Kinetics
Unit 6

Reaction rates/mechanisms
Collision Theory
Rate Expression
Activation Energy
Rates of Reaction:

- time vs. rate - what’s the difference?
  - units of each?
    - time - seconds
    - rate - 1/seconds

- reaction rate - describes how quickly a reaction happens
  - how quickly the reactants are converted into products
Rate of Reaction:

\[ \text{rate} = \frac{\text{change of product concentration}}{\text{time}} \]

units?

- concentration = mol dm\(^{-3}\)
- rate = 1/sec
- rate of reaction = mol dm\(^{-3}\) s\(^{-1}\)
Rate of Reaction

- how to find rate of reaction on a curve...
- use the tangent, will treat a curve as a single point
- gradient might be negative, rate will be positive (always)
What do you notice about the overall rate of reaction? the beginning of rxn.? the end?
Measuring rates of reaction

Different Techniques:

- change in volume of a gas
- change in mass
- change in transmission of light (colorimetry/spectrophotometry)
- Titration
- Conductivity
- Clock reactions
Change in Volume of Gas

measuring techniques:

- gas syringe
- inverted burette - bubble the gas through the liquid to minimize error use warm water (why?)
Change in mass

- use a porous membrane to allow gas to escape (cotton balls will work)
- measure the change
- doesn’t work well with hydrogen...why?
Change in color

- works with coloured solutions (transition metals...etc)
- change in absorbance of the solution is measured over time
Titration and Conductivity

Titration - measure the concentration of the reactants or products by titrating the solution with a ‘standard’ solution of known concentration.

Conductivity - can be measured and compared to the total number of ions in solution (side of the rxn with more ions will be more conductive).
Clock Reactions

Video!

Using something observable as an arbitrary ‘endpoint’
Collision Theory
Not all particles have the same KE (avg. KE – temperature)

Shown by Maxwell-Boltzmann distribution curve
Collisions...

how to have a successful collision...

what do we need?
Energy of collision

What’s the minimum amount of kinetic energy needed to react called?

Activation energy
Energy

Only certain particles will have the energy to reach the threshold and are able to complete the reaction.
Geometry of Collision

- Do they collide with the proper orientation?
- Will the collision be effective?
- Is geometry the only variable?
- Energy too!
Factors Affecting rate of reaction

You know these:

- Temperature
- Concentration
- Particle size

You may know these:

- Pressure
- Catalyst
Temperature

What happens to the kinetic energy if we increase the Temperature?

Look at the number of particles with sufficient energy to react after the temperature is increased.

Many reactions double their rate with a 10°C increase.
Concentration

Higher concentration has more particles involved and therefore will have more collisions and more of those collisions will be successful.
On April 5, 2010, metal mining equipment created a spark as it hit rock along a passage of the Upper Big Branch mine, then owned by Massey Energy Company. That spark ignited a pocket of methane gas, which ignited a large quantity of highly explosive coal dust. Twenty-nine miners died, two were injured and Massey Energy was engulfed in accusations of negligence and willful concealment of unsafe conditions.
Pressure

What do you think?

FIGURE 15-2. If the volume of a gas is halved, the number of collisions with the walls of the container doubles. Thus, the pressure in container (b) is twice that of container (a).
Catalyst

- A substance that increases the rate of a reaction without itself going through a chemical change.

- Provides an ‘alternate route for reaction’ - has a lower activation energy.
Catalysts

certain manufacturing processes use catalysts to increase efficiency and yield (many are a closely guarded secret)

Every biological reaction uses a catalyst...called enzymes

Used in making cheese

Field of biotechnology is developing these applications rapidly
In review - more particles will have the energy to "get over the hump" (activation energy) due to the fact a catalyst was used.
16.1 Rate Expression

This graph shows the absorbance of the decomposition of $\text{C}_6\text{O}_3$ over time.
Rate vs Absorbance

What's true about this chart?

Reaction rate is directly proportional to the concentration

rate $\propto [C_{60}O_3]$
We know: \( \text{rate} \propto [C_{60}O_3] \)

This can be converted to an equation using a constant:

\[
\text{reaction rate} = k [C_{60}O_3]
\]

This is called the rate expression or the rate law.

It is considered a first-order reaction because the concentration of the reactant is raised to the first power.
In general, the rate is proportional to the product of the concentration of the reactants, raised to a power.

\[ A + B \rightarrow \text{products} \]

\[ \text{Rate} \propto [A]^m[B]^n \quad \text{or} \quad \text{rate} = k [A]^m[B]^n \]

The powers to which the concentrations are raised in the rate expression, \( m \) and \( n \), are known as the \textit{orders} of reaction.

The \textit{overall order} for the reaction is \( m + n \).
Example

The reaction $2H_2(g) + 2NO(g) \rightarrow 2H_2O(g) + N_2(g)$ is shown to be the second order with respect to NO and first order with respect to $H_2$.

Give the rate expression for this reaction and its overall order.
The orders of reaction cannot be determined by looking at the coefficients of the reactants.

Reaction order can only be determined experimentally.

There is no prediction to be made by looking at the coefficients.
The rate expression for the reaction

\[ \text{NO}(g) + \text{O}_3(g) \rightarrow \text{NO}_2(g) + \text{O}_2(g) \]

is:

\[ \text{rate} = k[\text{NO}][\text{O}_3] \]

What is the order with respect to each reactant and what is the overall order of the reaction?
Units of $k$, the rate constant

Zero Order

Rate = $k$

$k = \text{units of rate}$

$= \text{mol dm}^{-3} \text{s}^{-1}$

First order

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

to the board...
Units of $k$, the rate constant

Second Order

- Rate = $k \ [A]^2$
- to the board...

Third Order

- Rate = $k \ [A]^3$
- again...
Example

A reaction has the rate expression:

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

Calculate the value of \( k \), including units, for the reaction when the concentrations of both \( A \) and \( B \) are \( 2.50 \times 10^{-2} \text{ mol dm}^{-3} \) and the rate is \( 7.75 \times 10^{-5} \text{ mol dm}^{-3} \text{ s}^{-1} \).
Graphical Representations...

Zero Order reactions

rate = k [A]^0  or  rate = k

concentration does not affect the rate

on page 291
First Order reactions

rate = k [A]

concentration is directly proportional to the rate

this graph shows a straight line with gradient, k

on page 292
Second Order reactions

rate = \( k [A]^2 \)

rate is proportional to the square of concentration of A

- steeper start than 1st order, levels off more
- is a parabola, gradient is proportional to concentration and is initially zero

on page 292
Putting it all together

conc.  rate

Time  Concentration

on page 291-292
**Half-life**

First order reactions have a constant half-life

- if the time is measured to decrease the amount of starting reactant by half, this interval is independent of the initial concentration

- Only true for 1st order reactions

- shorter the half life, faster the reaction rate
Determining the order of a reaction

Initial Rates Method

Involves carrying out different reactions by changing concentrations while holding others constant

Finding Order of Reaction

1. If changing the concentration of A has no effect on the rate, the rate must be zero order with respect to A

2. If changes in A produce proportional changes in rate, it must be first order with respect to A - i.e. doubling concentration doubles the rate

3. If changes in A leads to an increase equal to the square of the change, the reaction is second order with respect to A - i.e. doubling conc. leads to 4-fold increase
Use the data in the table below to work out the order of reaction with respect to A and B. Also, decipher the rate expression for the reaction.

<table>
<thead>
<tr>
<th>Experiment #</th>
<th>Initial Concentrations mol dm(^{-3})</th>
<th>Initial Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>[A]</td>
<td>[B]</td>
</tr>
<tr>
<td>1</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>2</td>
<td>0.2</td>
<td>0.1</td>
</tr>
<tr>
<td>3</td>
<td>0.3</td>
<td>0.1</td>
</tr>
<tr>
<td>4</td>
<td>0.3</td>
<td>0.2</td>
</tr>
<tr>
<td>5</td>
<td>0.3</td>
<td>0.3</td>
</tr>
</tbody>
</table>
Most reactions occur at a measurable rate that occur as a “series of steps”

Usually, the products of a single step are used as a reactant in a subsequent step - exist only as “intermediates”
Example:

\[
\text{NO}_2(g) + \text{CO}(g) \rightarrow \text{NO}(g) + \text{CO}_2(g)
\]

This reaction happens in the following steps:

- step 1: \(\text{NO}_2(g) + \text{NO}_2(g) \rightarrow \text{NO}(g) + \text{NO}_3(g)\)
- step 2: \(\text{NO}_3(g) + \text{CO}(g) \rightarrow \text{NO}_2(g) + \text{CO}_2(g)\)

the overall reaction can be found by canceling the common reactants/products
Molecularity - used in reference to the number of species involved

- unimolecular - uses a single reactant particle
- bimolecular - uses two reactant particles

In our reaction, both steps were bimolecular
Rate Determining Step

On your way to school...do you get stuck anywhere?

The slowest step in a chemical reaction will determine the overall rate - this is the rate determining step.
Rate Determining Step

1st step: rate-determining step

2nd step: fast step

$E_a$

$\Delta H$

Potential energy

Extent of reaction

Reactants

Products
Rate expression and Mechanism

Rate determining step - single molecular event

Collision theory - if a species has a concentration in a reaction, it must be a part of the rate law (expression)

<table>
<thead>
<tr>
<th>Equation for rate determining step</th>
<th>Molecularity</th>
<th>Rate law</th>
</tr>
</thead>
<tbody>
<tr>
<td>A → products</td>
<td>unimolecular</td>
<td>rate = $k [A]$</td>
</tr>
<tr>
<td>2A → products</td>
<td>bimolecular</td>
<td>rate = $k [A]^2$</td>
</tr>
<tr>
<td>A + B → products</td>
<td>bimolecular</td>
<td>rate = $k [A][B]$</td>
</tr>
</tbody>
</table>
Finding the Rate law

Rate law is dependent on rate determining step

$$2\text{NO}_2\text{Cl}_\text{(g)} \rightarrow 2\text{NO}_2\text(g) + \text{Cl}_2\text(g)$$

Mechanism:

- step 1: $\text{NO}_2\text{Cl}_\text{(g)} \rightarrow \text{NO}_2\text(g) + \text{Cl}_\text{(g)}$  
  slow - RDS

- step 2: $\text{NO}_2\text{Cl}_\text{(g)} + \text{Cl}_\text{(g)} \rightarrow \text{NO}_2\text(g) + \text{Cl}_2\text(g)$  
  fast
Which step determines the rate of reaction?

What will the rate expression for that step look like?

\[ \text{rate} = k \ [\text{NO}_2\text{Cl}] \]

first order reaction
What happens when the rate determining step doesn’t happen 1st?

\[ 2\text{NO}_2(g) + \text{O}_2(g) \rightarrow 2\text{NO}_2(g) \]

mechanism:

- step 1: \( \text{NO}_2(g) + \text{NO}_2(g) \rightarrow \text{N}_2\text{O}_2(g) \) fast
- step 2: \( \text{N}_2\text{O}_2(g) + \text{O}_2(g) \rightarrow 2\text{NO}_2(g) \) slow - RDS

So...rate depends on step 2

rate = \( k \ [\text{N}_2\text{O}_2] \ [\text{O}_2] \)
Cont’d...

rate = $k [N_2O_2][O_2]$

BUT! - $N_2O_2$ is a product of the first equation!

Substitute the rate expression from the first reaction:

rate = $k [NO]^2[O_2]$

∴ This is a third order reaction
Example

If the mechanism of a reaction is:

- $\text{AB}_2 + \text{AB}_2 \rightarrow \text{A}_2\text{B}_4$  \hspace{1cm} \text{slow}
- $\text{A}_2\text{B}_4 \rightarrow \text{A}_2 + 2\text{B}_2$  \hspace{1cm} \text{fast}

What is the overall equation for this reaction?

What is the rate expression for this reaction?

What units will the rate constant have in this reaction?
Activation Energy

Rate of reaction depends on:

- \( k \) - the rate constant
- the concentration of the reactants

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

Where does temperature fit in?
Activation energy

If activation energy is high, a small temperature change will cause a large increase in the number of particles with sufficient energy to react.

If activation energy is small, a small temperature change will not do much to change the overall rate.
Therefore, the temperature dependance of $k$ depends on the value of the activation energy

Equation Time!!
The fraction of molecules with enough energy to react (enough Activation energy, $E_a$) at temperature $T$ is proportional to $e^{-E_a/RT}$

$R = \text{gas constant} = 8.31 \text{ J K}^{-1} \text{ mol}^{-1}$

$T = \text{absolute temperature in Kelvin}$

$\therefore k \propto e^{-E_a/RT}$ or $k = A e^{-E_a/RT}$
Arrhenius Equation

\[ k = A e^{-E_a/RT} \]

- \( A \) - the Arrhenius constant

Let’s try to make sense of this...take the natural log of both sides

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

This equation will give a straight line with gradient \(-\frac{E_a}{R}\) and y-intercept, \(\ln A\) (y-axis = \(\ln k\), x-axis = \(1/T\))

Both equations are in IB Data Booklet...yay!
$2 \text{NO}_2 \rightarrow 2 \text{NO} + \text{O}_2$