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KINETICS

RATE OF A REACTION

A → B  A = ⬤  B = ⬤

t = time

What is happening to the number of blue dots as time proceeds?
What is happening to the number of red dots as time proceeds?
Is the total number of dots changing?
If each dot represents a molecule, what is the stoichiometry of the reaction?

Forty blue dots disappeared during the first minute (between t = 0 minutes and t = 1 minute). How many blue dots disappeared between t = 1 minute and t = 2 minutes? Between t = 2 minutes and t = 3 minutes? Between t = 3 minutes and t = 4 minutes? What does this tell you about the rate at which blue dots are disappearing?
On the previous page we show a molecular representation of a reaction $A \rightarrow B$ where $A$ is represented by blue circles and $B$ by red circles. Actual chemical concentrations are measured in moles per liter, which has the units $\text{mol L}^{-1}$.

Now we will give the original concentration of $A$ as $1 \text{ mol L}^{-1}$. This is shown by the width of the blue stripe on the ChemLog for $t = 0$ just below.

Using the ChemLogs at left, measure the concentration of $A$ (blue) at times 0 through 4 minutes. Plot those concentrations on the chart below, then draw a curve through the five points. Do the same for $B$ (red).

Now calculate the change in $A$ at one minute intervals. For example, 40 $A$'s change to $B$ during the interval between $t = 0$ minutes and $t = 1$ minute. Now we can say that the average rate at which $A$ changed to $B$ during the first minute was 40 $A$'s per minute. Do this for the intervals from $t = 1$ minute to $t = 2$ minutes, then from $t = 2$ minutes to $t = 3$ minutes, then from $t = 3$ minutes to $t = 4$ minutes. Compare and contrast the average rates for each of the four 1 minute intervals. What do you notice and why do you think this is happening?

Now calculate the time at which the original concentration of $A$ (1.0 mol L$^{-1}$) had been reduced to half (0.5 mol L$^{-1}$), then find the time at which the concentration of $A$ was 0.25 mol L$^{-1}$. The time it takes to reduce a substance to one half of its original concentration is called its half life. What can you deduce about this reaction by comparing its half life from 1.0 mol L$^{-1}$ to 0.5 mol L$^{-1}$, with the half life from 0.5 mol L$^{-1}$ to 0.25 mol L$^{-1}$?
KINETICS

RATE OF A REACTION

Suppose we have an \( A \rightarrow B \) reaction and we experimentally measure the concentrations at different times, which are given in the following table:

<table>
<thead>
<tr>
<th>time (minutes)</th>
<th>([A]) (mol L(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.00 mol L(^{-1})</td>
</tr>
<tr>
<td>1</td>
<td>0.70 mol L(^{-1})</td>
</tr>
<tr>
<td>2</td>
<td>0.50 mol L(^{-1})</td>
</tr>
<tr>
<td>3</td>
<td>0.34 mol L(^{-1})</td>
</tr>
<tr>
<td>4</td>
<td>0.24 mol L(^{-1})</td>
</tr>
</tbody>
</table>

We can plot the data on a graph:

The definition of the rate is how many moles per liter of \( A \) is lost per unit of time. We will determine this from our graph.

From our graph we can see that \([A]\) decreased by 0.36 moles per liter over the two minute interval between \( t = 1 \) minute and \( t = 3 \) minutes. We can calculate the average rate at which \([A]\) changes by

\[
\text{rate} = -\frac{0.36 \text{ mols L}^{-1}}{2 \text{ min}} = -0.18 \text{ mol L}^{-1} \text{ min}^{-1}
\]

By definition, the change in the vertical dimension of a curve divided by the change in the horizontal dimension of the curve is the average slope of that curve over that interval. You may recall from trigonometry that this is also the definition of the tangent.

We can, in fact, measure the instantaneous rate of change by drawing a tangent to the curve at any point and then measuring the slope of that tangent.

Find the instantaneous change in the rate of decrease of \([A]\) at \( t = 3 \) min. by measuring the slope of the tangent drawn on the graph. Draw a tangent to the curve at \( t = 1 \) min and use that tangent to determine the rate of decrease of \([A]\) at that time.

Compare the rates at \( t = 1 \) min and \( t = 3 \) min.

The last graph gives the concentration of \( A \) in moles per liter, \([A]\), at any time between \( t = 0 \) minutes and \( t = 5 \) minutes but we want to know the rate at which \([A]\) is changing.
On the previous page we introduced a set of experimental measurements of the concentration of a reactant, A, at successive times. From that we could graphically determine the rate of decrease in the concentration of A at any intermediate time. But what determines the varying rates? In fact, the only aspect of the situation which differs at the various times is the concentration of A itself. So we can try to find a rate law which shows how the rate of change in the concentration of A depends upon the concentration of A.

A simple possibility would be:

\[
\text{rate} = k[A]^n
\]

where \(k\) is some constant, \([A]\) is the concentration of A (in moles per liter) and \(n\) is some exponent of \([A]\).

If we can determine \(k\) and \(n\) from the data then we have found the rate law.

Using our last graph we can find the rate at \(t = 2\) minutes to be

\[
\text{rate}_2 = -0.18 \text{ mols L}^{-1} \text{ min}^{-1}
\]

and at \(t = 4\) minutes we find

\[
\text{rate}_4 = -0.09 \text{ mols L}^{-1} \text{ min}^{-1}
\]

Next we divide the rates

\[
\frac{\text{rate}_2}{\text{rate}_4} = \frac{-0.18 \text{ mols L}^{-1} \text{ min}^{-1}}{-0.09 \text{ mols L}^{-1} \text{ min}^{-1}} = 2
\]

but also

\[
\frac{\text{rate}_2}{\text{rate}_4} = \frac{k[A]^n}{k[A]^n} = \left(\frac{A_2}{A_4}\right)^n = \left(\frac{0.48 \text{ mols L}^{-1}}{0.24 \text{ mols L}^{-1}}\right)^n = 2.0^n
\]

from which we can reasonably conclude, within the limits of our measurements, that \(n = 1\) and

\[
\text{rate} = k[A]^1 = k[A]
\]

We can then find \(k\) by substituting data from any of our measurements, for example, at \(t = 2\) minutes we have

\[
\text{rate} = -0.18 \text{ mols L}^{-1} \text{ min}^{-1} = k(0.49 \text{ mols L}^{-1})
\]

giving

\[
k = -0.37 \text{ min}^{-1}
\]

And so we can write the rate law as

\[
\text{rate} = k[A] = (-0.37 \text{ min}^{-1})[A]
\]
KINETICS
FACTORS THAT AFFECT RATE

The ChemLog shows the reaction of $E \rightarrow F$. Each subsequent ChemLog shows the same reaction and how it is affected by certain changes. Compare the different ChemLogs in order to answer the following question for each factor - concentration change, temperature change, and the presence of a catalyst.

**Concentration Change**

**Temperature Change**

**Presence of a Catalyst**

Show your understanding of each ChemLog by stating how the changing factor affects the rate of the reaction and why the change affects the rate in the way it does?
KINETICS
A FIRST ORDER REACTION

The process is radioactive decay of Plutonium to Americium. The formula is \( \text{Pu} \rightarrow \text{Am} + e \). In the boxes below we show the Plutonium and the Americium.

Count the number of Plutonium atoms and the number of Americium atoms in each box.

<table>
<thead>
<tr>
<th>BOX</th>
<th>#Pu</th>
<th>#Am</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Plot the number of each kind of atom on the graph below.

Radioactive decay is an important example of a first order reaction. Since the chances of a nucleus decaying is unaffected by any normal external influence, the rate of decay clearly depends only upon the number of nuclei (atoms) present. Thus the rate law is first order and we have:

\[
\text{rate} = k[A]
\]

The HALF LIFE of a reaction is defined as the time required for half of the reactants to disappear. First order reactions (and only first order reactions) the half life does not depend upon the concentration or amount of the reactant and so we can measure the half life or specify it (from previous measurement) without referring to the amount or concentration of the reactant.

Given that the half life of the decay, \( \text{Pu} \rightarrow \text{Am} + e \), is 14.4 years, how long does it take to get from the situation in box 1 to the situation in box 2? box 3? box 4? box 5?

If a certain first order reaction has a half life of one year, how long will it take before one mole of the reactant becomes one half mole? one thirty-second of a mole? one atom?

Why can the last answer (for one atom) only be an approximation?
Suppose we have a situation in which two molecules of A combine to give one molecule of B. We write the stoichiometry as $2A \rightarrow B$. How does the concentration of A affect the rate of the reaction?

The pictures above show two different initial conditions. The concentration of A on the right is three times the concentration of A on the left. In a real chemical reaction the A molecules are moving at various velocities and when they collide they sometimes interact to form a B molecule.

Now we have isolated one molecule in each of the two situations. The circled molecule on the right will collide with one of the other molecules three times as often as the circle molecule on the left because the one on the right has three times as many molecules to collide with. This effect causes the rate of collisions to be multiplied by a factor of three. But notice also that we could have circled three times as many different molecules on the right as on the left, which means the rate of collisions will be multiplied by another factor of three. So we have three times as many molecules colliding three times as often. For this reaction the rate of collisions and thus of the reaction depends on the product of the concentration with itself and we can write the rate law as:

$$\text{rate} = k[A][A] = k[A]^2$$

This is called a second order reaction.
KINETICS

A + B → C

There are chemical reactions where the collision of two different molecules sometimes produces a third kind of molecule. We can write this as $A + B \rightarrow C$.

Assuming that we are describing an elementary step, what order is the reaction described on this page?
Write the rate law.

How will the half life of A relate to the half life of B?

Does your answer to the last question depend upon the fact that we have shown A and B having the same initial concentration in our examples?

The left picture above shows initial conditions for the reaction containing 33 blue and 33 red dots, representing molecules. The picture on the right has 99 blue and 99 red dots.

We have isolated one blue molecule in each of these pictures. Assuming that the average speed of the molecules is the same (same temperature) the blue dot on the right will collide with a red dot three times as often as the blue dot on the left.

The circled red dot on the right has three times as many blue dots to collide with as the circled dot on the left.
KINETICS

CHEMLOGS OF THE ORDERS

A → B
Order 0

A → B
Order 1

A → B
Order 2
This is strange! Remember A → B (page 8) where the rate got smaller and smaller with time?

What happens to the rate here?
How did you determine what happens to the rate?

In this reaction, rate DOES NOT depend on [C]!!

\[
rate = k \ [C]^0 \\
rate = k \times 1 \\
rate = k
\]

This is called a zero order reaction.

What is the value of k?
Using the method described earlier, we have determined the initial rates for you. They are:

<table>
<thead>
<tr>
<th>[E]</th>
<th>initial rates (mol L(^{-1}) min(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.8</td>
<td>5 \times 10(^{-5})</td>
</tr>
<tr>
<td>0.4</td>
<td>2.5 \times 10(^{-5})</td>
</tr>
</tbody>
</table>

Determine the rate law and calculate \( k \) for this reaction.
Using the method described earlier, we have determined the initial rates for you. They are:

<table>
<thead>
<tr>
<th>[I]</th>
<th>Initial rates (mol L(^{-1}) min(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.8</td>
<td>5 \times 10^{-5}</td>
</tr>
<tr>
<td>0.4</td>
<td>1.25 \times 10^{-5}</td>
</tr>
</tbody>
</table>

Determine the rate law and calculate \(k\) for this reaction.
These three sets of ChemLogs involve the same reaction over the same interval of time, but with different initial concentrations of the reactants. The first set establishes a reaction rate. Find the reaction rate.

In the ChemLog at left the initial concentration of reactant B has been halved. Compare the reaction rate to the first case above. Determine the order of the reaction in [B].

In the ChemLog at left the initial concentration of reactant A has been halved. Compare the reaction rate to the first case above. Determine the order of the reaction in [A].
KINETICS

REACTION RATES: THE COLLISION THEORY

The rate of any reaction is defined as the number of molecules reacting in a given period of time. This is normally measured in terms of the variation in concentration, \( c \), of either reactants or products with time, \( t \).

\[
\text{Rate of Reaction} = \frac{\text{change in concentration}}{\text{change in time}}
\]

\[
\text{Rate of Reaction} = \frac{\Delta c}{\Delta t} = \frac{c_2 - c_1}{t_2 - t_1}
\]

A Tentative Hypothesis

The problem is not quite so simple. Just because two molecules collide does not mean that they will necessarily react. The rate of reaction depends not only upon the collision frequency but also on the collision efficiency. The collision must be an effective one, in that the molecules must collide with sufficient energy to bring about reaction. The minimum energy required to bring about a reaction is known as the activation energy.

There is still another factor. Molecules have shape and the occurrence of a reaction often depends upon which parts of the reactant molecules collide.

A Modified Tentative Hypothesis

A Final Hypothesis – The Collision Theory

Is the reaction, whose enthalpies are shown in the picture above, exothermic or endothermic? Would it be thermodynamically spontaneous or nonspontaneous?

When two BrNO molecules collide, they will react according to \( 2\text{BrNO} \rightarrow \text{Br}_2 + 2\text{NO} \) if the bromine atoms collide but will just bounce off of each other otherwise. In the picture above, circle which of the collisions will cause a reaction.

The effect of molecular orientation upon reaction rates is called the steric factor. Is the steric factor larger or smaller than one?

<table>
<thead>
<tr>
<th>Reaction rate</th>
<th>Collision frequency</th>
<th>Fraction of collisions having sufficient energy</th>
<th>Collision energy factor</th>
<th>Collision geometry factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \Delta c )</td>
<td>( \Delta t )</td>
<td>( \frac{c_2 - c_1}{t_2 - t_1} )</td>
<td>( \frac{c_2 - c_1}{t_2 - t_1} )</td>
<td>( \frac{c_2 - c_1}{t_2 - t_1} )</td>
</tr>
</tbody>
</table>
**KINETICS**

**REACTION RATES: THE TRANSITION STATE THEORY**

When molecules collide with at least the minimum energy necessary for reaction and the right geometry, or orientation, it seems reasonable that they may unite momentarily to produce an unstable species, which can be called the *activated complex* or *transition state*. This activated product can then break apart to give the new reaction products, or it can break up to yield the original reactants. It is also assumed that the *activated complex is in equilibrium with the original reactants.*

![Diagram of reaction](attachment:reaction_diagram.png)

**Assumptions of the Transition State Theory**

1. An unstable transition state, called the activated complex, is formed.
2. The activated complex is in equilibrium with the original reactants.

![Free Energy Diagram](attachment:free_energy_diagram.png)

**Free Energy Diagram for the Reaction of H₂ and I₂ to form 2HI.**
KINETICS

THE ARRHENIUS EQUATION

In 1897 Gustave Arrenhius introduced an equation to fit the data relating reaction rate to activation energy and temperature. The equation, which is know by his name, is:

\[ k = Ae^{-\frac{E_a}{RT}} \]

k is the reaction rate in moles per second.
A is a constant depending upon the types of molecules.
e is the basis for the natural logarithms.
E_a is the activation energy in kiloJoules per mole.
R is the gas constant = 8.314 Joules per mole-Kelvin.
T is the temperature in Kelvin.

The graph above shows the influence of E_a on reaction rate. Actual reactions will also depend upon A. What is the approximate value of k/A for E_a = 20 kJ mol^{-1}? Extrapolate the graph to find the approximate value of k/A for E_a = 35 kJ mol^{-1}.

Your chemistry textbook shows you how to find the activation energy from the Arrhenius equation, by graphing a series of measurements of the reaction rate versus the temperature. It begins by taking the natural logarithm of the Arrhenius equation:

\[ \ln k = \ln A - \frac{E_a}{RT} \]

When ln k is chosen as the y-axis and 1/T is chosen as the x-axis, this is a linear equation with slope – E_a/R.

For additional insight we will show a similar method using algebra on two measurements: k_1 at T_1 and k_2 at T_2.

\[ \ln k_1 = \ln A - \frac{E_a}{RT_1} \]
\[ \ln k_2 = \ln A - \frac{E_a}{RT_2} \]
If we subtract the second equation from the first we get:

\[ \ln k_1 - \ln k_2 = \left( \frac{E_a}{R} \right) \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \]

solving for E_a, we get

\[ E_a = RT_1T_2 \frac{\ln k_1 - \ln k_2}{T_1 - T_2} \]

knowing either k, we can easily find A from the Arrhenius equation:

\[ A = k_1 e^{\frac{E_a}{RT_1}} \]

It may be better scientific practice to use the graphical method since it uses more data points (and is thus less susceptible to error) but this calculation may give you more insight into the graphical method.

We can summarize the affect of temperature on the rate of a reaction by stating that:
As temperature increases, rate increases because a larger proportion of molecules are moving faster, so a larger proportion of the colliding molecules have the minimum activation energy needed to react.

A good guide for affect of T on rate is that for a typical E_a, an increase in 10 K doubles the rate!
The Maxwell distribution describes what proportion of the molecules in a gas or liquid are in a given velocity range. It depends on the temperature and on another factor.

Using Picture 2, deduce what other factor the Maxwell distribution depends on.

Using Picture 2, what is the most common velocity for radon? for carbon dioxide? for dioxygen? for methane? for dihydrogen?

In Picture 4, the bottom curve is for 283 K (not 273 K) and the top curve is for 373 K. If these molecules take part in a reaction where the rate at 283 K is 1.00 moles per liter, then what is the rate at 373 K?
Since $\Delta H^A = \Delta H^B$ reactions A and B are thermodynamically equivalent. However, reaction B has a lower energy intermediate state than reaction A and thus requires less activation energy than A. In a collision driven reaction, more of the molecules will have a sufficient energy for B than for A and thus reaction B will proceed faster than reaction A.

Suppose you are working with a gas phase reaction. What factors would you change to speed it up?
Draw an arrow from each of the following items to the location of its scale (size or distance) on the chart at left. You may need to look up or measure some of these. (hint: Consider using the Internet.)

The distance to the galaxy Andromeda.
The distance to Pluto.
The diameter of Jupiter.
The distance to your home.
Your height.
Your shoe size.
The size of a dime.
The thickness of a human hair.
Amoeba Proteus
Lacto bacillus acidophilis.
A tobacco mosaic virus.
A water molecule.
**KINETICS**

**ENERGY SCALES**

<table>
<thead>
<tr>
<th>CHEMICALS in Moles</th>
<th>ENERGY in Joules</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sun’s Output for 0.25 s</td>
<td>$10^{26}$</td>
</tr>
<tr>
<td>Thunderstorm</td>
<td>$10^{21}$</td>
</tr>
<tr>
<td>Football Game</td>
<td>$10^{16}$</td>
</tr>
<tr>
<td>One Kg of Gasoline</td>
<td>$10^{11}$</td>
</tr>
<tr>
<td>One Kw-Hour</td>
<td>$10^6$</td>
</tr>
<tr>
<td>C$<em>6$H$</em>{12}$O$_6$ + 6O$_2$ → 6CO$_2$ + 6H$_2$O</td>
<td></td>
</tr>
<tr>
<td>2F$_2$(g) → F$_2$(g)</td>
<td></td>
</tr>
<tr>
<td>H$_2$O$_2$(g) → H$_2$O$_2$(l)</td>
<td></td>
</tr>
<tr>
<td>Lifting One Kg one Meter</td>
<td>$10^1$</td>
</tr>
<tr>
<td>Falling Snowflake</td>
<td>$10^{-4}$</td>
</tr>
<tr>
<td>Average 7-Ray</td>
<td>$10^{-9}$</td>
</tr>
<tr>
<td>Average X-Ray</td>
<td>$10^{-14}$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>CHEMICALS in Molecules or Atoms</th>
<th>ENERGY in Joules</th>
</tr>
</thead>
<tbody>
<tr>
<td>First ionization potential for H Balmer Red Line</td>
<td>$10^{-17}$</td>
</tr>
<tr>
<td>1 Quantum of Cosmic Background Radiation H spin Flip, i.e., 21 cm line</td>
<td>$10^{-22}$</td>
</tr>
<tr>
<td>1 Quantum of 100 Meter Long Radio Wave</td>
<td>$10^{-27}$</td>
</tr>
<tr>
<td>1 Quantum of 10$^4$ Meter long Radio Wave</td>
<td></td>
</tr>
</tbody>
</table>

The following quantities are for one mole of the given molecular reaction. Mark the location of each of them on the energy chart. If the energies are negative, use the absolute value.

- **A.** The enthalpy of formation of water = -286 kJ.
- **B.** Br$_2$(l) → Br$_2$(g) = 31 kJ
- **C.** Lattice energy of Lif = 1034 kJ
- **D.** H$_2$O$_2$(s) → H$_2$O$_2$(l) = 6 kJ
Draw an arrow from each of the following list of items to the position of its age or duration on the chart at left.

- The Permian-Triassic boundary.
- Cro-Magnon humans.
- Ur.
- The time since January 1, 1900.
- The time since January 1, 2000.
- A semester.
- A class period.
- A breath.
- A heartbeat.
- The time for sound to go one meter.