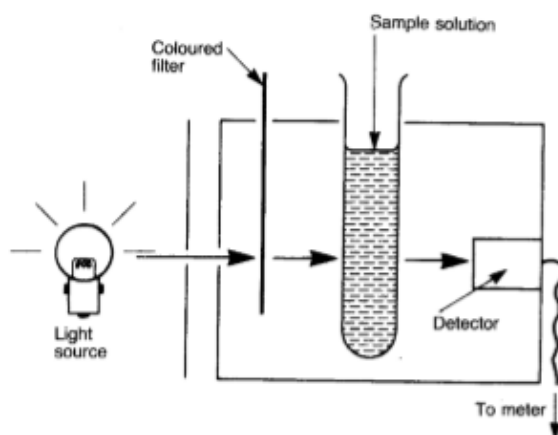


Chemical Kinetics II



A simplified diagram of a colorimeter

First Edition	Jan 2006
Second Edition	Jun 2009
Third Edition	Jun 2011
Fourth Edition	Jan 2019 (Revised New Syllabus)

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Chemical Kinetics

1. Define rate of reaction & Write its units, Hence explain how the rate can be positive or negative?

The rate of the reaction can be defined as the rate of change in concentration of reactants/products with time.

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

The average rate of reaction is defined as:-

$$\text{Rate} = \frac{\text{change in concentration of reactant/ product}}{\text{change in time}}$$

If the rate is expressed in terms of concentration of reactant then it is negative as the concentration decreases with time.

$$\text{Rate} = \frac{-\Delta [\text{Reactant}]}{\Delta \text{Time}} \quad \Delta = \text{Change} \quad [] = \text{Concentration}$$

If the rate is expressed in terms of concentration of products then it is positive as the concentration of products increases with time.

$$\text{Rate} = \frac{+\Delta [\text{Products}]}{\Delta \text{Time}}$$

Measuring the rates of reaction

2. State the different experimental techniques which can be used to determine the rate & how to decide which method to be used

There are several methods available. By examining the chemical equation, the choice of the most preferable method can be made.

The methods can be divided into two categories. The chemical methods and the physical method. The chemical method includes volumetric analysis, where analytical sampling of solutions is done to follow the progress of a reaction.

The physical method includes colorimetry, measurement of volume of gas evolved, Measuring the changes in pH, Electrical conductivity.

3. Explain how the volumetric method can be used to determine the rate of a reaction

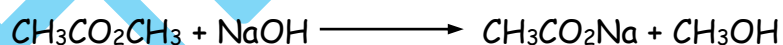
As the reaction proceeds, the concentration of reactants decrease, and the concentration of the products increase. The concentration of the specific reactant/product at regular time intervals, can be found as below.

The change in the concentration at given time intervals, can be found by pipetting out a known volume of the reaction mixture at frequent time intervals and titrating against a standard solution. As the reaction mixture is pipetted out to the conical flask, the reaction has to be stopped immediately. If the titration was carried out immediately, still the reaction will proceed, (between the original reactants) while the titration is being done.

To prevent further reaction, a small volume of the mixture is pipetted and transferred to ice cold water to quench the reaction. The time is recorded at the mid way of transferring, not at the initial pipetting out. Then the concentration of the specific reaction can be found by titrating against a suitable reagent. This can be repeated at regular time intervals. The gradient of the plot concentration vs. time will give us the rate of the reaction. Quenching can also be achieved by adding the solution from the reaction mixture to a solution that reacts with one of the reactants, in order to prevent further reaction taking place. The titre is proportional to the concentration of the reactant/ product being titrated.

When a reagent is used for quenching it should not react with one of the reagents to result the same product that is being measured.

Eg: Alkaline hydrolysis of methyl ethanoate.



A small known volume of reaction mixture is pipetted out at known time intervals and immediately quenched by transferring it to ice cold water. The NaOH concentration can be determined by titration against standard acid. The titre would decrease with time as the reaction proceeds.

OR

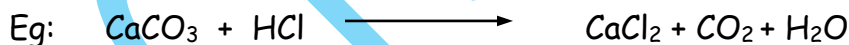
The change in concentration can also be found by reacting a known volume of reaction mixture with excess reagent at given time intervals and the remaining reagent can be found by titration.

Eg: In the above experiment, at regular time intervals, a known volume of reaction mixture can be placed in test tubes which contain a concentration and volume known HCl acid. The NaOH will react with HCl and the excess HCl can be found by titration with NaOH. Hence the titre (NaOH) would increase as the $[\text{OH}^-]$ decreases.

a. Explain how the rate can be measured in reactions where a gas is evolved as a product

The gas produced is collected in a graduated gas syringe or over water into a measuring cylinder attached to the reaction vessel. (note that the gas syringe has a greater degree of precision when smaller volumes are measured) The increase in volume of gas is recorded at regular time intervals and volume of gas evolved vs. time is plotted, to find the rate from the gradient. The rate obtained by this method is called the instantaneous reaction rate.

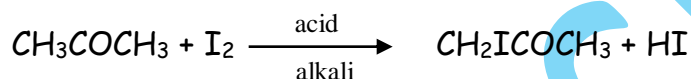
If a solid is used as the reactant the above method can be modified by measuring the loss of mass with time. As the gas is given off the mass decreases.



b. Explain how the rate can be measured in reactions where a colour change can be observed

If one of the reactant or product is coloured, then the decrease or increase in the intensity of the colour can be used to measure the rate. The apparatus used for this purpose is known as the colorimeter or a spectrophotometer. The amount of light of a particular frequency that is absorbed depends on the concentration of the coloured substance.

Eg: Reaction of iodine with propanone.



The coloured substance is I_2 which is a yellow-brown solution. As the rate proceeds, the concentration of I_2 decreases, hence the rate decreases. The rate of decrease in colour in I_2 is proportional to the rate of decrease in concentration of I_2 . The intensity of colour can be measured at regular time intervals by subjecting the sample to a colorimeter. The colorimeter gives the intensity of colour as a reading or if it is attached to a computer as a graph. This method is useful for fast reactions.

Eq:- Reaction between bromine & methanoic acid.

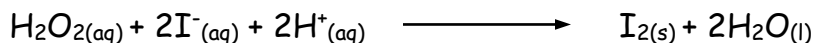


The reactants are mixed & the clock is started. As the reaction precedes the brown colour of Br_2 fades off gradually. The light absorbed is measured at regular time intervals by a spectrophotometer.

4. Clock Reactions.

The time taken to produce a fixed amount of product is measured & the reaction is repeated several times using different concentrations. A clock reaction helps to determine the initial rate more conveniently, by taking a single measurement per experiment.

□ The iodine clock : (Harcourt-Esson)



- Add few drops of starch indicator to a solution of H_2O_2 in a beaker.
- Known volume of KI solution & dilute sodium thiosulfate are placed in a second beaker.
- The contents of the two beakers are mixed & the time taken for the solution to turn blue is recorded.

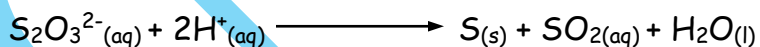
The reaction produced I_2 which then reacts with $\text{Na}_2\text{S}_2\text{O}_3$ when all sodium thiosulfate has been used up the remaining iodine reacts with starch producing an intense blue-black colour.

The purpose of adding Sodium thiosulfate is that it rapidly reacts with iodine as it is formed thus reduces the iodine concentration. This prevents the appearance of blue colour until a fixed amount of reaction has occurred.

- The experiment is repeated with different concentrations of H_2O_2 with the same volumes of KI & $\text{Na}_2\text{S}_2\text{O}_3$. The average rate of reaction in each experiment is proportional to $1/\text{time}$

NOTE: If sodium peroxodisulfate / persulfate ($\text{Na}_2\text{S}_2\text{O}_8$) instead of H_2O_2 , $\text{Na}_2\text{S}_2\text{O}_8$ get reduced to sulfate (SO_4^{2-})

□ The sulfur clock :



Add dilute HCl to $\text{Na}_2\text{S}_2\text{O}_3$ solution in a beaker standing on a piece of paper with a black cross on it. As the yellow precipitate of sulfur is formed the cross will be invisible. Measure the time taken for the cross to disappear with different concentrations of $\text{Na}_2\text{S}_2\text{O}_3$ or different temperatures at constant concentration. The average rate of reaction is proportional to $1/\text{time}$.

5. Explain with an example how rate of reaction can be measured in terms of electrical conductivity.

Electrical conductivity can be used in a reaction where total number of ions in a solution changes during a reaction.

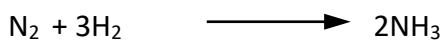
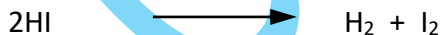


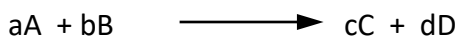
6. Write rate expressions to show the rate of reaction with respect to each reactant & product in the following reaction hence deduce their relationship



The rate of the reaction can be measured in terms of change of concentration of any species in the reaction at a given time. The rate at which reactants disappear or products appear in a unit time can be used to measure the rate.

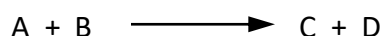
7. Similarly, write the rate equation for below reactions in terms of reactants & products & state their relationship in calculus notation.





8. State the Rate Law

9. Write the empirical rate equation (rate expression / kinetic expression) for the below reaction & define each term



10. Define the terms order of reaction & overall order of reaction

The coefficients 'm' or 'n' in the rate equation is known as the order of reaction (or partial order of reaction). m & n can be 0, 1 or 2.

The partial order/ order of one reactant is the power to which the concentration of that reactant is raised in the rate equation.

If m or n is	1	1 st order
	2	2 nd order
	0	zeroth order

The sum of the order of reaction is called the overall order of the reaction (m + n). It can also be defined as the sum of powers to which the concentrations are raised in the rate equation.

The order of the reaction m & n are not necessarily equal to the stoichiometric coefficients of the reactants. The order with respect to each reactant should be found experimentally and cannot be predicted by the equation

11. Explain why the order of reaction cannot be deduced directly from the Stoichiometric equation for a non-elementary reaction. (single step reaction)

The rate equation includes only those species involved in the rate determining step (slow step) in a multistep reaction and the order is determined by the mechanism. Whereas the stoichiometric equation includes all the reactants.

For elementary reaction (reaction where a single collision between the two reactant particles occur) the order can be deduced by the stoichiometric equation, which is the reacting molar ratio.

12. Define Rate constant & state its units

The constant (k) in the rate expression is called the rate constant and is equal to the rate of the reaction when all the reactants have unit concentration (zeroth order). The unit of the rate constant depends on the rate expression.

<u>Order</u>	<u>Units of k</u>
--------------	-------------------

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

First	s^{-1}
-------	-----------------

Second	$\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$
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Eg: 1st order: $\text{Rate (mol dm}^{-3} \text{ s}^{-1}) = k [\text{mol dm}^{-3}]$
 $k = \text{s}^{-1}$

2nd order: $\text{Rate (mol dm}^{-3} \text{ s}^{-1}) = k [\text{mol dm}^{-3}]^2$
 $k = \text{mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$

The value of rate constant depends on temperature & the Activation energy. Increased temperature will increase the value of the rate constant. The use of catalyst decreases the activation energy hence increases the rate constant. (Further explained under Arrhenius equation)

The rate constant is always represented by lower case 'k'. Upper case 'K' is the symbol for equilibrium constant.

13. Explain how the orders of the reactants can be found by experimental data

There are two experimental methods to determine the order. The continuous method and the initial rate method. In continuous method the order is found by the half-life of concentration vs time graph.(explained later) The initial rate method is described below.

Orders of reactants can be found by carrying out the same reaction several times, varying the concentration of one reactant at a time. Each time measure the initial reaction rate, thus the order of the reaction with respect to that reactant can be calculated as shown below.

First find the rate of a reaction, then repeat the reaction by doubling the concentration of one reactant. If the rate is doubled, then the order of the reaction with respect to that reactant is one.

Eg:

In short, we can predict the order without the above calculation in the following method, if the concentration of only one reactant is doubled. Then:

If the rate is doubled then $[X^2^1]$ the order is one.

If the rate is increased by factor 4, $[X^2^2]$ then the order is two.

If the rate was the same $[X^2^0]$ then the order is zero.

Likewise if the concentration of one reactant tripled, Then,

If the rate is tripled then $[3^1]$ the order is one

If the rate is increased by factor 9, $[3^2]$ then the order is two

14. It was found that doubling the concentration of both reactants increased the rate by a factor eight, but the doubling the concentration of one reactant (B) doubles the rate. Deduce the order of the reaction with respect to each reactant hence write the rate equation & the overall order of the reaction

15. Two gases A & B react according to the equation



A series of experiments carried out at 300K gave the following results

Experiment	Initial concentration / mol dm ⁻³		Initial rate / mol dm ⁻³ s ⁻¹
	[A]	[b]	
1	0.1	0.1	0.35
2	0.2	0.1	0.70
3	0.2	0.2	1.40

- i. Deduce the order of reaction with respect to each reactant & hence write the rate equation

ii. What is the order of the reaction & define overall order of the reaction

iii. Calculate the rate constant including its units

16. At a constant temperature the rate between a bromo alkane & hydroxide ions was investigated & the following data were obtained

[bromo alkane] / mol dm ⁻³	[OH ⁻] / mol dm ⁻³	Rate / mol dm ⁻³
0.10	0.10	1.20
0.20	0.10	2.40
0.30	0.20	3.60

Use the data to deduce the rate equation for the reaction between bromo alkane & hydroxide ions.
Hence the overall order of the reaction

17. Past Paper question 2003 June C5 Question 3

3. (a) In a rate of reaction experiment between two substances, A and B, the overall order of the reaction was found to be 2. Write three possible rate equations for such a second order reaction between A and B.

.....
.....
.....

(3)

- (b) At a certain temperature the rate of reaction between nitrogen monoxide, NO, and hydrogen, H₂, was investigated. The following data were obtained.

[NO]/mol dm ⁻³	[H ₂]/mol dm ⁻³	Rate/mol dm ⁻³ s ⁻¹
1.0	1.0	0.02
1.0	3.0	0.06
3.0	1.0	0.18

- (i) Use the data above to deduce the rate equation for this reaction.

(3)

- (ii) Use your answer to (b)(i) above to calculate the value of the rate constant, with units.

(2)

- (c) State the effect of an increase in temperature on the value of the rate constant

.....

(1)

18. Past Paper question 2006 June C5 Question 3 (b)

(b) Two gases, A and B, react according to the equation



A series of experiments carried out at 298 K gave the following results.

Experiment	Initial concentration of A /mol dm ⁻³	Initial concentration of B /mol dm ⁻³	Initial rate of reaction /mol dm ⁻³ min ⁻¹
1	0.100	0.100	0.00200
2	0.100	0.200	0.00798
3	0.200	0.100	0.00399

(i) State the order of reaction with respect to each of the reactants. Justify your answer.

Reactant A

.....

.....

Reactant B

.....

.....

(3)

(ii) Write the rate equation for the reaction between A and B.

.....

(1)

(iii) Use the experimental data from Experiment 1 to calculate the rate constant, including its units

(2)

19. Explain the transition state theory & represent the transition state & intermediate in an energy profile

The transition state is a state in between the reactants and the products. As reactants change into products, some of its old bonds break (leaving group) and new bonds are made at the same time. The transition state condition represents half broken old bonds and a half formed new bond. Transition state has no significant lifetime.

Eg: Hydrolysis of bromoalkane (S_N2 mechanism)

The transition state (Activated complex) is shown at the top of the activation energy hump of the energy profile.

Most of the reaction passes through a transition state. A transition state is not a species that can be isolated it changes immediately into the products.

The reaction profile for S_N1 hydrolysis of tertiary halo alkane is a two-step reaction which involves stable intermediate.

20. State the relationship between the rate constant (k), Temperature & Activation energy
[The Arrhenius equation]

As temperature is increased, the particles gain more energy, hence vibrate and collide frequently, resulting in a higher rate of reaction. Also, the kinetic energy of the particles increases, so more molecules with energy higher than activation energy, results in a higher rate. As a result, the rate constant (k) increases with increase in temperature. Also, if the activation energy barrier is large, the reaction will be slow. As a result, the reaction will have a small rate constant.

The relationship between the temperature, activation energy and the rate constant, was first found by Arrhenius and is represented by the Arrhenius equation.

$$k = Ae^{-E_a/RT}$$

k = Rate constant

A = Arrhenius constant (collision frequency)

e = Base of natural logarithms

E_a = Activation energy

R = Gas constant (8.314 J K⁻¹mol⁻¹)

T = Temperature

21. Simplify the Arrhenius equation hence show the effect of temperature & activation energy on rate constant

According to the Arrhenius equation increase activation energy will decrease the rate constant. Also by increasing the temperature will increase the value of the rate constant.

22. Plot a graph to show the relationship between $\ln k$ (& \log_{10}) vs. $1/T$ using the Arrhenius equation. Explain how this graph can be used to calculate the activation energy.

The Arrhenius equation is of the form of $y = mx+c$. Therefore a plot of $\ln k$ vs. $1/t$ should be a straight line if Arrhenius equation is obeyed.

The activation energy can be calculated once gradient & the gas constant is found as shown below;

If the graph was plotted $\log_{10}k$ vs. $1/t$ then the gradient will be $-E_a/R 2.303$

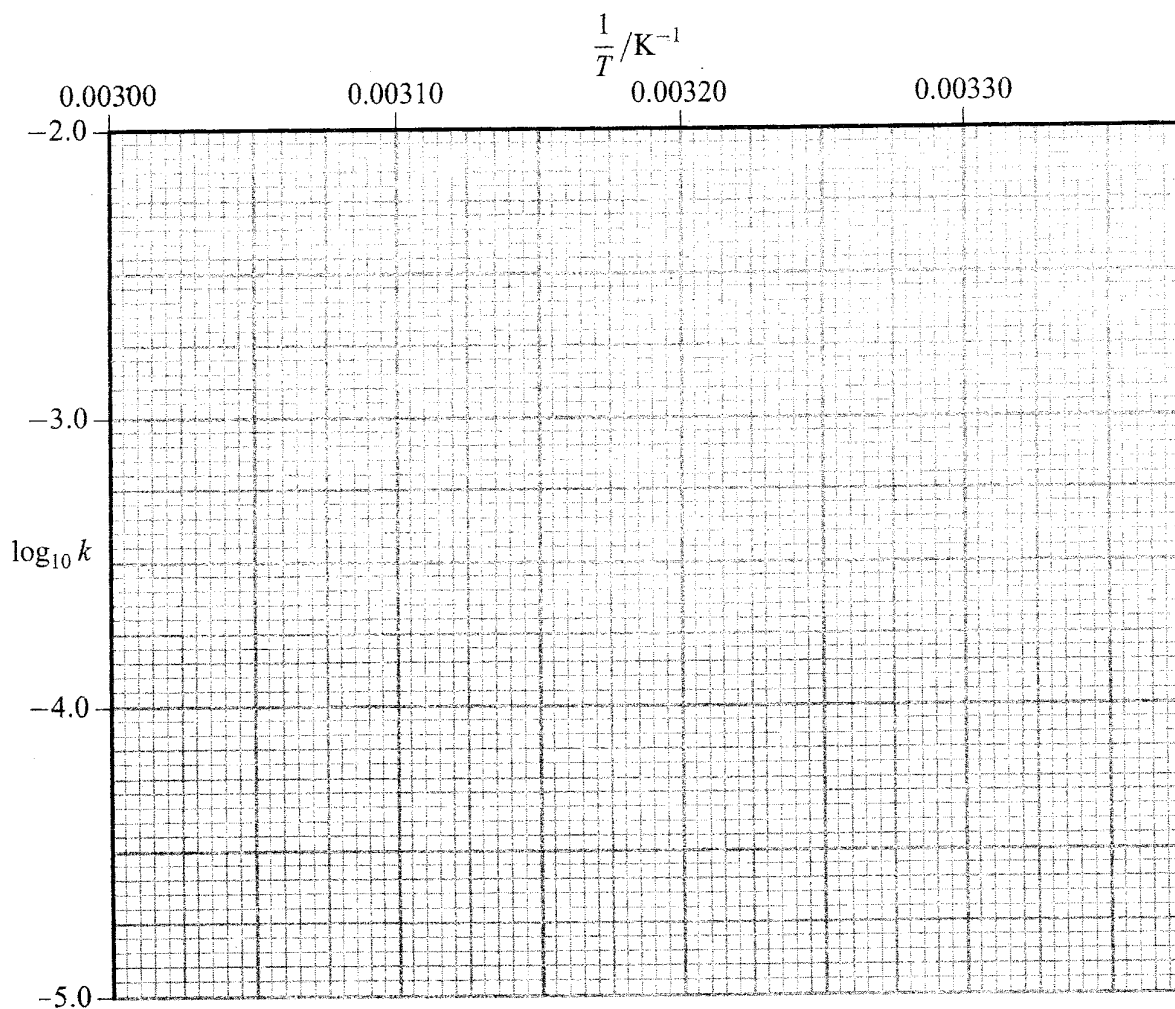
23. Past Paper question 2006 June C5 Question 3 (c)

(c) The rate constant, k , for the reaction in (b) was measured at different temperatures.

The following data were obtained.

$\log_{10} k$	$\frac{1}{T}/\text{K}^{-1}$
-2.70	0.00303
-3.39	0.00315
-4.09	0.00327
-4.43	0.00333

(i) Plot a graph of $\log_{10} k$ against $\frac{1}{T}$, on the grid below.



(2)

(ii) The Arrhenius equation can be written

$$\log_{10} k = \text{constant} - \frac{E_a}{2.30R} \left(\frac{1}{T} \right)$$

where $R = 8.31 \text{ J mol}^{-1} \text{ K}^{-1}$.

A graph of $\log_{10} k$ against $\frac{1}{T}$ has a gradient of $\frac{-E_a}{2.30R}$.

Calculate the gradient of the graph and hence calculate the value of activation energy, E_a .

(2)

21. Describe the experiment to find the activation energy of the reaction between phenol and bromine.

- Pipette 10ml of phenol solution and 10ml of bromide/ bromate solution in one boiling tube.
- Add few drops of methyl red indicator.
- Pipette 5ml of sulfuric acid solution into another boiling tube.
- Keep both boiling tubes in a water bath with a temperature of 75°C
- Mix the two boiling tubes and start the stop watch.
- Leave the boiling tube in the water bath till the colour of methyl red disappears.
- Record the time.
- Repeat the experiment at 5 different temperature each with a different of 10°C

Record the results in the table below. Plot a graph of $\ln 1/t$ (which is same as $\ln k$) on y-axis vs. $1/\text{temp}$ on x-axis. Gradient of the pot can be used to find the activation energy for the reaction.

Time /S	$1/\text{time}$ S^{-1}	$\ln(1/\text{time})$	Temp / $^{\circ}\text{C}$	Temp/K	$1/\text{Temp}$ K^{-1}

Bromide (Br^-) reacts with bromate (BrO_3^-) in the presence of acid to produce bromine. When all phenol is reacted, the bromine continuously produced in the first reaction will react with methyl red indicator thus bleach its colour.

22. How do we identify the rate-determining step in a multi-step reaction?

When the reaction is multi step, then the rate of the overall process is determined by the slowest step. The overall rate of the process is equal to the rate of the slowest step. This step is called the Rate-determining step.

For example, suppose we have to travel from A to C via B where A-B is a main road. A vehicle carrying 50 people, traveling at 40km/h, covers the distance of 40 km in 1 hour. A narrow road from B to C can only be crossed by a motorcycle carrying two people at a time at 20 km/h. It covers the distance of 20km in 1 hr.

Therefore, irrespective of how fast the 1st mode of transport is, the overall rate is determined by the second slow step. Therefore the 2nd step is the rate determining step.

Half Life ($t_{1/2}$)

1. Define Half-life ($t_{1/2}$)

Half life is defined as the time taken to reduce the initial concentration of a reactant to its half.

2. Describe how the half-life of a reaction can be found?

This can be done plotting a graph to show the variation of the concentration of a reactant with time. If the rate of the reaction is depended on the concentration of that reactant, then the rate of the reaction decreases (decreases in gradient) as the concentration decreases with time.

The time taken for the concentration of the reactant to decrease to half can be determined by the graph.

$t_{1/2}$ cannot be determined if the rate is unaffected by the concentration of the reactant. If the rate is constant with the decrease in concentration of the reactant, then it is a zeroth order reaction.

Rate $\propto [R]^0$

3. What can be concluded by finding the half-life of a reaction?

By finding the half life, we can determine the order of the reaction,(continuous method) thus the rate law. The half life depends on the initial concentration in a characteristic way, for reactions with different orders.

Eg: The first order reaction has a constant half life.

The second order reaction does not have a constant half life, rather it increases in a regular manner

The zeroth order reaction graph of concentration vs. time is a straight line and the successive half-lives decrease with time.

4. Describe the characteristics of a first order reaction graph

The graph for a 1st order reaction of concentration vs. time is always a curve, and has a constant half life. The time taken for the concentrations to drop to its half value each time, is the same.

According to this graph, the time taken for the concentration to drop from 240 to 120 units, 120 to 60, 60 to 30, is 100S each time.

Therefore the half life $t_{1/2} = 100S$

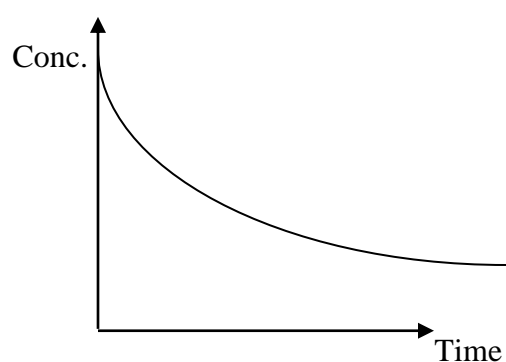
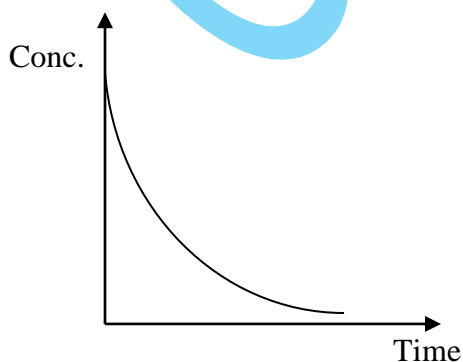
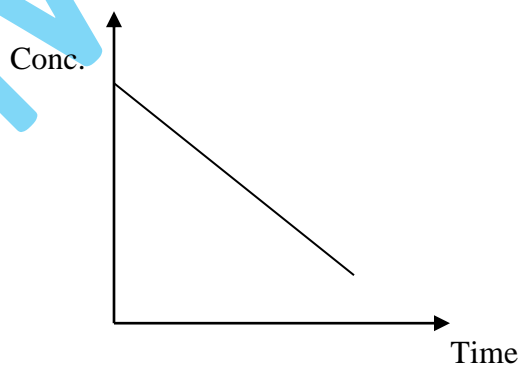
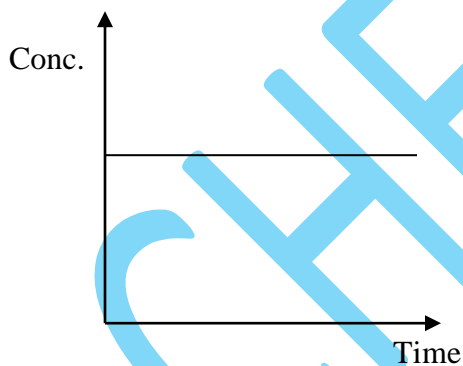
5. State an equation to show the relationship between the half life & the rate constant of a first order reaction.

$$kt_{1/2} = \ln 2$$

OR

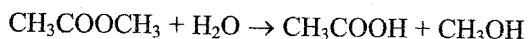
$$t_{1/2} = 0.693/k$$

6. Predict the order of below concentration vs. time graphs.



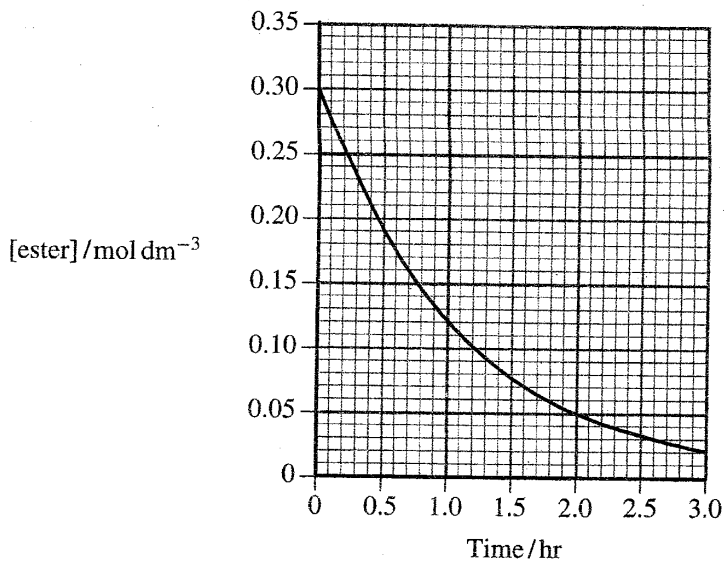
7. Past Paper question 2004 June C5 Question 3 (a)

The ester methyl ethanoate reacts with water as follows:



An experiment to investigate the kinetics of this hydrolysis showed that the concentration of methyl ethanoate varied as shown in the graph below.

The water in this reaction is not only a reagent but is also the solvent and is therefore in large excess.



(i) Show, under these conditions, that the reaction is first order in methyl ethanoate.

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(2)

(ii) Explain with a reason whether or not the overall order of reaction must also be one.

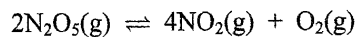
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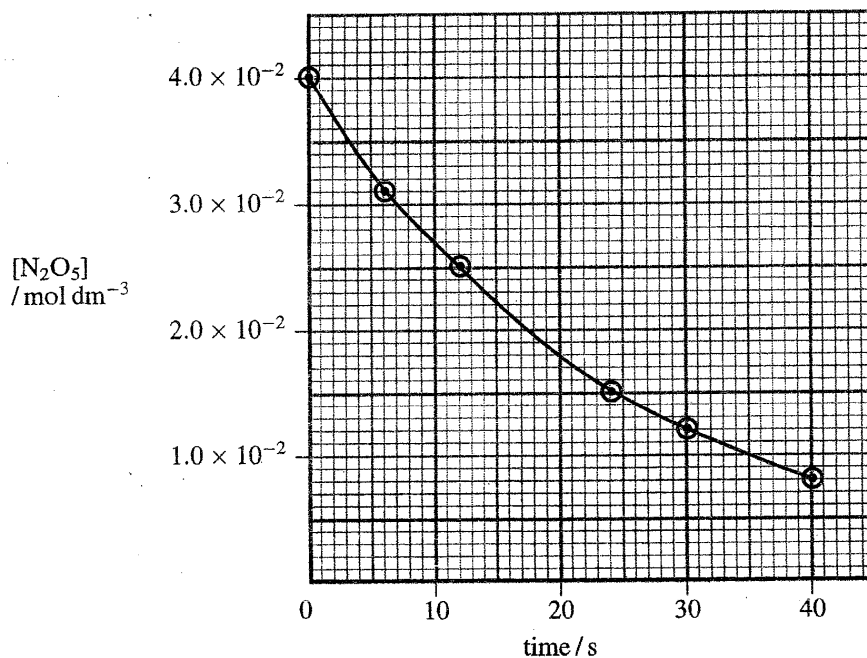
(iii) Assuming the reaction is first order, use the graph to calculate the rate constant, k . Include the units in your answer.

8. Past Paper question 2005 January C5 Question 1 (a)

1. Nitrogen(V) oxide, N_2O_5 , decomposes when heated according to the equation:



(a) The concentration of N_2O_5 at a temperature of 52°C was measured at different times, and the results are shown in the graph below



(i) Use the graph above to calculate two values for the half-life. State the order of the reaction and give a reason for your answer.

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(4)

(ii) Explain what the order of reaction you obtained in (i) suggests about the mechanism of the reaction.

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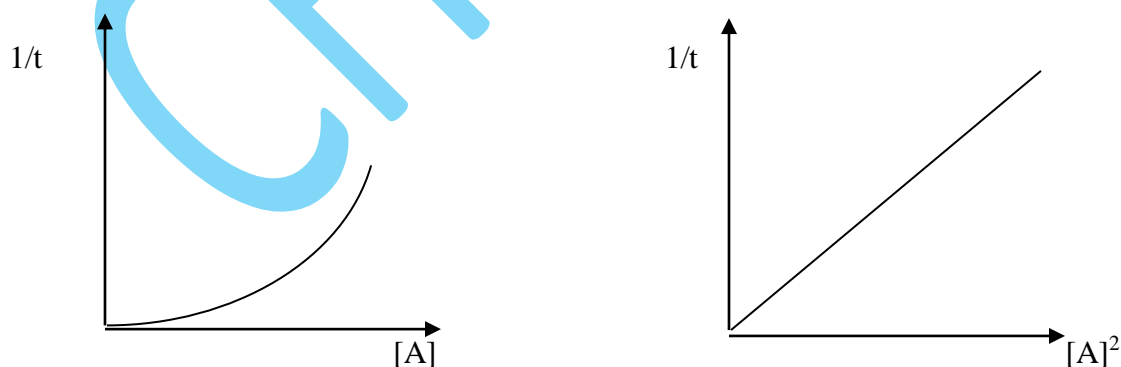
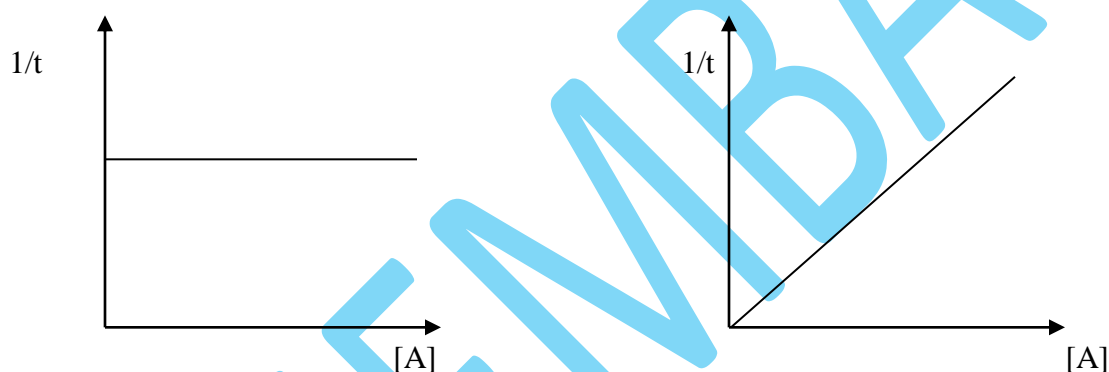
(2)

9. Explain how to find the order of reaction using rate-concentration graphs.

The order with respect to a given reactant can be found if the concentration of that reactant is plotted against rate or some quantity which is proportional to rate such as $1/\text{Time}$. $1/\text{Time}$ is often used as a measure of the rate.

- If the graph of rate or $1/\text{Time}$ vs. the concentration of a given reactant is a straight line, then the reaction is first order with respect to that reactant.
- If the graph of rate or $1/\text{Time}$ vs. $[\text{reactant}]^2$ is a straight line the reaction is 2nd order with respect to that reactant. Or upwardly curved line when plotted against concentration.

Predict the order of below concentration – rate graphs.



- Explain how information regarding the mechanism of a reaction can be deduced from kinetic data

The rate equation shows the reactants that take part in the rate determining step (slowest step). If the reactant is shown in the rate equation, it means that the order with respect to that reactant is not zero. If it is zero it will not be shown in the rate expression.

The rate equation also helps to find out the stoichiometry of the slowest step. The order with respect to each reactant gives the number of molecules which take part in the slow step.

Also, if the half-life graph contains a constant half life that means the reaction is in the 1st order. Hence the reaction must take place in two or more steps. Only one molecule will appear in the mechanism in the rate determining and the other molecule will appear in the mechanism after R.D.S.

eg:- S_N1 reaction. The reaction is zero order with respect to the nucleophile as the nucleophile enters after the rate determining step.

If the reaction is in the 2nd order, then the mechanism involves a transition state where both reactants take part and vice versa.

Eg:- S_N2 reaction. Such reactions take place in one single step.

- Explain how to predict the order of single step & multi step reactions using the reaction between aqueous hydroxide ions & halo alkane hence write the rate equation.

- Single step reactions:-

Mechanism:

Rate Equation:

The powers to which the concentration terms are raised in the rate equation for a single step reaction is the same as the stoichiometry.

- Multi step reactions:-

Mechanism:

Rate Equation:

The overall rate depends on the step 1 which is the slowest step (RDS)

- Explain the reaction of iodine with propanone in acid thus obtain data for the order with respect to the reactants & hydrogen ions. Hence write the mechanism for the reaction.

Acid catalyzed reaction of propanone with iodine is a three step reaction where iodine enters the mechanism after the rate determining step.

The rate Equation is:

As iodine enters the mechanism after the RDS its partial order is zero. Therefore the reaction is second order overall and zeroth order with respect to iodine.

Step 1: protonation of the carbonyl oxygen atom. (RDS step)

Step 2 : Loss of H^+

Step 3 : Addition of iodine followed by loss of H^+

- Draw possible reaction profile diagrams for multi step reactions showing the intermediate & comment on the rate determining step.

In a multistep reaction the stable intermediate is usually at a lower energy level than the reactants. But the activation energy barrier may differ as shown below which determines the rate determining step.

When the E_a is high then the reaction step will be slow thus it will be the rate determining step.

Clarification of Iodine, Propanone Reaction.

In this experiment you will study the kinetics of the reaction between 2-propanone (acetone) and iodine:



The rate of this reaction is found to be dependent on the concentration of hydrogen ion in solution as well as presumably the concentrations of the two reactants. Hydrogen ion could be thought of as a kind of "auto-catalyst". The rate law might thus be:

$$\text{Rate} = k [\text{CH}_3\text{COCH}_3]^m [\text{I}_2]^n [\text{H}^+]^p$$

Where m , n and p are the orders of the reaction with respect to 2-propanone, iodine and hydrogen ion respectively, and k is the rate constant for this reaction.

A convenient way to measure the rate for this reaction is in terms of the disappearance of I_2 :

$$\text{Rate} = -\Delta[\text{I}_2] / \Delta t$$

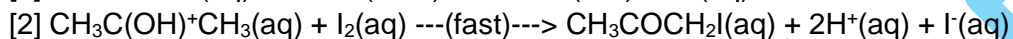
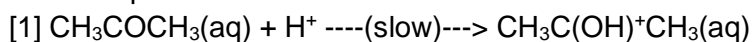
This expression alone will be sufficient since the reaction turns out to be zero order with respect to iodine concentration (i.e., $n=0$). Thus the rate of the reaction does not depend on I_2 and we can study the rate by making iodine the limiting reagent, having the 2-propanone and hydrogen ion present in large excesses so that their concentrations do not change appreciably by the time all the iodine is gone and therefore the rate remains fairly constant. Under such circumstances, if it takes t seconds for the color of the I_2 to disappear, the rate would be:

$$\text{Rate} = [\text{I}_2]_0 / t$$

where $[I_2]_0$ is the initial iodine concentration in the mixture. Since I_2 is colored in aqueous solution (reddish brown I_3^-), the rate can be determined by measuring the time it takes for the color of a solution with a known amount of I_2 to fade.

In summary, since the reaction is first order with respect to each of propanone and hydrogen ions, and is zero order with respect to iodine, this implies that the "slowest step" is the one involving a collision between one propanone and one hydrogen ion.

The accepted mechanism is therefore:



The first (slow) stage is a protonation of the propanone.

The second stage can be broken down into three separate (fast) steps, which finally involve proton removal.

In principle this could be done simply by looking at the solution, comparing it to water. There are a couple of problems with this approach. As the reaction approaches completion, the color fades rather rapidly, becoming pale yellow. It is difficult to distinguish just when the color is gone. Also, the final mixture is not perfectly clear like water. Therefore we will employ the colorimeter used before to determine the concentration of the solution.

2010 January Ch4 Question no.(23)

Iodine and propanone react in the presence of an aqueous acid catalyst as follows



To determine the rate equation for the reaction, propanone is reacted with iodine in the presence of aqueous hydrochloric acid at constant temperature. Samples are withdrawn at known times, quenched with sodium hydrogen carbonate solution, and the iodine remaining titrated with a standard solution of sodium thiosulfate.

The rate equation for the reaction is

$$\text{Rate} = k [\text{CH}_3\text{COCH}_3]^1 [\text{H}^+]^1 [\text{I}_2]^0$$

(a) The graph of $[I_2]$ against time is a straight line, showing that the order of reaction with respect to iodine is zero.

(i) Explain why the propanone and the hydrogen ions must be in large excess in this experiment in order to give this straight line. **(2 marks)**

ANSWER

First mark:

(ensures that) $[H^+]$ and [propanone] (virtually) constant
OR so that the $[H^+]$ and [propanone] do not affect the rate

(1)

Second mark:

the $[I_2]$ / iodine concentration changes
OR so that the overall order (of reaction) is not determined
OR otherwise a curve (graph) is obtained

(1)

January 2011 Ch4 Question no.19(c)

In this experiment the concentration of the iodine was $0.020 \text{ mol dm}^{-3}$ and the concentrations of propanone and sulfuric acid were both 1.00 mol dm^{-3} . Why was the iodine solution used much less concentrated than the propanone and sulfuric acid? (2 marks)

ANSWER

First mark

So that [propanone] and [acid] are (virtually) constant
OR so that the [propanone] and $[H^+]$ do not affect the rate
OR Propanone and acid are in excess so **changes in concentration** don't affect rate

(1)

Second mark

And therefore rate changes would only depend on [iodine]
OR so that the overall order is not determined
ALLOW [Iodine] is the limiting factor

(1)

10. Explain qualitatively the effect of temperature change on the rate constant and hence the rate of reaction.

Like equilibrium constant, the value of rate constant depends on temperature. As the temperature is increased, the particles gain more energy, hence vibrate and collide frequently, thus the kinetic energy of the particles increases, so more molecules with energy higher than activation energy, results in a higher rate.

Increase temperature does not cause the concentration term in the rate expression to change thus, the rate constant (k) increases with increase in temperature.

Practical Skills.

- Describe the experimental procedure of the acid catalyzed reaction of iodination of propanone.



Procedure:

- Mix 25ml of 1M aqueous propanone with sulfuric acid of same volume and molality.
- Add 50ml of 0.02M iodine solution and start the stop watch immediately.
- Using a pipette, withdraw 10ml sample of the reaction mixture into conical flask and quench the reaction by adding spatula measure of sodium bi carbonate. Note the time. (NaHCO_3 reacts with acids hence quench the reaction)
- Titrate the mixture with 0.01 sodium thiosulfate using starch indicator to find the iodine concentration.
- Replete the above procedure for about 8 minutes and obtain atleast 4 readings.

Results:

Plot a graph of Concentration of Iodine vs. Time. (May plot against volume of iodine as the titre volume is proportional to the concentration of iodine)

Deduce the order from the graph.

- Define Heterogeneous & Homogeneous catalyst giving suitable examples

- Heterogeneous Catalysts:-

The catalysts are not in the same state as the reactants. Eg: Gas or liquid reactants used with a solid catalyst. These catalysts work by acting as a surface which the reaction can occur at a faster rate. (use of Iron catalyst in the Haber process)

- Homogeneous catalyst:-

The catalyst is in the same state as the reactants. Eg: gaseous reactant with a gaseous catalyst or liquid reactant with a liquid catalyst

Eg: The catalytic role of nitrogen monoxide in the oxidation of atmospheric Sulphur dioxide)

Eg: Acid catalyzed reaction of iodine with propanone.

1. Outline the different modes of action of homogeneous & heterogeneous catalysis in below reactions.

- I. **Haber Process:**

Industrial manufacture of ammonia gas from Hydrogen & Nitrogen gases are carried out by Haber process. Nitrogen & Hydrogen gases are mixed in 1:3 volume ratio at the presence of Iron Catalyst at 450°C & 200 atm pressure.

Iron is acting as a heterogeneous catalyst as it is a solid & the reactants are gases.

- II. **The catalytic removal of oxides of nitrogen of exhaust fumes**

Vehicle exhaust fumes contain pollutant gases such as 'CO', 'NO' produced by the combustion of hydrocarbon fuels. The catalytic converter attached to the vehicle exhaust pipe converts these to less harmful products such as nitrogen gas & carbon dioxide.

The catalytic converter contains a thin coating of 'Pt' & 'Rh' catalysts with tiny pores which provides a large surface area.

The Pt/Rh catalysts acts as a heterogeneous catalysts in the above process.

- III. **The catalytic role of atmospheric oxides of nitrogen in the oxidation of atmospheric Sulphur dioxide**

Nitrogen monoxide produced by vehicle exhaust fumes act as a catalyst to oxidize atmospheric SO_2 to SO_3

IV. Catalytic role of Fe^{3+} in the $\text{I}^-/\text{S}_2\text{O}_8^{2-}$ (peroxodisulphate) reaction

The above reaction is very slow as it requires two negative ions to collide. Thus the reaction is catalyzed by Fe^{3+} ions or Fe^{2+} ions as shown below.

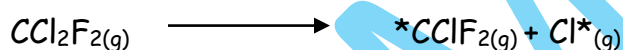
Fe^{3+} ions oxidizes I^- ions to I_2 thus Fe^{3+} get reduced to Fe^{2+}

In the second step Fe^{2+} Reduces $\text{S}_2\text{O}_8^{2-}$ ions to SO_4^{2-} ions thus itself get oxidizes back to Fe^{3+} hence acts as a homogeneous catalyst.

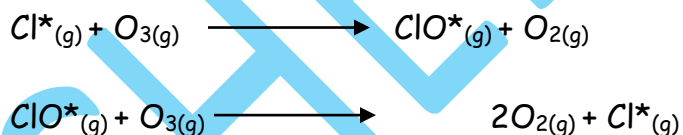
With Fe^{2+} ions as catalyst the steps 1 & 2 take place in the reverse order.

- iv. Catalytic role of chlorine free radicals in the destruction of the ozone layer by chloro fluoro carbon (CFC)

The UV radiation from sun produces chlorine free radicals from CFC as shown below:



The chlorine free radicals take part in a chain reaction with ozone and get reproduced at the end as shown below; Thus acting as a homogeneous catalysts.



- Explain the catalytic activity of heterogeneous catalyst using the terms Adsorption & Desorption.

The efficiency of a heterogeneous catalysts depends on the surface area of the catalyst. The reactant molecules get adsorbed (not absorb) on to the surface of the catalyst. The reactant molecules at the active site of the catalyst (site where reaction takes place between reactants) get positioned in a way that enable them to react together. Once the product is produced it leaves the catalyst (desorption).

The rate of reaction is controlled by how fast the reactants are adsorbed and how fast the products are desorbed.



Further suggested practicals:

- The catalysis by a cobalt (II) salt of potassium sodium tartrate and hydrogen peroxide.

This reaction involves the oxidation of potassium sodium tartrate by hydrogen peroxide using a cobalt salt as a catalyst.

Chemicals required:

Potassium sodium tartrate (Rochelle salt), $\text{KNaC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}(\text{s})$

Hydrogen peroxide solution, $\text{H}_2\text{O}_2(\text{aq})$, (IRRITANT)

Cobalt(II) chloride solution, $\text{CoCl}_2(\text{aq})$, (TOXIC, DANGEROUS FOR THE ENVIRONMENT)

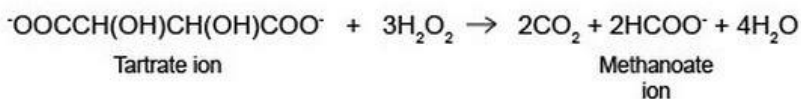
Procedure :

- Weigh 5 g of the potassium sodium tartrate into a 250 cm³ beaker. Add 60 cm³ of distilled water and stir to dissolve the solid.
- Add 20 cm³ of 20 volume hydrogen peroxide solution to the solution in the beaker. Note any signs of reaction.
- Put the beaker on the tripod and gauze and heat the mixture in the beaker to about 70 °C. Note any signs of reaction.
- Add 5 cm³ of cobalt(II) chloride solution to the mixture in the beaker. Take care to avoid skin contact. Note any colour changes and gas produced.

Discussion:

This is an impressive demonstration of how a catalyst is involved in the progress of a reaction.

The reaction is an oxidation of the tartrate ion (IUPAC name 2,3-dihydroxybutandioate ion) to carbon dioxide gas and the methanoate ion. Hydrogen peroxide oxidises the tartrate ion very slowly if there is no catalyst, even at elevated temperatures.



Cobalt (II) ions are pink. The hydrogen peroxide initially oxidizes the cobalt (II), Co^{2+} , to cobalt (III), Co^{3+} , which is green. The cobalt (III) bonds to the tartrate ion, allowing the oxidation to take place. The Co^{3+} is then reduced back to Co^{2+} and the pink colour returns. The cobalt catalyst provides an alternative route for the reaction to occur. This alternative route has a lower activation energy and the reaction proceeds much more quickly.