6.1.3 Analyzing rate data from graphs

To measure the rate of a reaction a change in some property (e.g. concentration, mass and volume) needs to be measured with time between the start and end of the reaction.

Analyzing rate data from graphs qualitatively
Consider the reaction for the decomposition of hydrogen peroxide:

\[ 2 \text{H}_2\text{O}_2(\text{aq}) \rightarrow 2 \text{H}_2\text{O}(\text{l}) + \text{O}_2(\text{g}) \]

The graph on page 2 shows the change in concentration with time. The rate of a reaction is indicated by the slope (gradient) of the line. The steeper the slope the faster the rate.

Initial rate
Initially at time zero the concentration is of hydrogen peroxide is high because the number of moles of the hydrogen peroxide is the greatest. This increases the frequency of collisions between the molecules increasing the rate at which they are converted into products, indicated by a steep initial slope.

Initially at time zero the concentration of the water and oxygen is zero because they have not been formed yet. With time their concentrations increase as hydrogen peroxide molecules are converted into water and oxygen gas. Initially the rate at which they are formed increases rapidly, indicated by the steep slope of the line. This is because there is more moles of hydrogen peroxide initially which means that more products will be formed.

During the reaction
As time proceeds the hydrogen peroxide get converted into products and its concentration starts to decrease. Because it is an aqueous solution the solution becomes more dilute. The decreasing frequency of collisions between hydrogen peroxide molecules decreases the rate of the reaction. The slope becomes less steep.

The concentration of water and oxygen also starts to decrease, because there are fewer moles of hydrogen peroxide left. The decreasing frequency of collisions between the hydrogen peroxide molecules, decreases the frequency with which they are converted into products. Their slopes become less steep.

At the end of the reaction
Eventually the lines will flatten out (remain constant) indicating that the concentrations do not change with time. The concentration of hydrogen peroxide no longer changes because no more collisions are possible. All the moles of hydrogen peroxide have been used up and the reaction is complete. With no more moles of hydrogen peroxide available, no more moles of water and oxygen will be produced, so their concentrations will remain constant as well.

The overall rate of the reaction is negative with respect to the hydrogen peroxide because its concentration decreases with time and positive with respect to the water and oxygen because their concentrations increase with time.
The graphs below show how changing the concentration, temperature and surface area of a reactant will change the time taken for the reaction between calcium carbonate and hydrochloric acid to go to completion.

Increasing the surface area of a solid reactant (CaCO$_3$) by grinding it into a powder increases the frequency of collisions between the reactants. The initial rate of the reaction will increase, indicated by the steeper slope.

Increasing the temperature of the hydrochloric acid increases the average kinetic energy of the hydrogen ions (reactive part of an acid) increasing the frequency of collisions between the HCl and CaCO$_3$ because a greater proportion of the molecules have energy, $E \geq$ activation energy, $E_a$. The initial rate of the reaction will increase, indicated by the steeper slope.

Increasing the concentration of HCl will increase the number of moles of hydrogen ions increasing the frequency of collisions between with CaCO$_3$. The initial rate of the reaction will increase, indicated by the steeper slope.

Notice how the graphs flatten out and the reaction ends earlier when the concentration, temperature and surface area are increased. In each case the calcium carbonate is the limiting reactant, so the same total volume of carbon dioxide gas will be produced.
Analysing rate data from graphs quantitatively

Calculating Initial rate
The graph below shows the change in the concentration of oxygen gas with time during the decomposition of hydrogen peroxide. The initial rate of the reaction at the start is where the slope/gradient is the steepest. It is found by drawing a tangent to the curve when the time is zero and determining the slope of this tangent. Initial rates are often determined because it is the easiest slope to calculate because the curve is usually the most linear at the start of the reaction. Initial rate is commonly used to determine how the rate of a reaction depends on concentration or temperature.

The graph below shows how changing the concentration of hydrogen peroxide changes the rate at which oxygen is produced with time. Notice how the initial rate is greater at the higher concentration and that the final volume of O$_2$ gas produced with 0.16 moldm$^{-3}$ H$_2$O$_2$ is half that produced with 0.32 moldm$^{-3}$ H$_2$O$_2$.

The reaction can be analyzed further by plotting the initial rate at each concentration against the concentration of hydrogen peroxide. The graph shows that the concentration is proportional to the initial rate, because as the concentration doubles the rate doubles.
Calculating Instantaneous rate
The graph below shows how to calculate the instantaneous rate at a particular time in the decomposition of hydrogen peroxide. Notice how it decreases as the reaction proceeds. The instantaneous rate is found by drawing a tangent to the curve at the time of interest and then determining the slope of this tangent.

Rate at time t = slope at that time.
Calculating Average rate
This is the average rate over the entire duration of the reaction.

\[
\text{Average rate} = \frac{\Delta \text{concentration}}{\Delta \text{time}}
\]

For example in the graph above the average rate between 0 and 40 s is:

\[
\text{Average rate} = \frac{\Delta \text{concentration}}{\Delta \text{time}} = \frac{0.40 - 0.15}{40 - 0} = -0.0065 \text{ moldm}^{-3}\text{s}^{-1}
\]

The rate is negative rate because the concentration of the reactants is decreasing with time.