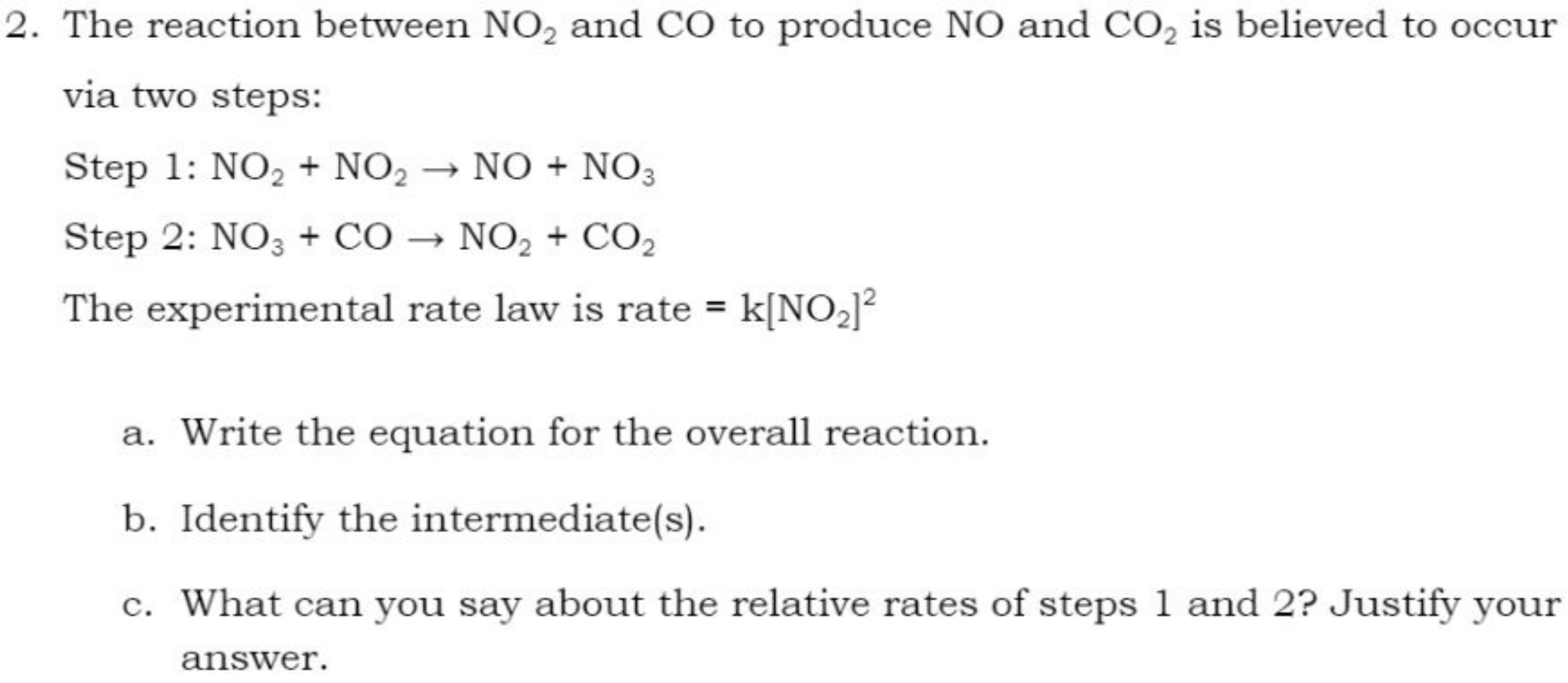


1. Given the following elementary steps, what is the overall reaction and what is the rate law for elementary step 1?

$$2\ HI_{(g)} \rightarrow H_2I_{2(g)}$$

$$H_2I_{2(g)} \rightarrow H_{2(g)} + I_{2(g)}$$

YOU DO, WE REVIEW



2. The reaction between NO_2 and CO to produce NO and CO_2 is believed to occur via two steps:

Step 1: $NO_2 + NO_2 \rightarrow NO + NO_3$

Step 2: $NO_3 + CO \rightarrow NO_2 + CO_2$

The experimental rate law is rate = $k[NO_2]^2$

a. Write the equation for the overall reaction.

b. Identify the intermediate(s).

c. What can you say about the relative rates of steps 1 and 2? Justify your answer.

Agenda

- Bellwork
- 5.5
- 5.6
- Crystal Violet Lab

5.5 Collision Model

ENDURING UNDERSTANDING:

TRA-4	There is a relationship between the speed of a reaction and the collision frequency of particle collisions.

LEARNING OBJECTIVE:

TRA-4.B	Explain the relationship between the rate of an elementary reaction and the frequency, energy, and orientation of molecular collisions.

COLLISION MODEL

Molecules must collide to react.

The greater the number of collisions per second, the greater the reaction rate.

As reactant concentration increases, therefore, the number of collisions increases, leading to an increase in reaction rate.

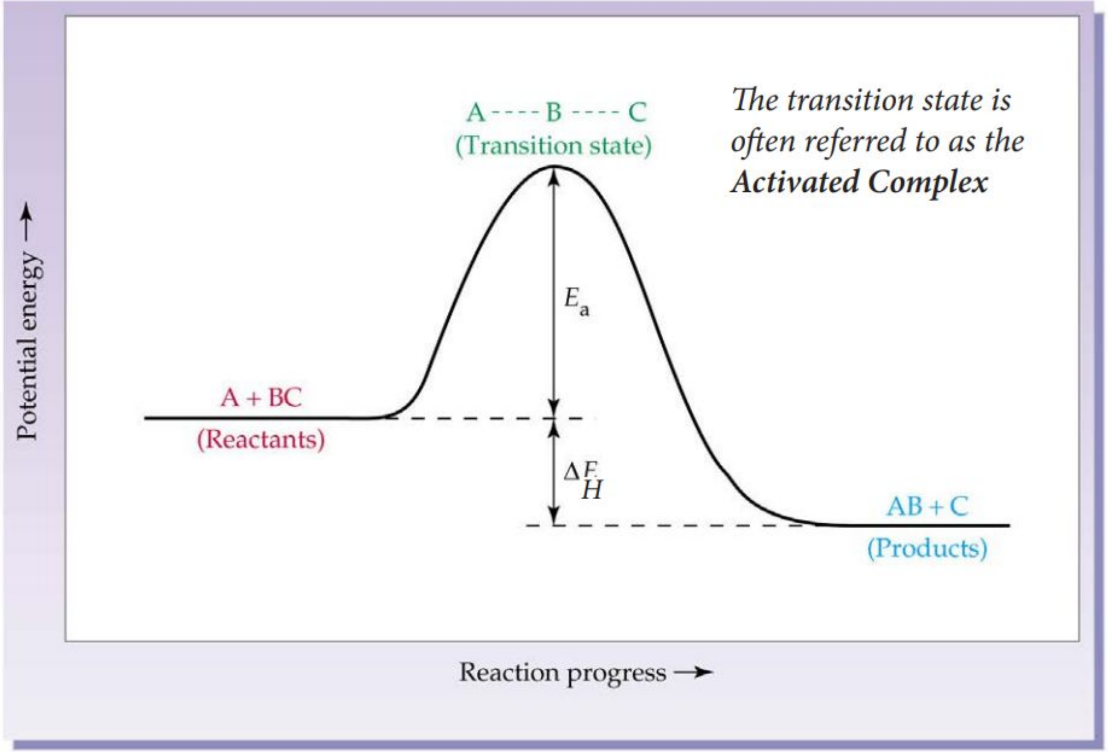
COLLISION MODEL

Collision theory states that in order for a reaction to take place the following things must occur:

1. Particles must collide. (The **rate of the reaction is dependent of the frequency of the collisions**)
2. They must have sufficient energy. (This is known as the **activation energy** and corresponds to the amount of energy needed to break the requisite bonds)
3. The particles must be in the **correct orientation**. (Certain parts on one molecule and certain parts on another molecule must meet in order for the reaction to occur)

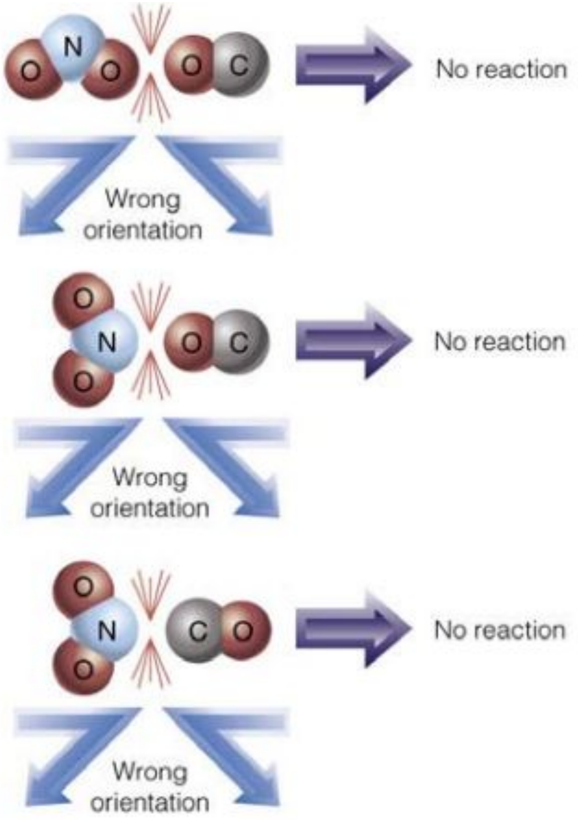
ACTIVATION ENERGY

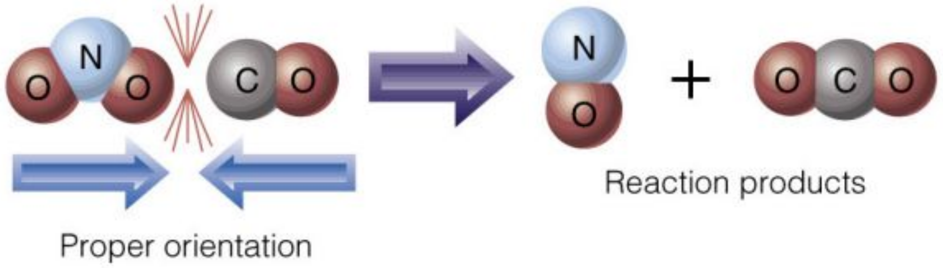
If sufficient kinetic energy → potential energy then the molecules will be able to form a **transition state** in which reactant bonds will be breaking and product bonds will be forming.



The transition state is often referred to as the ***Activated Complex***

Orientation





Even when molecules collide with sufficient energy, activation energy or above, a successful collision is not guaranteed.

In most reactions, molecules must be oriented in a certain way during collision for a reaction to occur.

COLLISIONS

Collisions occur all the time but not all collisions result in a reaction.

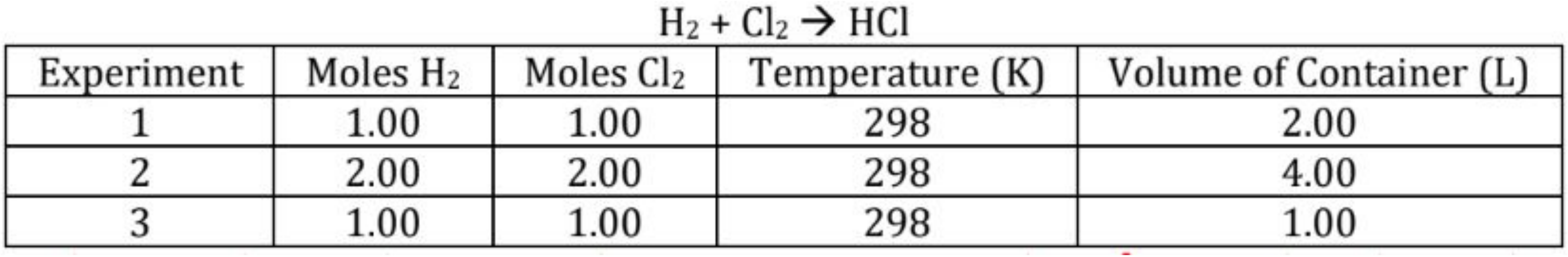
This helps us to explain why a **bimolecular** reaction can occur, because the chance of two molecules colliding is high, but why a **trimolecular** (or higher) reaction is unlikely to occur as three particles colliding simultaneously is much more unlikely.

FACTORS AFFECTING REACTION RATE (WE SAW THESE IN 5.1)

- Increase Surface Area → Increase Reaction Rate
- Increase Concentration → Increase Reaction Rate
- Increase Pressure → Increase Reaction Rate
- Increase Temperature → Increase Reaction Rate
- Add a catalyst → Increase Reaction Rate

TOGETHER

Given the following reaction, which set of reaction conditions will result in the highest reaction rate? Explain in terms of collision theory.

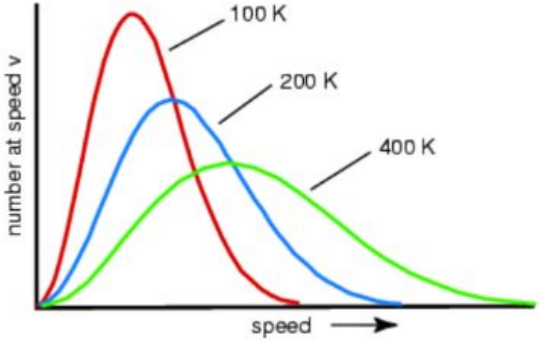


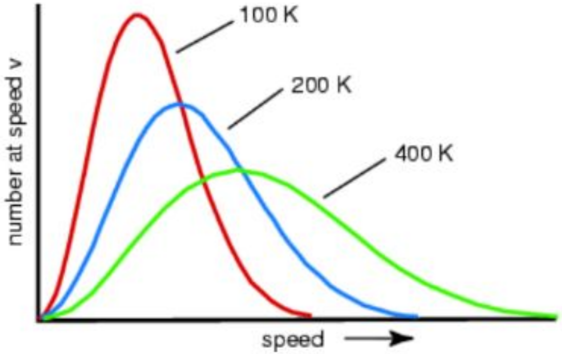
$H_2 + Cl_2 \rightarrow HCl$

Experiment	Moles H_2	Moles Cl_2	Temperature (K)	Volume of Container (L)
1	1.00	1.00	298	2.00
2	2.00	2.00	298	4.00
3	1.00	1.00	298	1.00

YOU DO, WE REVIEW

The graph below shows a Maxwell-Boltzmann distribution for a reaction at three temperatures.





a. On the first graph add a vertical line to represent very low activation energy.

b. On the second graph add a vertical line to represent high activation energy.

c. Explain why you don’t see a large increase to the reaction rate when the temperature is increased if the activation energy is low.

5.6 Reaction Profile Diagram

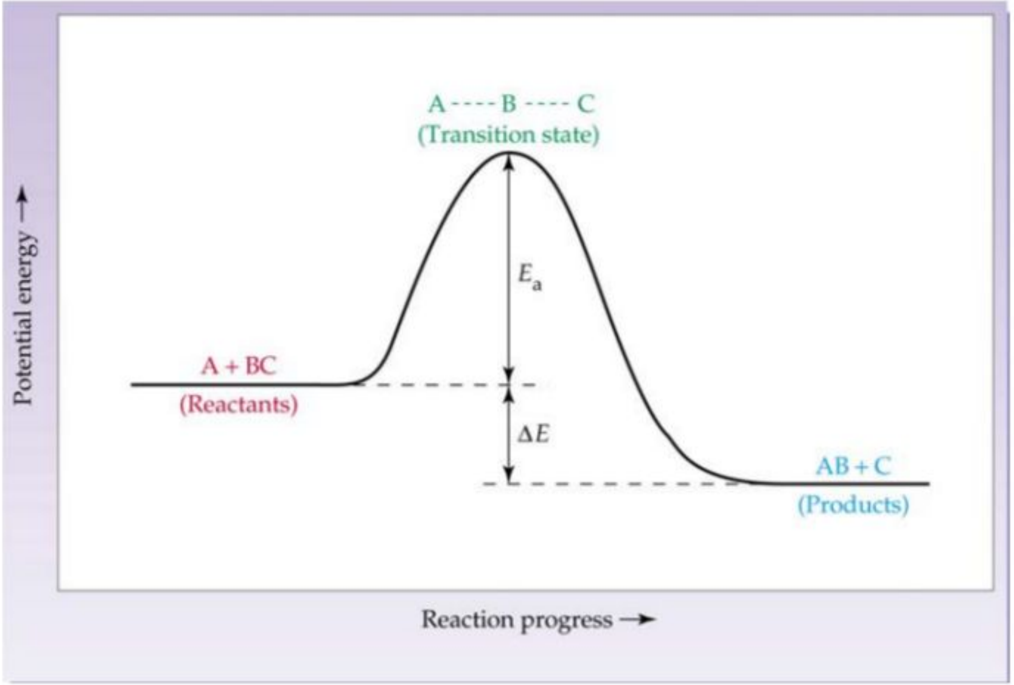
ENDURING UNDERSTANDING:	
TRA-4	There is a relationship between the speed of a reaction and the collision frequency of particle collisions
LEARNING OBJECTIVE:	
TRA-4.C	Represent the activation energy and the overall energy change in an elementary reaction using a reaction energy profile

REACTION PROFILE

Reaction energy profiles are a way to graphically represent a reaction.

The Y-axis is generally the potential energy (often in kJ/mol) and the X-axis is the reaction coordinate, which shows the progress of the reaction.

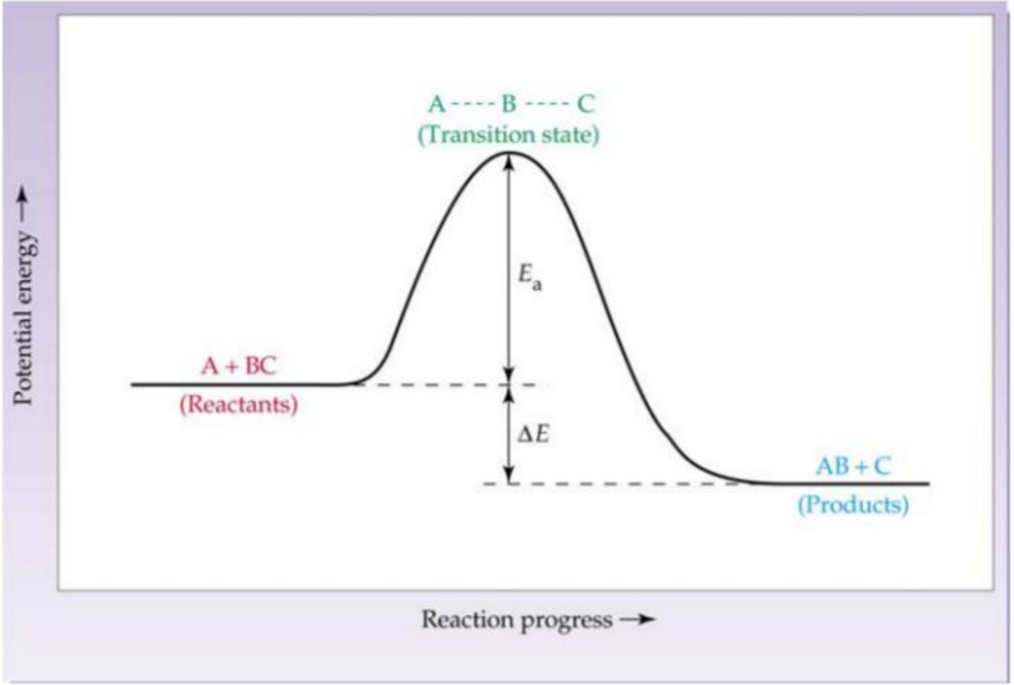
The graph shows the energy of the chemicals as the reaction proceeds from reactants to products.



ACTIVATION ENERGY

Collision theory says for a reaction to occur, a collision between molecules must occur with the correct orientation of molecules and with sufficient energy.

This energy, known as the **activation energy**, is determined by the energy of the **transition state**, also known as the **activated complex**.

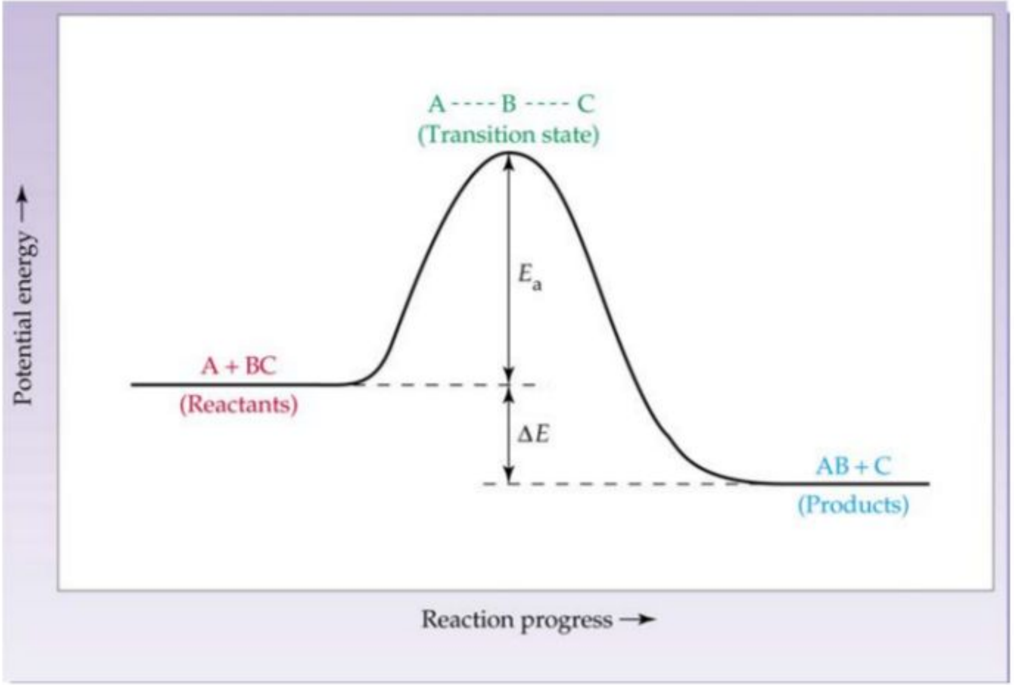


TRANSITION STATE (ACTIVATED COMPLEX)

The transition state is the intermediate point between two stable compounds.

When reactants **collide with enough energy**, they can proceed over this transition state energy hump to the products.

If the energy of a transition state is greater, the reaction rate will be slower because fewer collisions will have enough energy to pass this hump.



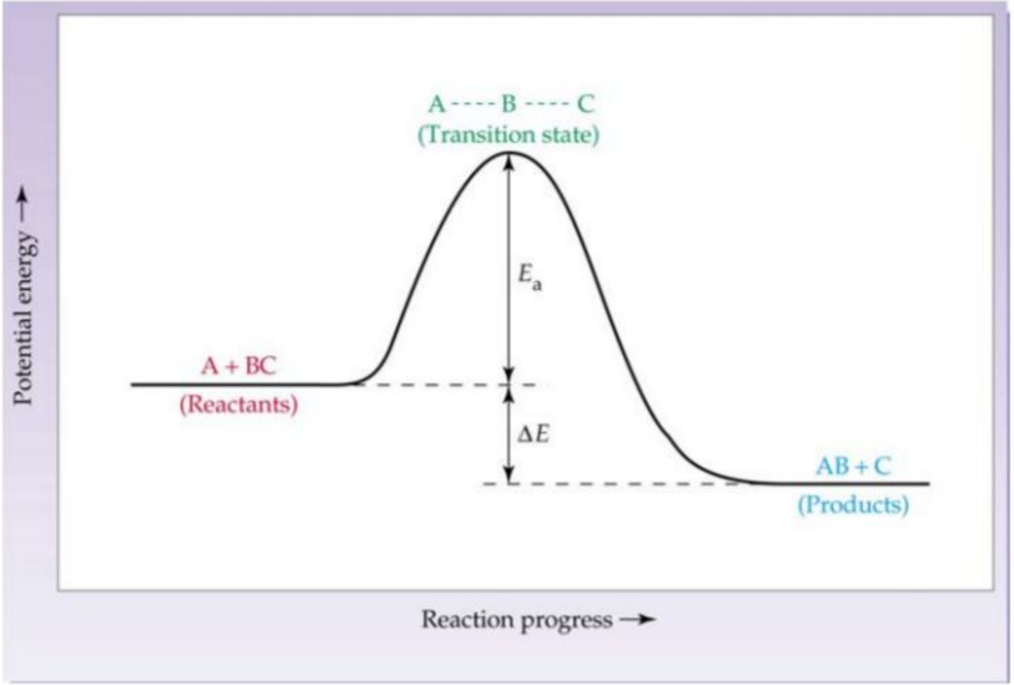
ACTIVATION ENERGY EQUATIONS

The activation energy (E_A) for the forward reaction is:

$$E_A = E_{TS} - E_{Reactants}$$

The activation energy of the reverse reaction is:

$$E_A = E_{TS} - E_{Products}$$

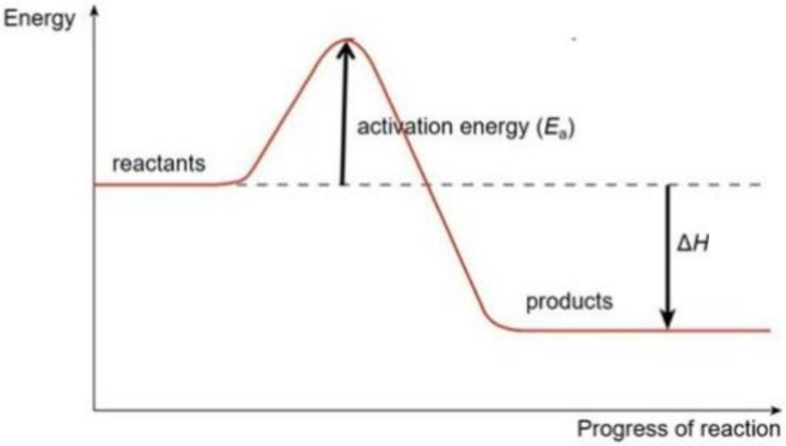


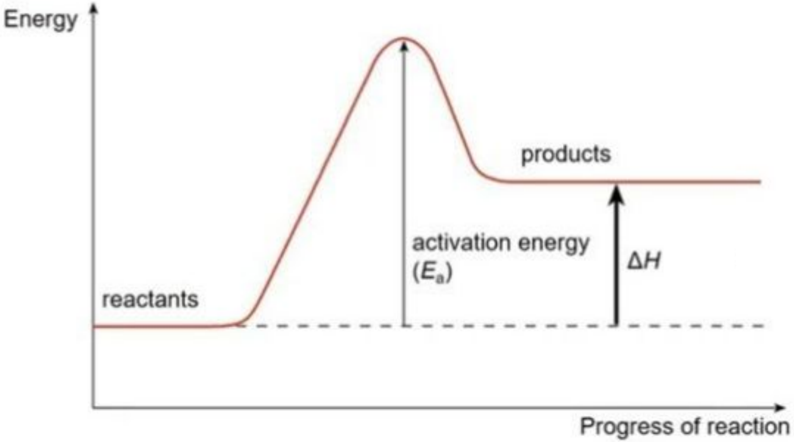
ENTHALPY

The **enthalpy of a reaction (ΔH)** is the potential energy difference between the products and the reactants.

For now, know that an **exothermic** reaction releases energy, and an **endothermic** reaction absorbs energy. By definition, the enthalpy of a reaction is:

$\Delta H = E_{Products} - E_{Reactants}$ **−ΔH = exothermic, +ΔH = endothermic**



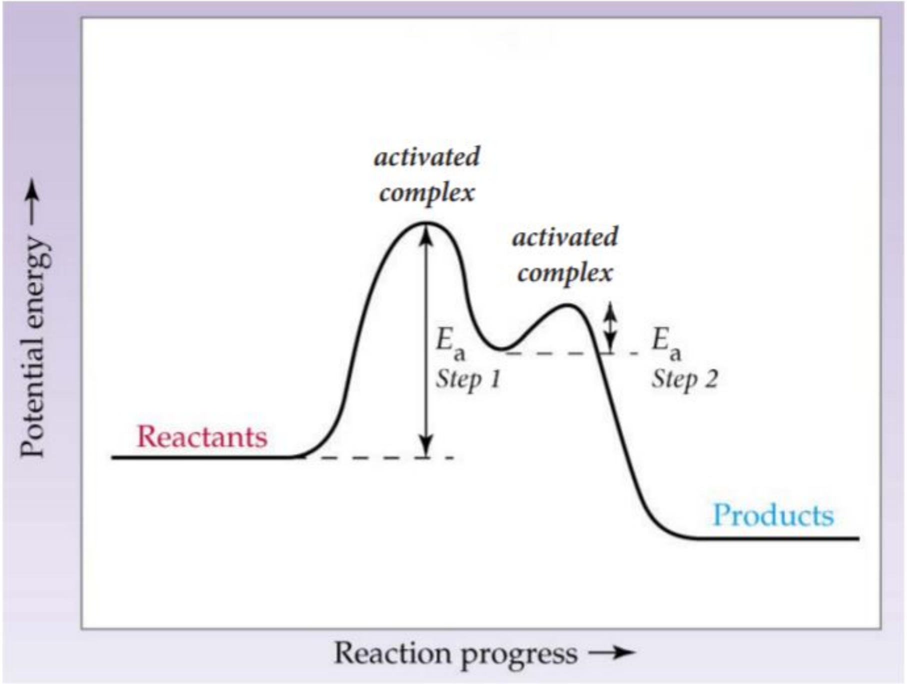


MULTIPLE STEPS

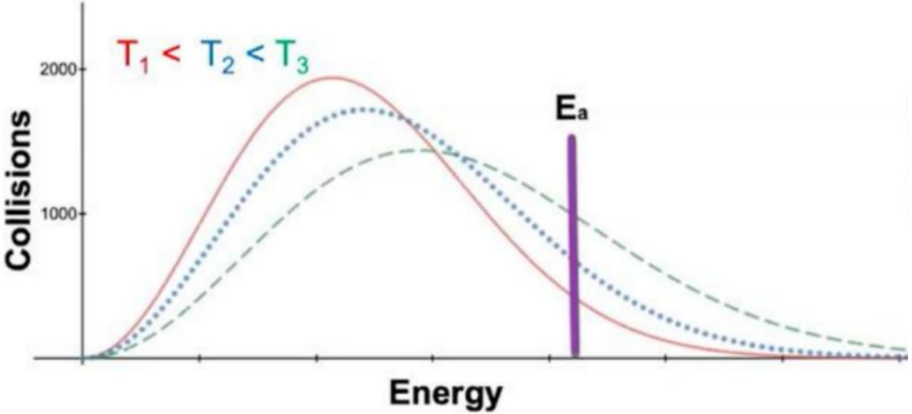
Most reactions proceed by a series of **elementary steps** - the **reaction mechanism**.

The slowest step (the rate determining step) is likely to have the highest activation energy.

- Which step would be the rate determining step in the reaction profile on the right?



Temperature



Recall that the rate law is:

Rate = $k[A]^m[B]^n$

The value of k changes with temperature.

Changes in temperature are proportional to changes in the kinetic energy of molecules.

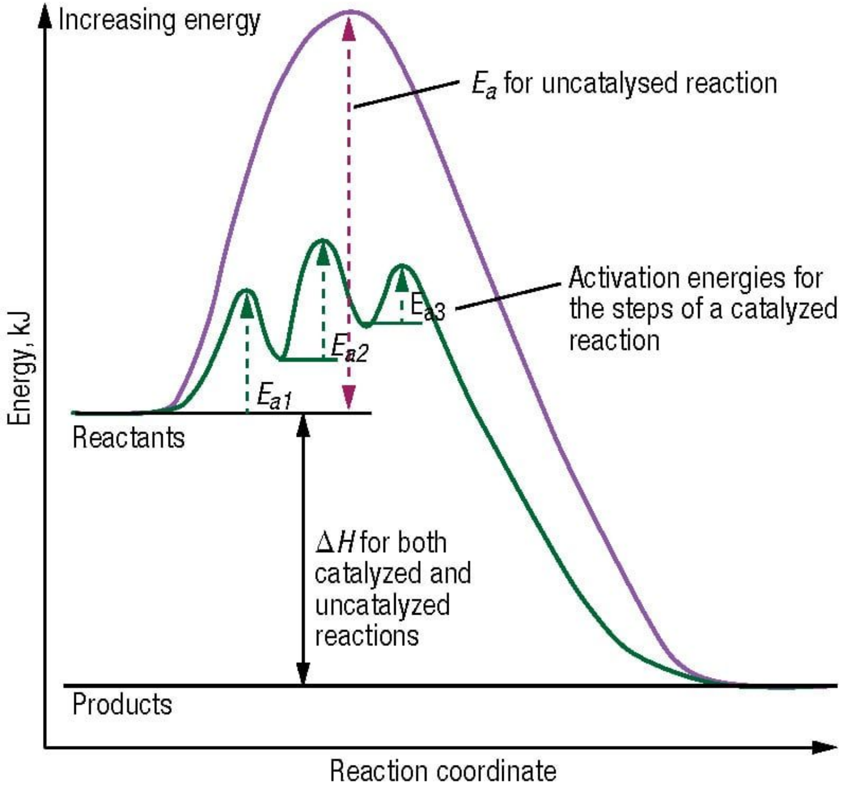
This **DOES NOT** change the reaction mechanism, so the **energy of the transition state remains unchanged**.

Instead, the different value of k can be accounted for by the larger proportion of molecules that have enough energy to get over the hump.

CATALYSTS

Catalysts changes the reaction pathway by **lowering the activation energy**.

This often results in a multistep reaction pathway.



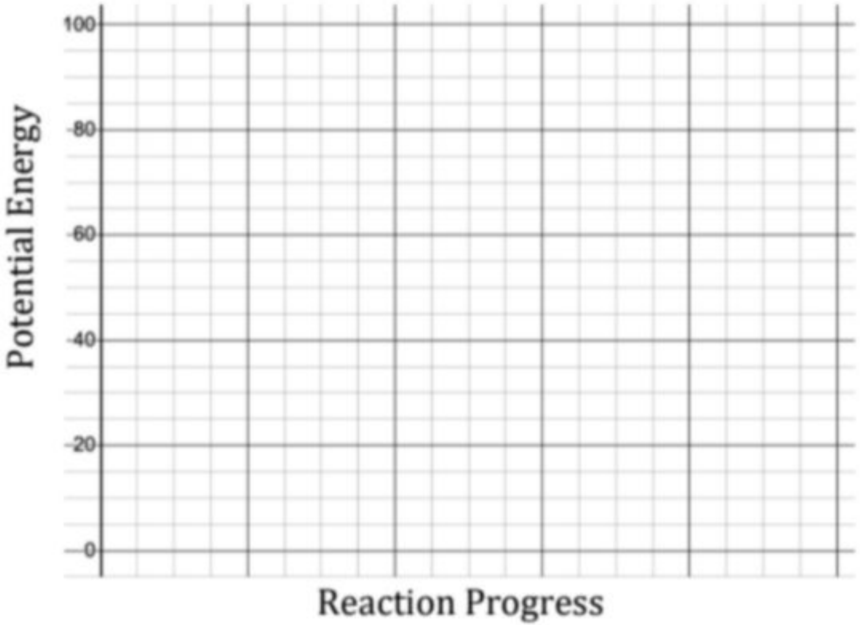
TOGETHER

1. Sketch a reaction diagram of an endothermic reaction.

YOU DO, WE REVIEW

2. On the graph below, draw a reaction energy profile of a reaction with the following:

Compound	Energy (kJ/mol)
Reactants	20
Transition State	80
Products	50



Bellwork

Agenda:

- Finish 5.6
- Lab design
- Run through lab

PBO

SWBAT use experimental data, <u>reaction mechanisms,</u> and graphs IOT determine the <u>rate law</u> of a reaction.

WITH YOUR GROUP

- Brainstorms ways that we could discover the rate law for a reaction by obtaining data in the lab
- Be prepared to share your thoughts with the class

If you get stuck, list the different ways we have learned to find the rate law

Crystal Violet Lab

- We will be discovering the rate law for a reaction of crystal violet and NaOH
- We will do this using a colorimeter
- We will make 3 different graphs to discover if the reaction is 0, 1, or 2 order

What will we be graphing instead of concentration

Read through the Safety notes and procedure

- Then answer the prelab questions with your group

Lab Safety

- Goggles must be worn the whole time
- Wash hands before leaving the lab or if you get any chemicals on you

Lab Notes

- Our volume measurements do not need to be precise so we can use a disposable pipet

MAKING THE GRAPHS ON THE LABQUEST

- First check the curve fit of the absorbance vs time
    - Go to graph, click analyze, click curve fit, select absorbance, make sure linear is checked
- Then check ln
    - Go to the table, click new calculated column, select AlnX, make sure A is 1 and X is absorbance. Then go to graph, click analyze, click curve fit, select whatever you named your column

5.7 Introduction to Reaction Mechanisms & 5.8 Reaction Mechanisms and Rate Law

ENDURING UNDERSTANDING:

TRA-5	Many chemical reactions occur through a series of elementary reactions. These elementary reactions when combined form a chemical equation.

LEARNING OBJECTIVES:

TRA-5.A	Identify the components of a reaction mechanism.
TRA-5.B	Identify the rate law for a reaction from a mechanism in which the first step is rate limiting.

REACTION MECHANISMS

The decomposition of hydrogen peroxide is facilitated by iodide ions. The overall reaction is:

$$2H_2O_{2(aq)} \longrightarrow 2H_2O_{(l)} + O_{2(g)}$$

By experiment, the rate law is found to be:

$$rate = k[H_2O_2][I^-]$$

What is the reaction order with respect to hydrogen peroxide?

What is the reaction order with respect to iodine ion?

BREAK IT DOWN INTO ELEMENTARY STEPS

We can account for the observed rate law by assuming that the reaction takes place in two separate elementary steps, each of which is bimolecular:

Step 1: $H_2O_{2(aq)} + I^-_{(aq)} \longrightarrow H_2O_{(l)} + IO^-_{(g)}$

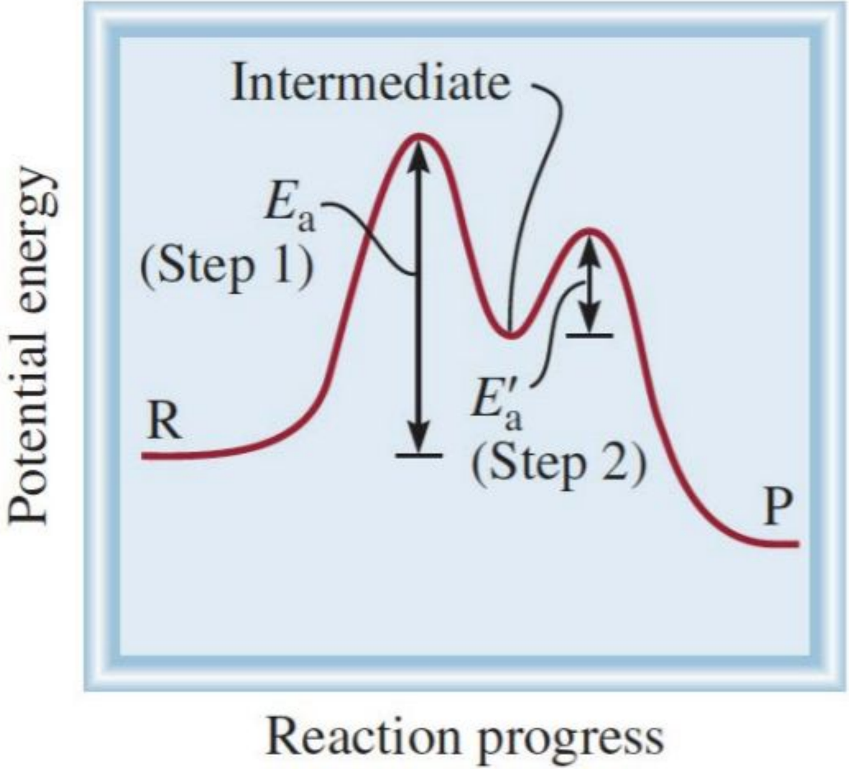
Step 2: $H_2O_{2(aq)} + IO^-_{(aq)} \longrightarrow H_2O_{(l)} + O_{2(g)} + I^-_{(aq)}$

Identify any intermediates and/or catalysts.

CONCENTRATIONS OF INTERMEDIATES AND CATALYSTS

Intermediates: The [IO^-] remains very low as Step 2 will use up any IO^- as quickly as it forms.

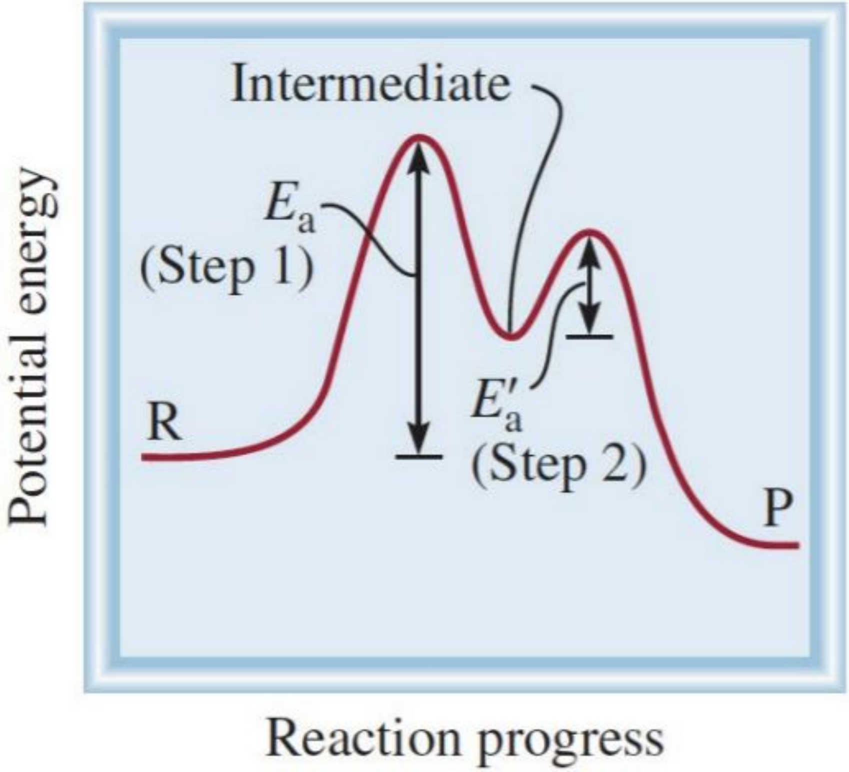
Catalysts: The [I^-] will be unchanged by the end of the reaction. Catalysts are NOT consumed by the reaction.



Rate Law and activation Energy

Given that the rate law is rate = $k[H_2O_2][I^-]$ we would presume that Step 1 has the higher activation energy.

*Confirmation of the mechanism would require some method (usually spectroscopy) for detecting the presence of the IO^- intermediate, even though it is short-lived.



RATE LAWS FROM MECHANISMS

The speed of a reaction is limited by the speed of the slowest step in the reaction mechanism.

The slowest step is called the rate-limiting (or rate determining) step because it determines the rate of the overall reaction.

In the case where the first step is rate-limiting, or where all reactions are irreversible, the rate law of the overall reaction is determined by the rate law of the slowest step.

*Remember: the rate law of each elementary reaction can be inferred from the stoichiometry of the molecules participating in the collision.

RATE LAWS FROM MECHANISMS

Consider the reaction mechanism below:

Step 1: $NO(g) + Cl_2(g) \rightarrow NOCl_2(g)$ *slow*
Step 2: $NOCl_2(g) + NO(g) \rightarrow 2NOCl(g)$ *fast*

- The first step is the slow step = rate limiting step.
- By examining the collisions of the first step of this mechanism, we know the rate law for step 1 is rate = $k[NO][Cl_2]$.
- Because the first step is the slow step of this mechanism it can be inferred that the rate law for the overall reaction is also rate = $k[NO][Cl_2]$.

RATE LAWS FROM MECHANISMS

If the rate law of the overall reaction is known, a mechanism can be supported or rejected based on the rate law of the slow step.

$$2H_2(g) + 2NO(g) \rightarrow N_2(g) + 2H_2O(g)$$

If the rate law of the reaction shown above is experimentally determined to be rate = $k[H_2][NO]^2$
cand the following proposed mechanism be correct?

Step 1: $H_2(g) + NO(g) \rightarrow H_2O(g) + N$ *slow*
Step 2: $N + NO(g) \rightarrow N_2(g) + O$ *fast*
Step 3: $O + H_2(g) \rightarrow H_2O(g)$ *fast*

TOGETHER (5.7)

1. Write the overall reaction represented by the mechanism shown below.

   Step 1: $N_2O_{(g)} \rightarrow N_{2\,(g)} + O_{(g)}$
   Step 2: $N_2O_{(g)} + O_{(g)} \rightarrow N_{2\,(g)} + O_{2\,(g)}$

   Identify any intermediates and/or catalysts for the mechanism above.

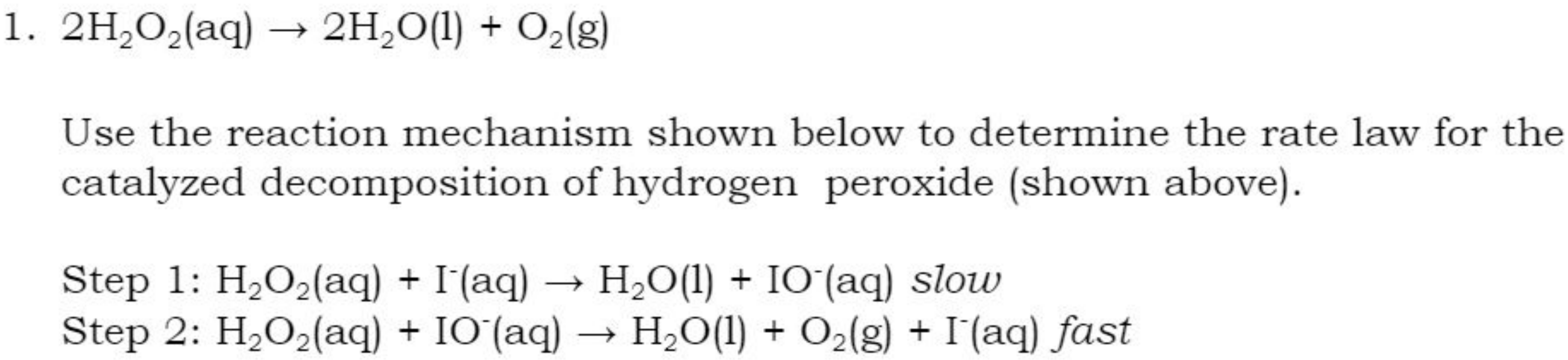
TOGETHER (5.8)

1. $2H_2O_2(aq) \rightarrow 2H_2O(l) + O_2(g)$

   Use the reaction mechanism shown below to determine the rate law for the catalyzed decomposition of hydrogen peroxide (shown above).

   Step 1: $H_2O_2(aq) + I^-(aq) \rightarrow H_2O(l) + IO^-(aq)$ *slow*
   Step 2: $H_2O_2(aq) + IO^-(aq) \rightarrow H_2O(l) + O_2(g) + I^-(aq)$ *fast*

TOGETHER (5.8)



1. $2H_2O_2(aq) \rightarrow 2H_2O(l) + O_2(g)$

   Use the reaction mechanism shown below to determine the rate law for the catalyzed decomposition of hydrogen peroxide (shown above).

   Step 1: $H_2O_2(aq) + I^-(aq) \rightarrow H_2O(l) + IO^-(aq)$ *slow*
   Step 2: $H_2O_2(aq) + IO^-(aq) \rightarrow H_2O(l) + O_2(g) + I^-(aq)$ *fast*

Agenda

- Bellwork
- 5.9 notes
- 5.9 practice problems
- Finish relay packet AND CHECK WORK
- 5.10 and 5.11

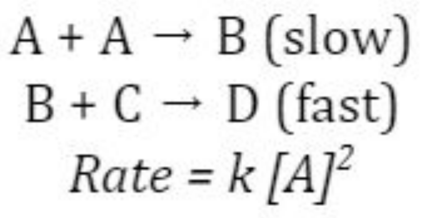
5.9 Steady-State Approximation

ENDURING UNDERSTANDING:	
TRA-5	Many chemical reactions occur through a series of elementary reactions. These elementary reactions when combined form a chemical equation.
LEARNING OBJECTIVE:	
TRA-5.C	Identify the rate law for a reaction from a mechanism in which the first step is not rate limiting

Rate Determining Step

The slowest step of the reaction determines the rate of the reaction. If the first step is slow, then the overall rate for the reaction will be based on the stoichiometry of the first elementary reaction.

Example:



$$A + A \rightarrow B \text{ (slow)}$$

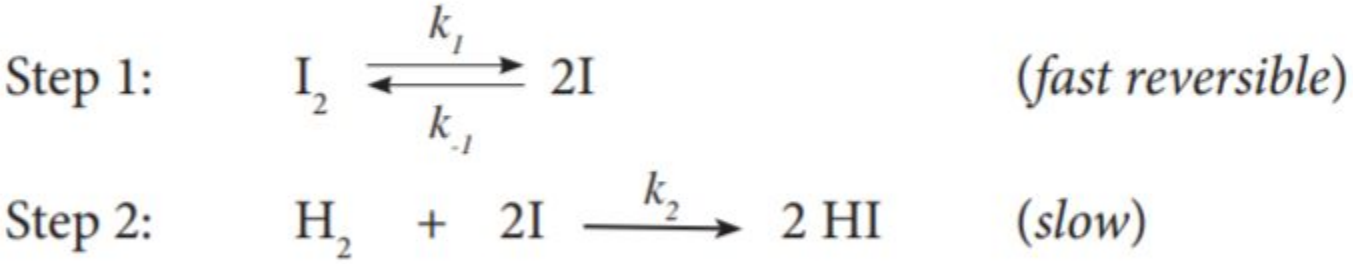
$$B + C \rightarrow D \text{ (fast)}$$

$$Rate = k\,[A]^2$$

RATE DETERMINING STEP NOT THE 1ST STEP

For many reactions, the slowest (rate determining) step is not the first step.

A common reaction mechanism is one that involves at least two elementary steps, the first of which is very rapid in both the forward and reverse directions compared with the second step.



Step 1: $I_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2I$ (*fast reversible*)

Step 2: $H_2 + 2I \xrightarrow{k_2} 2\,HI$ (*slow*)

EXAMPLE

An example is the reaction between molecular hydrogen and molecular iodine to produce hydrogen iodide:

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

$$rate = k\,[H_2][I_2]$$

In the 1960s chemists found that the actual mechanism is more complicated than previously believed. A two-step mechanism was proposed:

$$\text{Step 1:} \quad I_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2I \qquad (\textit{fast reversible})$$

$$\text{Step 2:} \quad H_2 + 2I \xrightarrow{k_2} 2\,HI \qquad (\textit{slow})$$

Step 1: $I_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2I$ *(fast reversible)*

Step 2: $H_2 + 2I \xrightarrow{k_2} 2\,HI$ *(slow)*

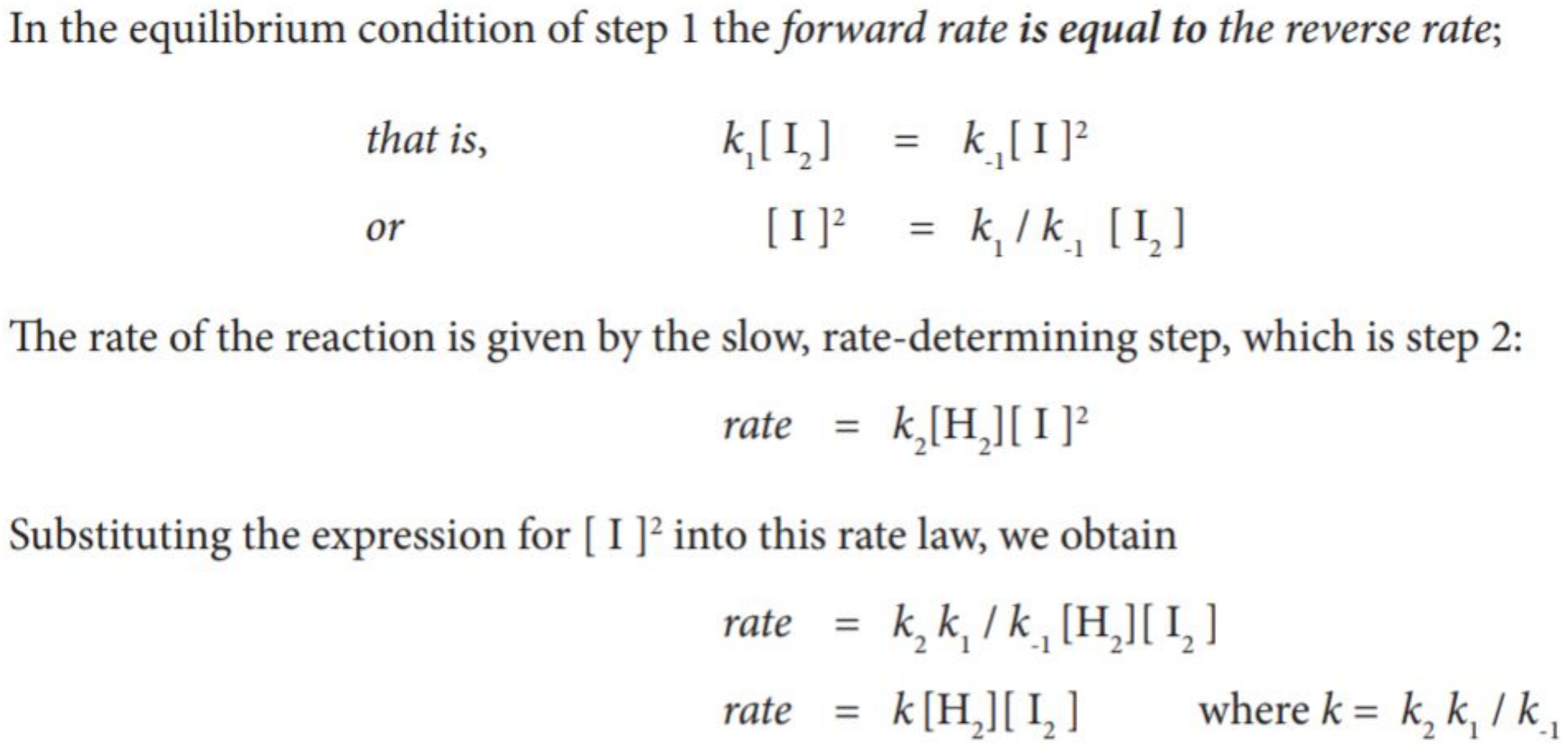
When the reaction begins, there are very few I atoms present.

As I_2 dissociates, [I] increases. Therefore, the forward rate of step 1 decreases and the reverse rate increases.

Soon the two rates become equal, and a **chemical equilibrium** is established.

Because the elementary reactions in step 1 are much faster than the one in step 2, equilibrium is reached before any significant reaction with hydrogen occurs, and it persists throughout the reaction - **steady state approximation**.

THE MATH OF IT ALL



In the equilibrium condition of step 1 the *forward rate **is equal** to the reverse rate*;

that is, $$k_1[\,\mathrm{I}_2\,] = k_{-1}[\,\mathrm{I}\,]^2$$

or $$[\,\mathrm{I}\,]^2 = k_1 / k_{-1}\ [\,\mathrm{I}_2\,]$$

The rate of the reaction is given by the slow, rate-determining step, which is step 2:

$$\textit{rate} = k_2[\mathrm{H}_2][\,\mathrm{I}\,]^2$$

Substituting the expression for $[\,\mathrm{I}\,]^2$ into this rate law, we obtain

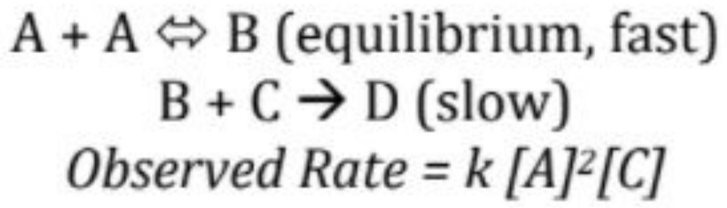
$$\textit{rate} = k_2\,k_1 / k_{-1}\,[\mathrm{H}_2][\,\mathrm{I}_2\,]$$

$$\textit{rate} = k\,[\mathrm{H}_2][\,\mathrm{I}_2\,] \qquad \text{where } k = k_2\,k_1 / k_{-1}$$

Steady State Approximation

1. Start with the slow step. Any reactants (not intermediates!) in this step should be included in Rate Law as normal.
2. consider prior steps that 'feed into' the slow step. Any reactants in this step should be included in Rate Law normal.
3. If an intermediate produced in this step is not consumed until after the slow step, then it should be included inversely in the Rate Law. (RARE)
4. Any reactants in later steps should be excluded from the Rate Law.

EXAMPLE

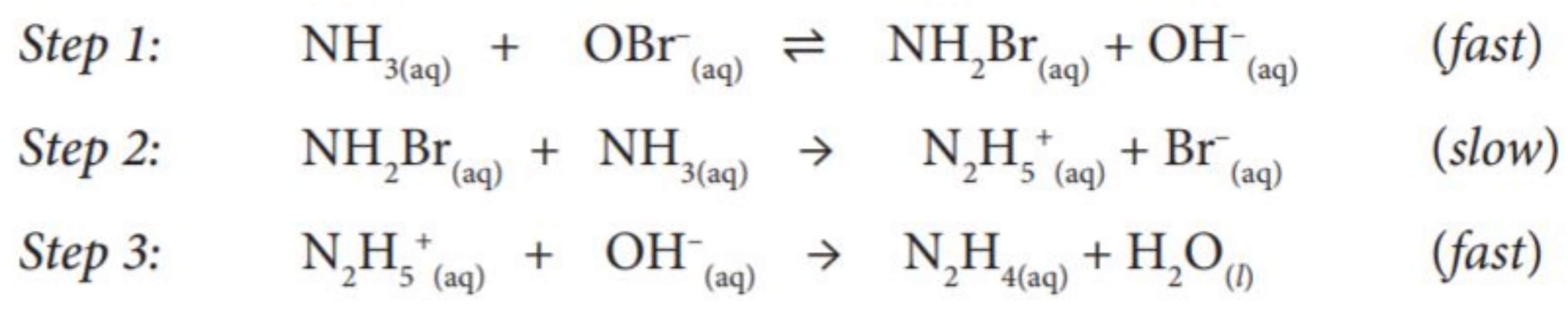


$A + A \Leftrightarrow B$ (equilibrium, fast)

$B + C \rightarrow D$ (slow)

Observed Rate $= k\,[A]^2[C]$

TOGETHER:



Step 1:	$NH_{3(aq)} + OBr^-_{(aq)} \rightleftharpoons NH_2Br_{(aq)} + OH^-_{(aq)}$	(*fast*)
Step 2:	$NH_2Br_{(aq)} + NH_{3(aq)} \rightarrow N_2H_5^+{}_{(aq)} + Br^-_{(aq)}$	(*slow*)
Step 3:	$N_2H_5^+{}_{(aq)} + OH^-_{(aq)} \rightarrow N_2H_{4(aq)} + H_2O_{(l)}$	(*fast*)

TOGETHER

1. Ozone naturally decomposes into oxygen according to the following reaction:

$$2\ O_{3\,(g)} \rightarrow 3\ O_{2\,(g)}$$

The experimentally observed rate law for this reaction is: $Rate = \frac{k[O_3]^2}{[O_2]}$

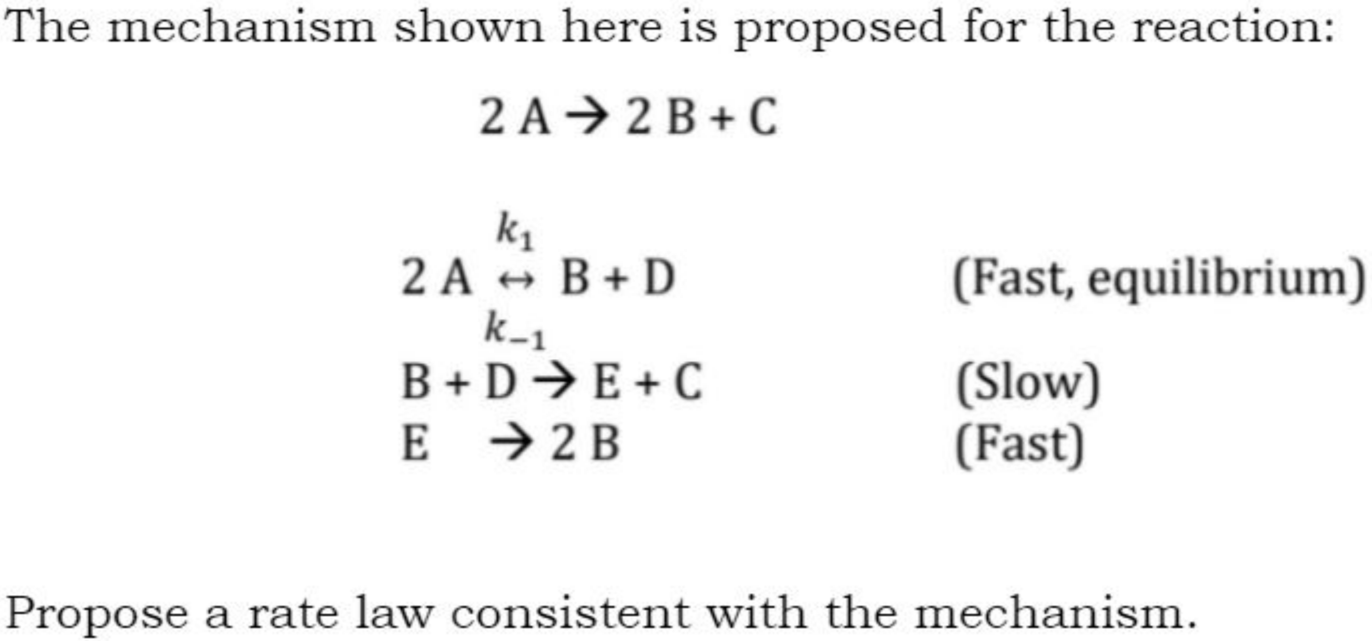
The reaction occurs in two steps, which is the rate limiting step?

$$O_{3\,(g)} \underset{k_{-1}}{\overset{k_1}{\leftrightarrow}} O_{2\,(g)} + O_{(g)}$$

$$O_{(g)} + O_{3\,(g)} \overset{k_2}{\rightarrow} 2\ O_{2\,(g)}$$

Show that the rate law for the slow step agrees with the experimentally observed rate law.

YOU DO, WE REVIEW



The mechanism shown here is proposed for the reaction:

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

$2\,A \underset{k_{-1}}{\overset{k_1}{\leftrightarrow}} B + D$ (Fast, equilibrium)

$B + D \rightarrow E + C$ (Slow)

$E \rightarrow 2\,B$ (Fast)

Propose a rate law consistent with the mechanism.

Relay Packet

- Go through your relay packet
  - Check your work
  - Make sure your rate laws are correct
    - Did you use the slow step?
    - If the slow step is not first did you use steady state approximation?

5.10 & 5.11 Multistep Reaction Profile Diagram & Catalysis

ENDURING UNDERSTANDINGS:	
TRA-5	Many chemical reactions occur through a series of elementary reactions. These elementary reactions when combined form a chemical equation.
ENE-1	The speed at which a reaction occurs can be influenced by a catalyst.
LEARNING OBJECTIVES:	
TRA-5.D	Represent the activation energy and the overall energy change in a multistep reaction with a reaction energy profile
ENE-1.A	Explain the relationship between the effect of a catalyst on a reaction and changes in the reaction mechanism.

MULTISTEP REACTION PROFILE DIAGRAMS

Reaction energy profiles can also be used to illustrate a multistep reaction, as long as the energetics for each step are known.

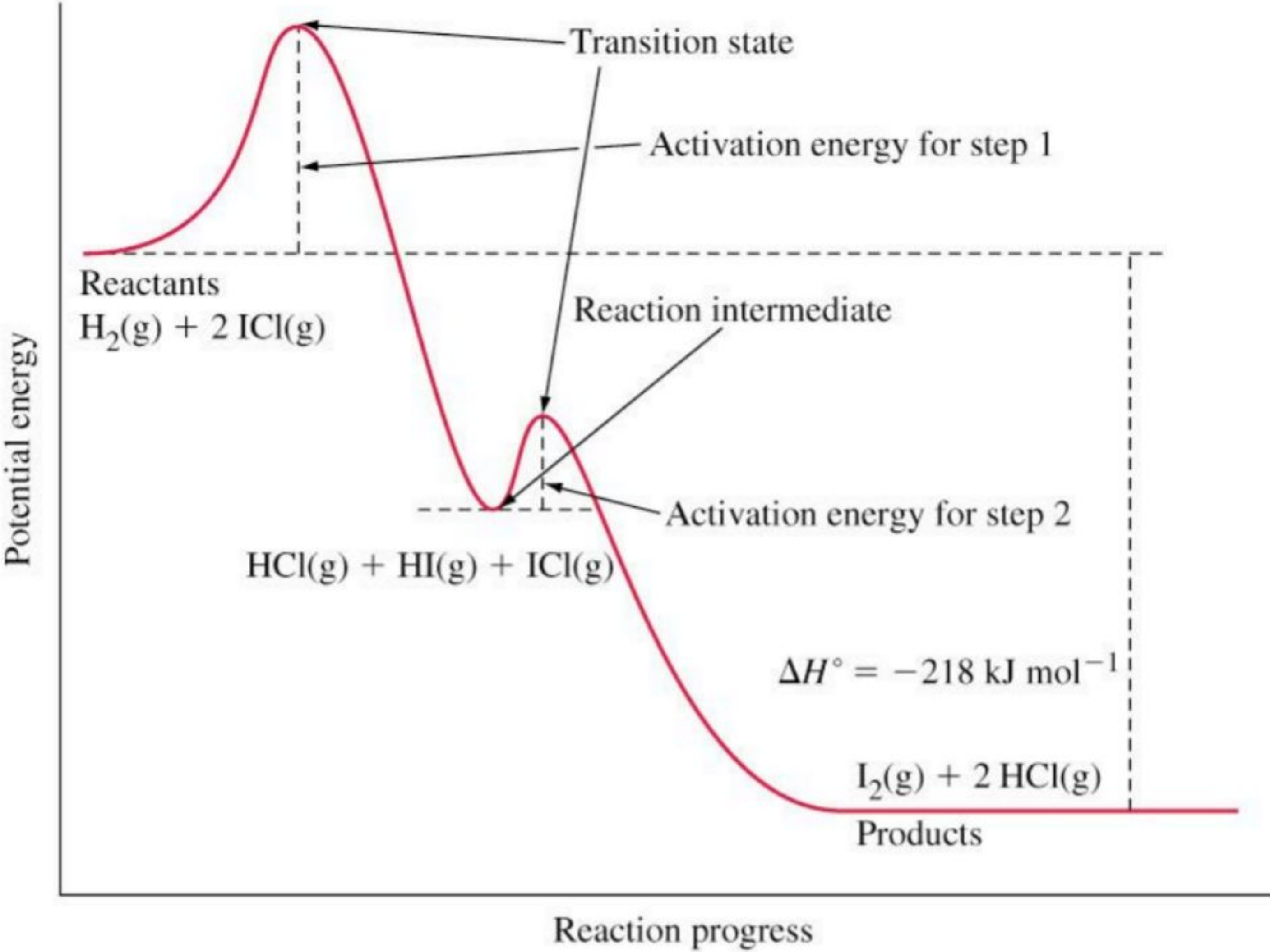
In a two-step reaction, two transition states are shown. In a three-step mechanism, three transition states are shown.

The rate determining step is illustrated by the energy of the transition states, where the largest activation energy corresponds to the slowest step.

Intermediates are shown as valleys between the reactants and products. The placement of the intermediates is dependent on the energetics of each step.

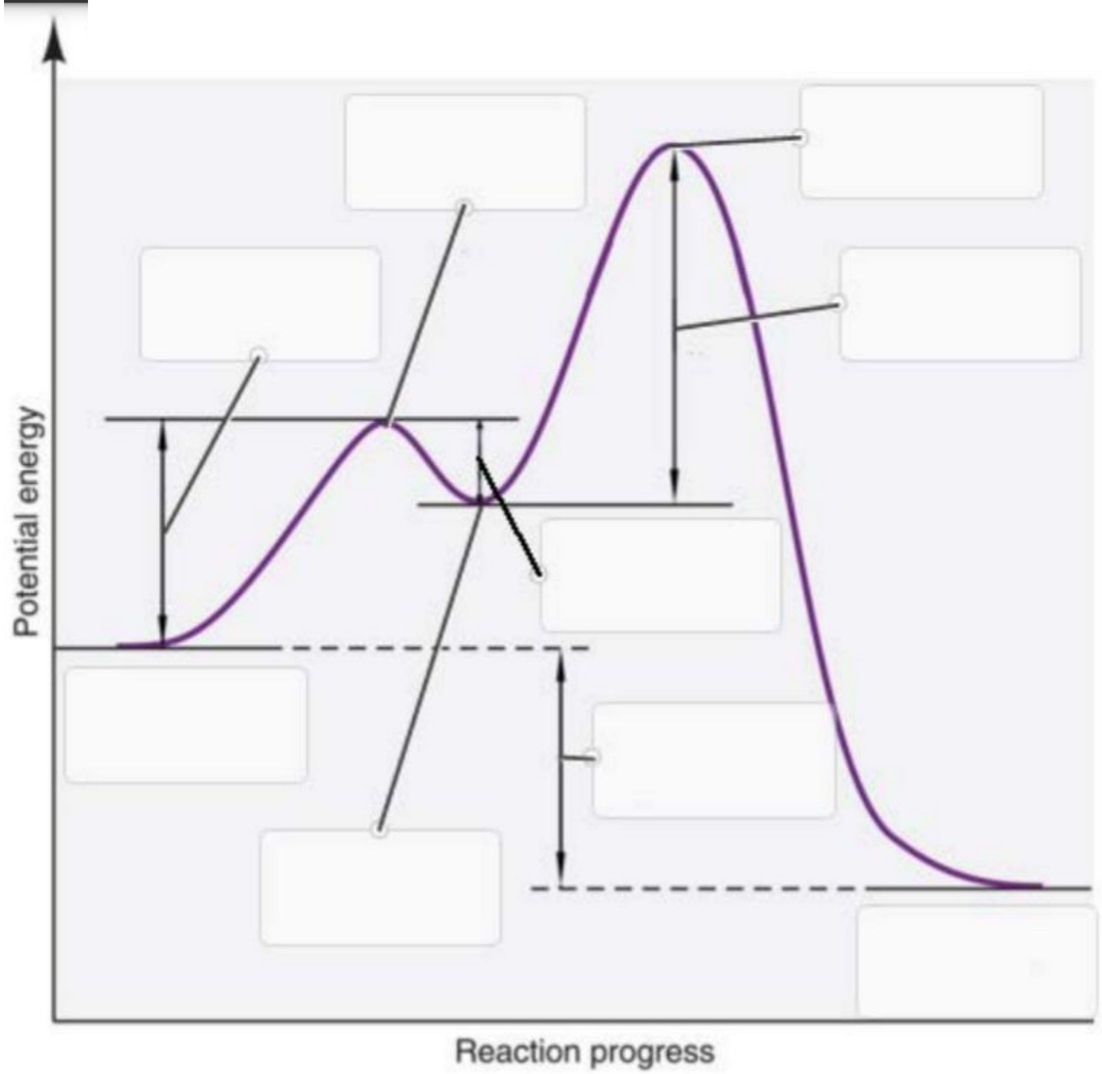
2 STEP RXN

- Which step is rate limiting?
- Is the rxn endothermic or exothermic?



FILL IN THE BLANKS

- Which step is rate limiting?
- Is step 1 endothermic or exothermic?
- Is the reaction endothermic or exothermic?



CATALYSIS

A **catalyst** is a material that is used to speed up a chemical reaction but is not consumed by the reaction.

Catalysts work in one of two ways:

- alter the rate of reaction by **changing the number of effective collisions**
- **altering the chemical pathway** to one that requires less energy (particularly for the rate determining step).

Three Types of Catalysts

There are three categories of catalysts:

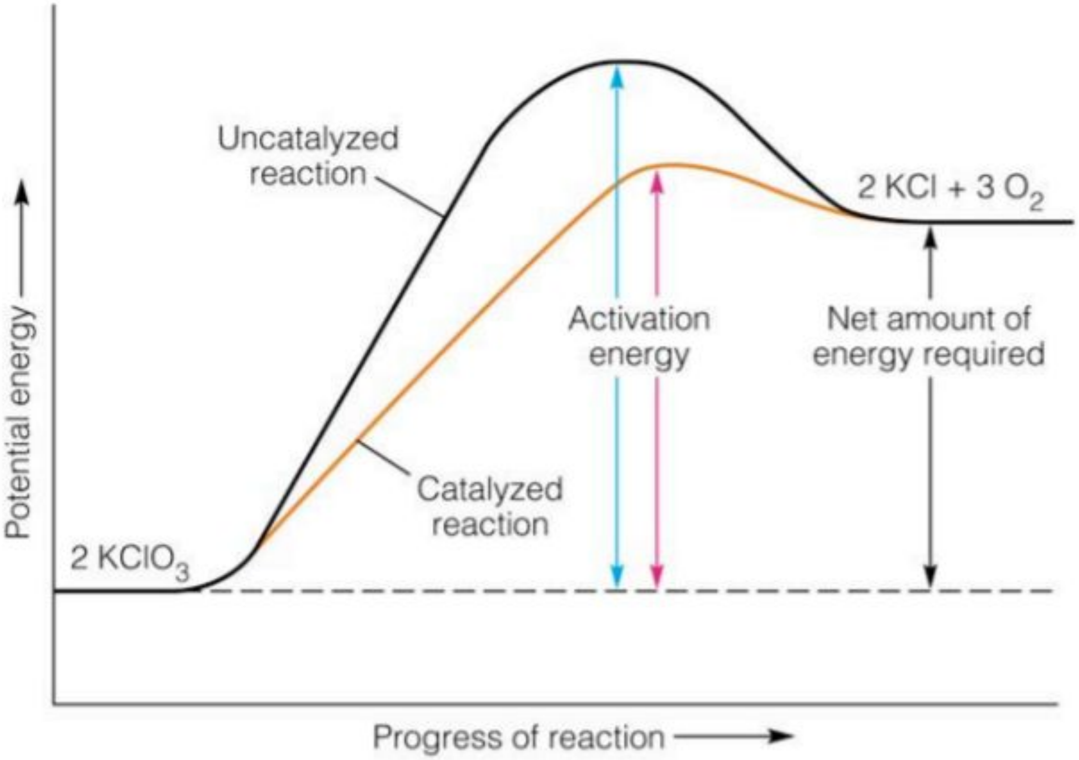
- **homogeneous catalysts** - in the same phase as the reactants and can mix with them uniformly
- **heterogeneous catalysts** - in a different phase from the reacting particles, such as a solid catalyst with gaseous reactants
- **Enzymatic catalysts** - speeds up the reaction by binding with one or more of the reactants - either creating a more favorable orientation or lowering the amount of energy required to react

Homogeneous Example: Decomposition of $KClO_3$ using MnO_2

This is an endothermic reaction but the presence of a catalyst can still reduce activation energy.

$$2KClO_{3(s)} \xrightarrow[MnO_2]{\Delta} 2KCl_{(s)} + 3O_{2(g)}$$

Both $KClO_3$ and MnO_2 are solids = homogeneous catalyst.

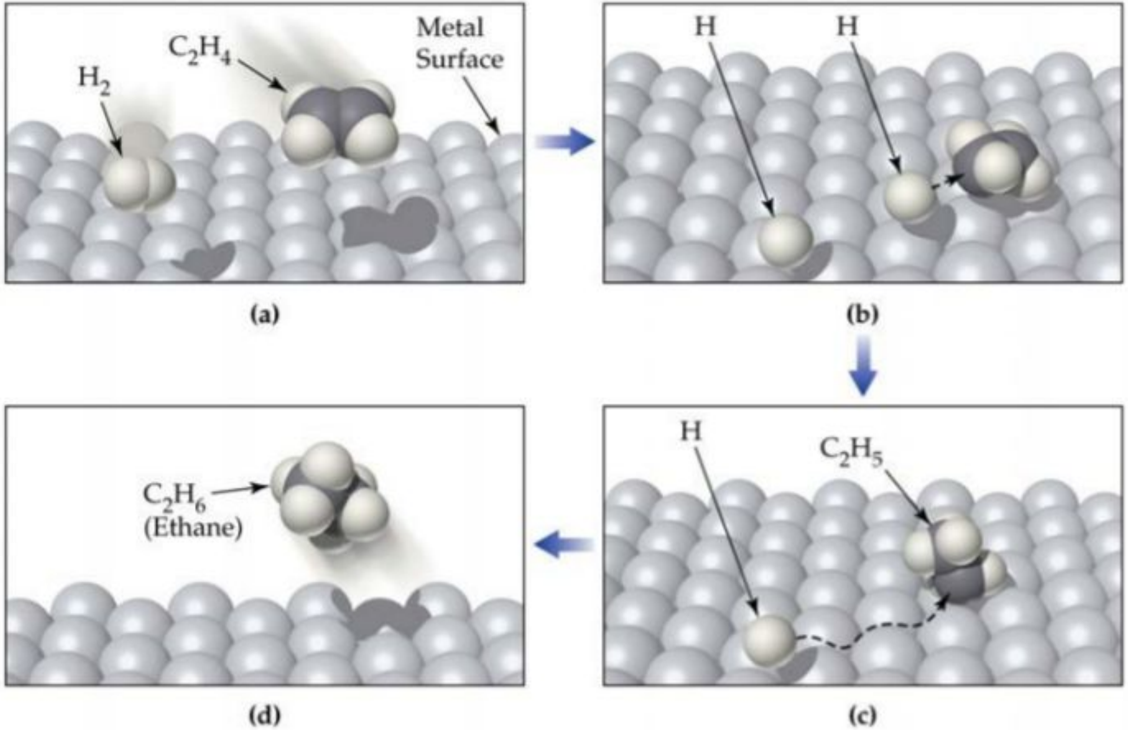


Heterogeneous Example 1: hydrogenation of ethene using nickel

The need for collisions to occur with the correct orientation is removed.

With bonds already broken, less violent collisions between hydrogen atoms and carbon atoms.

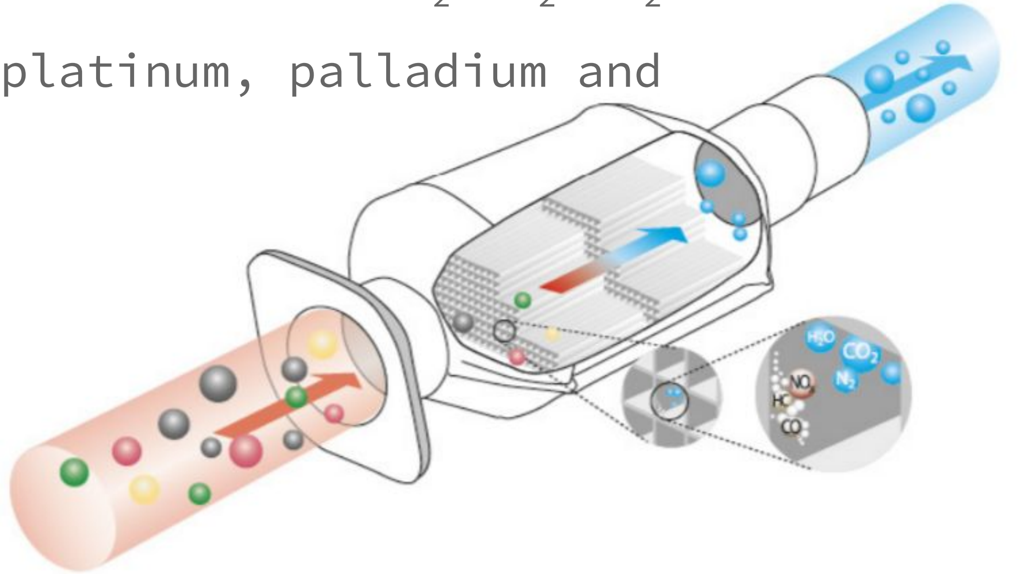
The reaction can proceed by an alternative mechanism with lower activation energy.



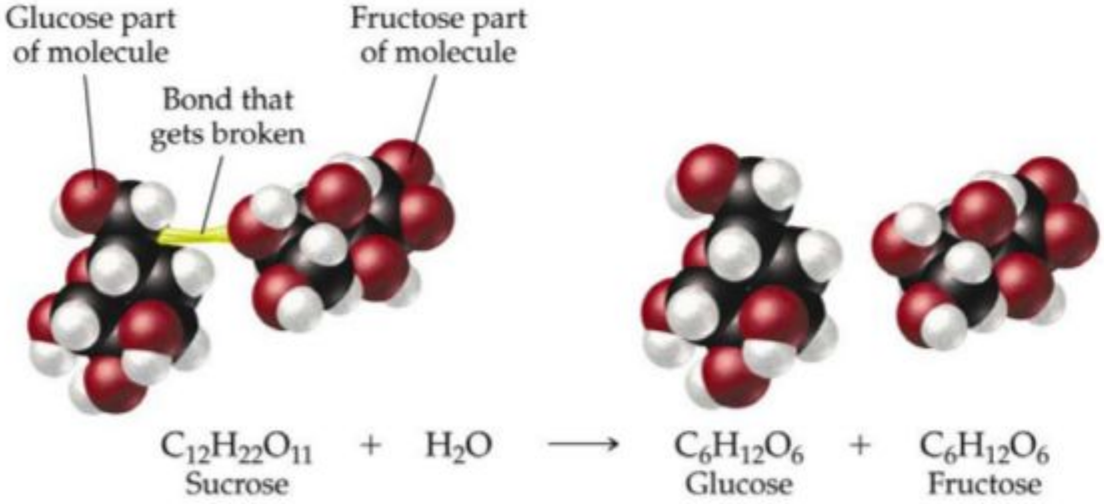
Heterogeneous Example 2: Catalytic Converters

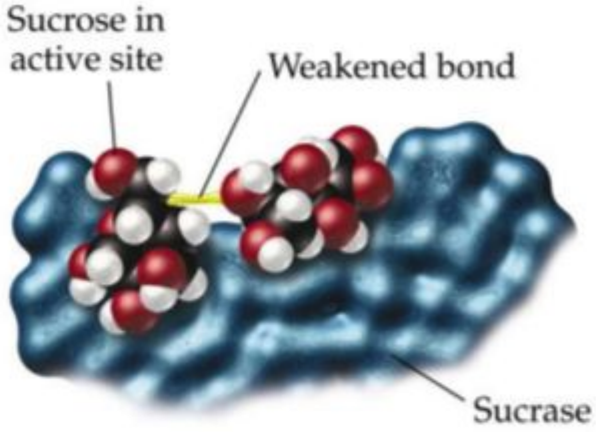
Catalytic converters are used in cars to convert harmful gases (CO, NO, NO_2, partially reacted hydrocarbons) into less harmful gases (CO_2, N_2, H_2O).

Transition metals such as platinum, palladium and rhodium are used.



ENZYMATIC EXAMPLE: HYDROLYSIS OF SUCROSE USING SUCRASE

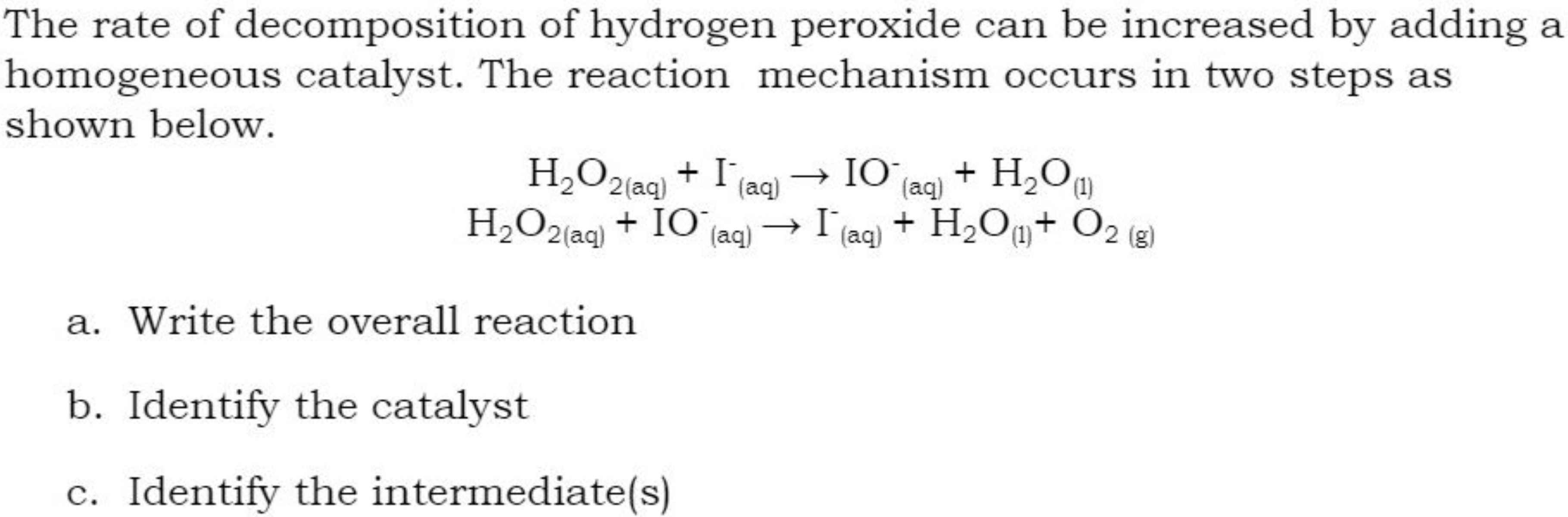




TOGETHER (5.10)

Sketch a reaction diagram for a three-step mechanism that is exothermic overall:

TOGETHER (5.11)



The rate of decomposition of hydrogen peroxide can be increased by adding a homogeneous catalyst. The reaction mechanism occurs in two steps as shown below.

$$H_2O_{2(aq)} + I^-_{(aq)} \rightarrow IO^-_{(aq)} + H_2O_{(l)}$$
$$H_2O_{2(aq)} + IO^-_{(aq)} \rightarrow I^-_{(aq)} + H_2O_{(l)} + O_{2\,(g)}$$

a. Write the overall reaction

b. Identify the catalyst

c. Identify the intermediate(s)