Investigating the Rate of the Reaction between Bromide and Bromate Ions in Acid Solution

In this investigation, I aim to fully investigate the factors affecting the rate of the reaction between bromide ions and bromate ions in acid solution. The equation of this reaction is given below:

$$5Br^-_{(aq)} + BrO_3^-{}_{(aq)} + 6H^+_{(aq)} \rightarrow 3Br_{2\,(aq)} + 3H_2O_{(l)} \qquad \text{(Reaction 1.0.1)}$$

I will attempt to find the rate equation for the reaction, in the form:

$$\text{rate} = k[Br^-]^x[BrO_3{}^-]^y[H^+]^z \qquad \text{(Reaction 1.0.2)}$$

where k is the rate constant and x, y, and z are the orders of reaction with respect to Br^-, BrO_3^- and H^+ respectively. I will also attempt to find a suitable catalyst for the reaction, as well as the activation enthalpy for the reaction with and without a catalyst.

The reaction is a redox reaction: the bromide is oxidised to bromine and the bromate is reduced to bromine. This can be shown by the oxidation states of bromide, bromate and bromine:

$$5Br^-_{(aq)} + BrO_3^-{}_{(aq)} + 6H^+_{(aq)} \rightarrow 3Br_{2\,(aq)} + 3H_2O_{(l)}$$

Oxidation State: -1 +5 -2 +1 0 +1 -2

I shall be using solutions of Potassium Bromide (KBr) and Potassium Bromate ($KBrO_3$) as sources of bromide and bromate ions for the reaction, and Sulphuric Acid (H_2SO_4) as a source of H^+ ions. A solution methyl orange shall be used as an indicator, which will change colour from pink (in acid solution) to colourless when Bromide ions are produced. In order to be able to measure the amount of time it takes for the indicator to change colour, a small amount of Phenol (C_6H_5OH) is added to the solution. Phenol reacts instantly with any Bromine produced, returning bromide ions:

$$3Br_{2\,(aq)} + C_6H_5OH_{(aq)} \rightarrow C_6H_2Br_3OH_{(aq)} + 3H^+_{(aq)} + 3Br^-_{(aq)} \qquad \text{(Reaction 1.0.3)}$$

As soon as all the Phenol has reacted with the Bromine produced, the excess Bromine causes the methyl orange to change colour. The time it takes for this to happen is proportional to the initial rate of the reaction between Bromide and Bromate ions.

1) Background Chemistry for the Investigation

1.1 – Rates of Reaction

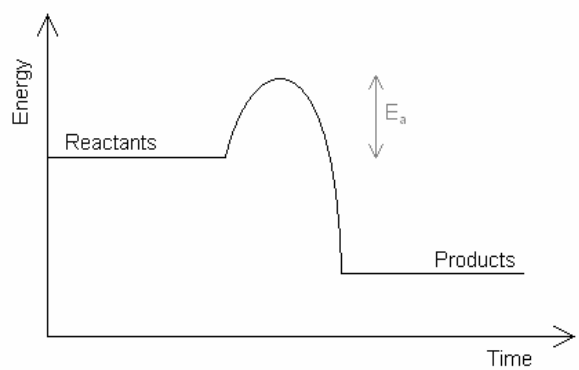
The rate of a chemical reaction is a measure of how a property changes in a reaction over time.[i] For example, the rate could be measured as the change in concentration of a substance over time. In this case, the units of the rate would be mol dm^{-3} s^{-1}.

There are several factors which can affect the rate of a reaction:

- The temperature at which a reaction takes place
- The concentration of a reacting solution
- The surface area of a reacting solid
- The pressure of a reacting gas
- The effect of radiation on reactants
- The use of a catalyst

1.2 – Measuring the Rate of Reaction

The way in which the rate of a reaction is measured depends very much on the reaction being studied. For example, if the reaction produces a gas, the volume of gas produced can be measured. If the reaction is a neutralisation reaction or involves the production of an acid or alkali, the change in pH can be measured. Colorimetry can be used to measure the intensity of a coloured substance.



1.3 – Collision Theory of Reactions

All substances are made up of moving particles. For a reaction to occur, the particles must collide with sufficient energy to react. The amount of energy they require is known as the Activation Energy (E_a). This can explain many of the factors which affect rate of reaction. Increasing the concentration or the pressure of a reactant means that there are more reacting particles in the same volume of solution, so collisions are more likely, meaning that more collisions happen in a given amount of time. Reactions involving solids happen on the surface of the solid, so increasing the surface area of a solid causes more area to be available for collisions to take place, leading to an increase in the rate of the reaction. In certain substances, radiation causes particles to move up vibrational energy levels, meaning

Figure 1.3. [illegible] to the [illegible] exothermic reaction, showing the activation energy, E_a.

that they have more energy, so are more likely to have the activation energy required for the reaction to take place.[1]

1.4 – Order of Reaction and the Rate Equation[ii]

The order of a reaction describes the relationship between the concentration of a reactant and the rate of the reaction. It is only possible to know the order of a reaction by performing experiments with different concentrations of reactions and looking at the relationship between concentration and rate.

- If the concentration of a reactant has no affect on the rate of reaction, the reaction is said to be zero-order with respect to that reactant.
- If the concentration of a reactant is directly proportional to the change in the rate of reactant, the reaction is said to be first order with respect to that reactant.
- If the square of the concentration of a reactant is directly proportional to the change in the rate of reactant, the reaction is said to be second order with respect to that reactant.

In general, if;

$$\textbf{rate} \propto [\textbf{reactant}]^{\textbf{n}} \qquad \text{Equation 5.1}$$

where [reactant] is the concentration of a reactant, then the reaction is n order with respect to that reactant.

Graphs can be drawn of the rate against the concentration to find the order of the reaction:

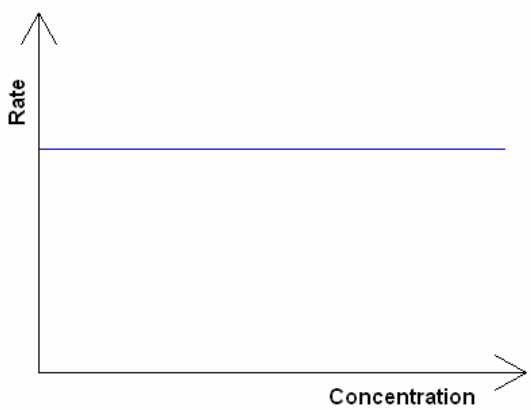


Figure 5.1: A zero order reaction

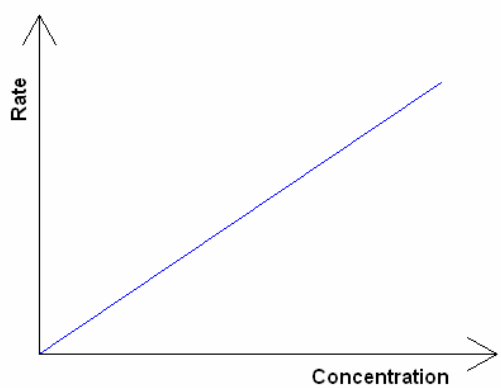


Figure 5.2: A first order reaction

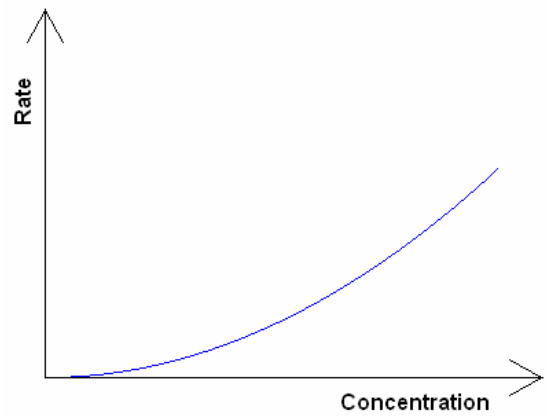


Figure 5.3: A second order reaction curve

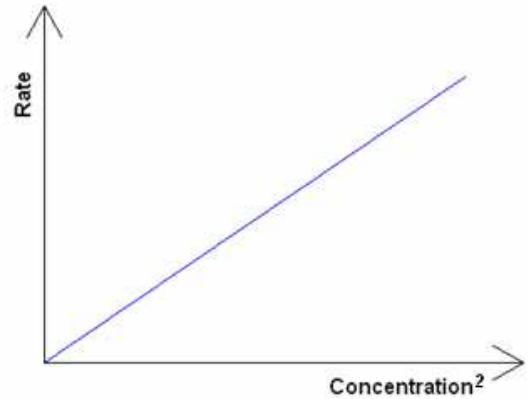


Figure 5.4: A second order reaction – rate vs squared concentration gives a straight line

Consider the reaction;

$$\mathbf{A + B \rightarrow C + D} \qquad \text{(Reaction 5.2)}$$

If the reaction is found to be x order with respect to A and y order with respect to y, then:

$$\mathbf{rate} \propto [\mathbf{A}]^x[\mathbf{B}]^y \qquad \text{(Reaction 5.3)}$$

The rate equation can be derived from this:

$$\mathbf{rate} = k[\mathbf{A}]^x[\mathbf{B}]^y \qquad \text{(Reaction 5.4)}$$

where k is the rate constant for the reaction. The overall order of the reaction is the sum of the orders of reaction of the separate reactants, so reaction is *(x+y)* order overall.

Similarly to the orders of reaction, the value of the rate constant can only be found by experiment. If the orders of reaction with respect to the reactants (in this case A and B) are found, then, using the values for the concentration of the reactants and the initial rate of reaction, the value of k is given by:

$$k = \frac{\mathbf{initial\ rate}}{[\mathbf{A}]^x[\mathbf{B}]^y} \qquad \text{(Reaction 5.5)}$$

The units of k depend upon the orders of reaction with respect to the reactants; rate is measured in mol dm^{-3} s^{-1} and concentration is measured in mol dm^{-3}; the units of k are found using Equation t and these units.

1.5 – Rate Determining Step

The majority of chemical reactions do not take place in a single step. The separate steps which form the reaction are known as the reaction mechanism. The reaction mechanism can only be hypothesised from results of experiments – there is no way to "prove" that it is how the reaction takes place. Therefore a mechanism can never be certain. The different steps of the reaction mechanism all take place at different rates

and are affected by the concentration in different ways. In many reactions, one of the steps is a lot slower than the others: this is known as the rate determining step.

If a reaction is zero order with respect to one of the reactants, this implies that the concentration of this reactant has no affect on the rate of reaction. When considering the reaction mechanism, this means that the step involving this reactant happens very fast regardless of the concentration, so this step is not the rate determining step. However, if the reaction is first order with respect to another reactant, then this reactant is involved in the rate determining step of the reaction.

The rate equation for a reaction can suggest a possible rate determining step. This involves the molecularity of an elementary reaction step.[iii] If a reaction step is unimolecular, then it involves one molecule changing (by, for example, dissociation) and forming products. Unimolecular reactions suggest that the reaction is first order. Similarly, a bimolecular reaction involves two atoms, molecules, ions or radicals reacting together to form products. These reactions suggest a rate equation of the form, where A and B are the reactants, rate = [A][B]. Termolecular (involving three reactants) and higher molecularity reactions are unlikely, since these require three or more reacting particles to collide at the same instant. Hence, a rate equation can suggest the molecularity and the mechanism of a rate determining step, but this can only be theorised.

1.6 – The Effect of Temperature on Rate of Reaction

The temperature of a substance is a measure of the kinetic energy of a substance – something feels warmer if the particles are moving faster. Therefore, collision theory would suggest that temperature affects the rate of a reaction since particles move faster, and hence collide more often, leading to an increase in the rate of reaction. However, this can be shown to be incorrect as the only factor in temperature increasing the rate of reaction.

A general approximation for the effect of temperature on the rate of a reaction is that, if the temperature increases by 10K, then the rate of reaction doubles. Temperature is proportional to kinetic energy, and kinetic energy is given by $\frac{1}{2}mv^2$, where m is the mass of a particle, and v is the particle's speed. Therefore temperature is proportional to the speed squared. Suppose a particle has a speed v_1 at a temperature of 300K and a speed v_2 at a temperature of 310K. Therefore:

$$\frac{v_2^{\,2}}{v_1^{\,2}} = \frac{310}{300}$$

Figure 1.4.1: The Maxwell-Boltzmann distribution of kinetic energy at [illegible]

This means that the ratio of the speeds is given by:

$$\frac{v_2}{v_1} = \sqrt{\frac{310}{300}} = 1.02$$

(Equation 1.4.2)

Since the ratio of the speeds is not 2:1, the rate of reaction has not doubled, suggesting that temperature affects the rate of reaction in a different way.

In fact, the temperature causes an increase in the rate of a reaction by increasing the number of particles with sufficient energy to react. The energy of particles is distributed with a Maxwell-Boltzmann distribution. The number of particles with energy greater than or equal to the activation energy is proportional to the area under the curve from the activation energy (E_a) to infinity (see fig. 1.4.1). At higher temperatures, more particles have a higher speed, and hence a higher kinetic energy. Therefore, the number of particles with energy greater than or equal to the activation energy is higher at higher temperatures (see fig. 1.4.2). As there are more particles with sufficient energy to react, there is a greater chance that a collision will cause a reaction, so there is an increase in the rate of the reaction.[1]

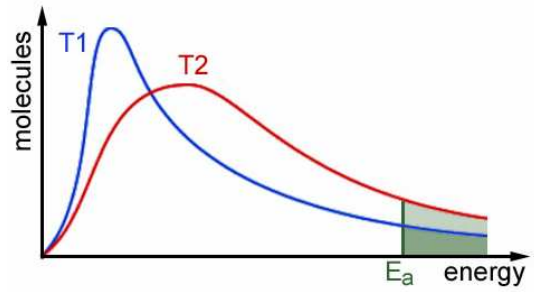
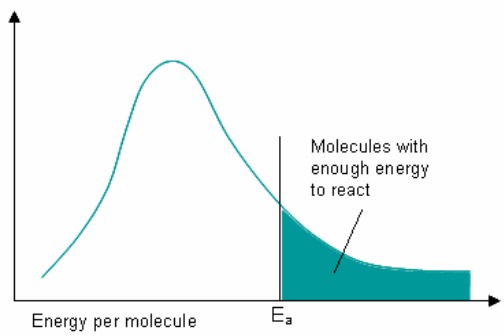


Fig. 1.4.2: Kinetic energy distribution curves for two temperatures, T1 and T2. The area below the curve, which represents the number of molecules with energy greater than E_a is shaded.

Note that the approximate rule that an increase in temperature leads to a doubling in rate of reaction is only valid for reactions for which the activation energy is around 50 kJ mol^{-1} and with a temperature rise from 300K to 310K.

1.7 – The Effect of Catalysts on the Rate of Reaction



A catalyst is a substance which changes the rate of a reaction without being used up itself. In general, a catalyst provides an alternative route for the reaction with a lower activation energy, hence increasing the rate of reaction. There are two types of catalyst: heterogeneous catalysts and homogeneous catalysts.

A heterogeneous catalyst is a catalyst which is in a different physical state to the reactants; for example, a solid catalyst in a solution. These catalysts work by forming temporary weak bonds between the catalyst surface and the reactants – the reactant is adsorbed onto the catalyst surface (see fig. 1.7.1). This causes bonds in the reactant to weaken and break. New bonds can then form between the reactants on the surface of the catalyst;

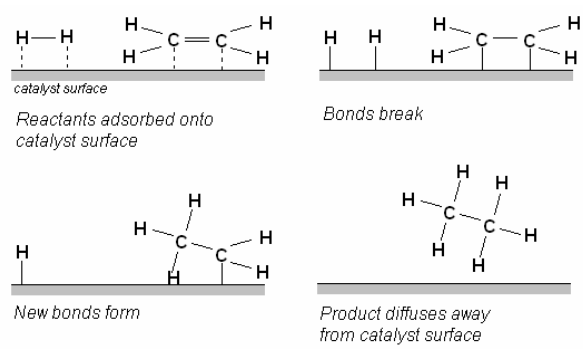


Fig. 1.7.1: An example of heterogeneous catalysis, in which ethene undergoes addition of hydrogen.[6]

when these bonds have formed, the temporary bonds break and the products diffuse away from the catalyst surface. Examples of heterogeneous catalysis include the Haber process, which uses an iron catalyst to produce ammonia, and catalytic converters in cars, which use a platinum catalyst to convert nitrogen oxides to nitrogen and oxygen.[vii]

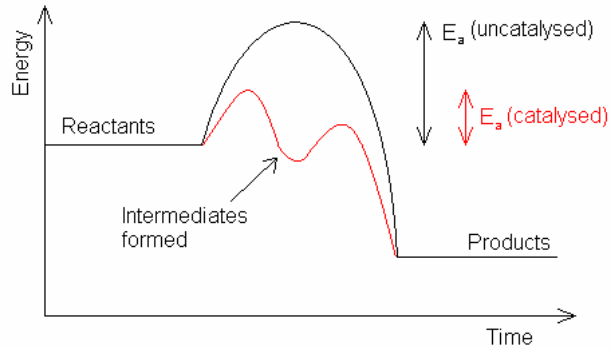


Figure 1.7.2 – Diagram to show the energy changes in catalysed and uncatalysed reactions.

A homogeneous catalyst is a catalyst which is in the same physical state as the reactants, which is usually a liquid or a solution. The catalysts that I will test in the reaction between bromide and bromate ions will be homogeneous, in this case solutions of transition metal ions. Homogeneous catalysts work by forming an intermediate compound with one or more of the reactants, which then breaks down to form the products and reform the catalyst – so none of the catalyst is used up in the reaction. The step to form the intermediate has a lower activation energy than the uncatalysed reaction (see fig. 1.7.2), so the reaction can happen faster. An example of heterogeneous catalysis is the destruction of ozone in the atmosphere, which is catalysed by chlorine radicals.[1]

Transition metals and transition metal ions are often particularly good as both heterogeneous and homogeneous catalysts. This is due to the incomplete 3d and 4s sub-shells in these ions, as well as their ability to have variable oxidation states. In heterogeneous catalysts, the empty electron orbitals in the 3d and 4s sub-shells allow for weak bonds to be formed on the surface of the metal. When transition metal ions act as homogeneous catalysts, the ion forms an intermediate with one or more of the reactants. The transition metal will often be in a different oxidation state in the intermediate, before changing back to the original oxidation state when the intermediate breaks down. This makes transition metal ions particularly good in redox reactions (such as the reaction between bromine and bromate ions in acid solution), as they can readily move from one oxidation state to another.[viii]

1.8 – The Arrhenius Equation

The Arrhenius Equation gives an expression for the value of the rate constant k, as shown in Equation 1.8.1:[ix]

$$k = Ae^{-\frac{E_a}{RT}}$$

Equation 1.8.1

where A is the pre-exponential factor (constant), e is the exponential constant ($e \approx 2.71828\ldots$), E_a is the activation energy for the reaction, R is the molar gas constant ($R \approx 8.31\ldots$), and T is the temperature at which the reaction takes place (in Kelvin). Taking logarithms of both sides of Equation 1.8.1 gives:

$$\ln k = \ln\left(Ae^{-\frac{E_a}{RT}}\right) \qquad \text{(Equation 1.8.2)}$$

Simplifying Equation 1.8.2 using the laws of logarithms gives:

$$\ln k = \ln A - \frac{E_a}{RT} \qquad \text{(Equation 1.8.3)}$$

From Equation 1.8.3, it is clear that if a graph was drawn of $\ln k$ against $^1/_T$, the relationship would be a straight line. If the rate equation of the reaction is found, the value of k for different values of T can be found if the rate of reaction is found at different temperatures. Hence, the activation energy of the reaction can be found using:

$$E_a = -mR \qquad \text{(Equation 1.8.4)}$$

where m is the gradient of the line of the graph of $\ln k$ against $^1/_T$.

2) Method

In order to investigate the rate of the reaction between bromide and bromate ions in acid solution, I will need to carry out the reaction several times under different conditions. To find the rate equation for the reaction, I will need to find the order of the reaction with respect to Br^- ions, BrO_3^- ions and H^+ ions. To do this, I will:

- Measure the time taken for the methyl orange to change colour with five different concentrations of bromide solution
- Measure the time taken for the methyl orange to change colour with five different concentrations of bromate solution
- Measure the time taken for the methyl orange to change colour with five different concentrations of acid solution

I can plot a graph of 1/time taken against concentration of solution to find the order of the reaction with respect to each of the reactants (see above – page 8). I will then choose set concentrations of each reactant and measure the time taken for the methyl orange to change colour with different temperatures. This, with the Arrhenius Equation, can be used to find the activation enthalpy of the reaction (see above – page 12).

I will then repeat the reaction using the same set concentrations, but adding ten drops of a transition metal ion solution, which could work as a catalyst. I will try five different solutions and compare their effect on the rate of the reaction. Choosing one of these solutions, I will repeat my method for changing the temperature to find the activation enthalpy of the reaction with that catalyst.

2.1 – Equipment List

This is a list of all the chemicals, glassware and other apparatus that I will require for my investigation. Firstly, all the chemicals that I will require:

- Potassium bromide (KBr)
- Potassium bromate ($KBrO_3$)
- Phenol (C_6H_5OH)
- Methyl orange
- Sulphuric acid solution (H_2SO_4)
- 0.20M copper (II) sulphate solution ($CuSO_4.5H_2O$)
- 0.20M cobalt (II) nitrate solution ($Co(NO_3)_2.6H_2O$)
- 0.20M nickel (II) chloride solution ($NiCl_2.6H_20$)
- 0.20M iron (III) sulphate solution ($Fe_2(SO_4)_3$)
- 0.20M manganese (II) sulphate solution ($MnSO_4.4H_2O$)
- Deionised water

All glassware that I will require:

- 3x 2000cm^3 volumetric flasks (±0.60cm^3)
- 4x 1000cm^3 volumetric flask (±0.40cm^3)
- 5x 100cm^3 volumetric flasks (±0.10cm^3)
- 8x 50cm^3 burettes (±0.05cm^3)
- 1x 10cm^3 pipette (±0.04cm^3)
- 1x 100cm^3 pipette (±0.15cm^3)
- At least 5 beakers (50cm^3 to 250cm^3)
- 1x 800cm^3 beaker
- 2x boiling tubes

Other apparatus I will require:

- Safety goggles
- Balance (±0.01g)
- Glass rod
- Funnel
- Dropping pipette
- Clamp stand and 8 clamps (to hold the burettes)
- Stopwatch
- Thermometer
- Boiling tube rack
- Bunsen burner
- Heat-proof mat
- Tripod
- Gauze

2.2 – Risk Assessment[x]

Below are detailed the risks associated with my investigation, and what I shall do to minimise these risks. Firstly, some general rules that I will follow at all times during my experiments to minimise potential risks:

- Wear safety goggles at all times, including when setting up and clearing away
- Report any instances of harmful chemicals coming into contact with the skin, eyes or mouth immediately and take appropriate action
- Report any spillages and breakages immediately and clear them up as quickly as possible
- When using a Bunsen burner, keep air hole closed when not in use, keep hair and clothes away from flame

Next, instructions on what to do in certain emergencies (for certain chemicals, further instruction is required, see below):

- **Chemicals in eye:** Immediately wash the eye with gently-running water for at least 10 minutes. Hold back the eyelids to rinse underneath. Contact lenses must be removed. If the first aider has any concerns, send for an ambulance.
- **Chemicals in mouth:** Even if swallowed, do no more than wash out the casualty's mouth. Do not induce vomiting. Sips of water may help cool the throat and help keep the airway open. If the first aider has concerns after treatment, seek medical help.
- **Chemicals on clothes:** Remove contaminated clothing immediately and wash the contaminated area. Take steps to ventilate the area of the spill. If necessary, take contaminated clothing outside.
- **Chemical splashes on skin:** Brush off any solids. Wash the skin for 5 minutes or until all traces of the chemical have disappeared. Remove clothing as necessary. If the chemical adheres to the skin, wash gently with soap. For chemical burns, irrigate for 20 minutes. If the first aider has concerns after treatment, especially if blistering occurs, seek medical help.
- **Toxic gas:** If more than a sniff is inhaled, sit the casualty down in uncontaminated air. If the first aider has concerns after treatment, seek medical help.
- **Hair on fire:** Smother with a fire blanket, thick cloth or coat, whatever is close to hand.
- **Clothing on fire:** Stop, drop and roll. This means stop the casualty moving around and make her/him lie down on the floor. Then either roll the casualty to smother the flames or, with the flames on top, cover with a fire blanket, thick cloth or coat, whatever is close to hand.
- **Burns:** Cool under gently-running water for 10 minutes or until heat is no longer felt. Call a first aider if there are concerns.

Next, I have examined in turn the risks each of the chemical substances that I will use in my experiments pose, as well as those produced as a result of the reactions that take place:

- **Potassium bromide, KBr, solid, aqueous**
  - Risks: Low hazard; minimal risk
  - Disposal: Dilute in water, pour down sink

- **Potassium bromate, $KBrO_3$, solid, aqueous**

  - Risks: Solutions of concentration 0.005 mol dm^{-3} are TOXIC, OXIDISING; explosive when mixed with combustible material; toxic if swallowed; may cause cancer
  - Disposal: Dilute in water to concentration of less than 0.1%, pour down foul-water sink

- **Sulphuric acid, H_2SO_4, aqueous**

  - Risks: IRRITANT at low concentrations used in experiment; can cause severe burns

- Emergencies: If spilt on skin or clothes, remove contaminated clothing and quickly wipe as much liquid as possible off the skin with a dry cloth before drenching the area with a large excess of water. If a large area is affected or blistering occurs, seek medical attention
- Dangerous with: water, a vigorous reaction occurs when the concentrated acid is diluted
- Disposal: Dilute in water, pour down foul-water sink

- **Phenol, C_6H_5OH, solid, aqueous**
  - Risks: TOXIC by inhalation, in contact with skin and if swallowed; CORROSIVE, causes burns; potential carcinogen, possible risk of irreversible effects

  - Emergencies: If spilt on skin or clothes, Remove all contaminated clothing as quickly as possible. Small amounts of water may increase absorption. Flood the area with water for at least 15 minutes (preferably in a shower). If immediately available, swab repeatedly with glycerol, then with soap and water. Seek medical attention as soon as possible. Phenol burns are very serious.
  - Disposal: Dilute in water to concentration of less than 0.1%, pour down foul-water sink

- **Methyl orange indicator, aqueous**
  - Risks: TOXIC if swallowed

  - Disposal: Dilute in water to concentration of less than 0.1%, pour down foul-water sink

- **Water, H_2O, liquid**
  - Risks: No risk at small volumes used/produced in experiment

- **Bromine, Br_2, aqueous**
  - Risks: Solutions of concentration 0.06 mol dm^{-3} are TOXIC, IRRITANT; VERY TOXIC by inhalation; IRRITATING to eyes; solutions of concentration 0.006 mol dm^{-3} are HARMFUL, IRRITANT; HARMFUL by inhalation, in contact with skin and if swallowed, IRRITATING to eyes

  - Disposal: Add slowly to 1 mol dm-3 sodium carbonate solution. Heat may be produced. The resulting solution should be tested for alkalinity with litmus solution and, when just alkaline, poured down a foul-water drain with further dilution. Carry out in a fume cupboard

- **Bromophenol, $C_6H_5Br_3OH$, aqueous**
  - Risks: See phenol;

also FLAMMABLE, IRRITATING to the skin
    - Disposal: Dilute in water, pour down sink

- **Hydrated copper (II) sulphate, $CuSO_4.5H_2O$, solid, aqueous**

    - Risks: HARMFUL; HARMFUL if swallowed; IRRITATING to eyes and skin
    - Disposal: Dilute to less than 0.4 mol dm-3 or dissolve 100 g in 1 litre of water before pouring the solution down a foul-water drain

- **Hydrated cobalt (II) nitrate, $Co(NO_3)_2.6H_2O$, solid, aqueous**

    - Risks: HARMFUL, OXIDISING, HARMFUL if swallowed, causes sensation by inhalation and skin contact, strong oxidising agent
    - Dangerous with: Flammable materials
    - Disposal: Dilute with water, pour down foul-water drain

- **Nickel (II) chloride, $NiCl_2.6H_2O$, solid, aqueous**

    - Risks: HARMFUL; HARMFUL if swallowed; may cause sensitisation by inhalation and skin contact; limited evidence of a carcinogenic effect
    - Disposal: Dilute to less than 0.5 mol dm-3 before pouring down a foul-water drain

- **Iron (III) sulphate, $Fe_2(SO_4)_3$, solid, aqueous**
    - Risks: IRRITANT, IRRITATING to eyes and skin
    - Disposal: Dilute in water, pour down sink

- **Manganese (II) sulphate, $MnSO_4.4H_2O$**

    - Risks: HARMFUL; danger of serous damage to health by prolonged exposure through inhalation and if swallowed
    - Disposal: Dilute to less than 0.3 mol dm-3 before pouring down a foul-water drain

2.3 – Making up Solutions

This is a list of all the solutions that I will need to make up (Since school policy does not permit students to make up acid solutions, the sulphuric acid that I will require will be made up by the school):

- 0.01M potassium bromide solution (KBr)
- 0.005M potassium bromate solution ($KBrO_3$)

- 0.20M potassium bromate solution ($KBrO_3$)
- 0.0001M phenol solution (C_6H_5OH)
- "Solution C" – acidified methyl orange solution (0.001%)
- "Solution D" – methyl orange solution (0.001%) in 0.40M potassium bromide solution
- 0.20M copper (II) sulphate solution ($CuSO_4.5H_2O$)
- 0.20M cobalt (II) nitrate solution ($Co(NO_3)_2.6H_2O$)
- 0.20M nickel (II) chloride solution ($NiCl_2.6H_20$)
- 0.20M iron (III) sulphate solution ($Fe_2(SO_4)_3$)
- 0.20M manganese (II) sulphate solution ($MnSO_4.4H_2O$)

Since large amounts of these solutions will be required and to reduce errors, I will make up 2000cm^3 of 0.01M potassium bromide, 0.005M potassium bromate and 0.20M potassium bromate. Similarly, I will make up solutions C and D in batches of 1000cm^3. For the phenol solution, due to the concentration being so low, the small mass of solid phenol required would lead to very large percentage errors if 0.0001M phenol was made up. Hence I will make up a solution of 0.01M phenol and dilute this to make a solution of 0.0001M phenol. I will make up 100cm^3 of each of the catalyst solutions (solutions of transition metal ions), since I will only require a few drops at a time of each of these, and if I made up less than 100cm^3, then the percentage error would be too high.

I need to work out the mass of each substance I will require to make up the required volume of solution at the required concentration. To do this, I will first work out the number of moles of the substance I require in my solution:

$$\mathbf{moles} = \frac{\mathbf{concentration} \times \mathbf{volume}}{\mathbf{1000}} \qquad \text{Equation 2.3.1}$$

where the concentration is measured in mol dm^{-3} (M) and volume is measured in cm^3. To find the mass of solution required for this number of moles I will use:

$$\mathbf{mass} = \mathbf{moles} \times \mathbf{R.F.M.} \qquad \text{Equation 2.3.2)}$$

where R.F.M. is the relative formula mass of the substance, and both the mass and the R.F.M. are measured in grams. The results of these calculations for each substance are shown in the table below (excluding solutions C and D – see below):

Substance	**R.F.M. /g**	**Required Concentration /mol dm^{-3}**	**Required Volume /cm^3**	**Required Mass /g**
KBr	119	0.01	2000	2.38
$KBrO_3$	167	0.005	2000	1.67
		0.20	2000	66.8
C_6H_5OH	94	0.01	1000	0.94
$CuSO_4.5H_2O$	249.68	0.20	100	4.99
$Co(NO_3)_2.6H_2O$	291	0.20	100	5.82
$NiCl_2.6H_20$	237.69	0.20	100	4.75
$Fe_2(SO_4)_3$	400	0.20	100	4
$MnSO_4.4H_2O$	223	0.20	100	4.46

The method used to make up all of these solutions is the same:

1. Put on safety goggles
2. Measure out the required mass of the substance in a beaker using a balance
3. Add some deionised water to the beaker and dissolve the substance in the water using a glass rod
4. When all of the substance has dissolved, use a funnel to pour the solution into a volumetric flask of the desired volume
5. Wash out the beaker and the glass rod with deionised water at least three times into the volumetric flask, to ensure that all the substance is in the volumetric flask
6. Fill the volumetric flask up to the mark with deionised water, using a dropping pipette to add the last few drops
7. Stopper the flask, label it and invert it ten times to ensure the concentration is the same in the whole solution

Solutions C and D are slightly more complicated. I will have a solution of 5 g dm^{-3} methyl orange to use, and in both solutions C and D this needs to be 0.001%. Since the relative formula mass of methyl orange is 327.34g, this means that I will require 20cm^3 of 5 g dm^{-3} of methyl orange in each 1000cm^3 of solution C and D that I make up. I will use 400cm^3 of 1M sulphuric acid in each 1000cm^3 of solution C, to give me a concentration of 0.40 mol dm^{-3} of sulphuric acid in solution C. This is the method that I will use to make up solution C:

1. Put on safety goggles
2. Measure out 20cm^3 of methyl orange solution (5 g dm^{-3}) using a pipette into a beaker
3. Measure out 400cm^3 of 1M sulphuric acid solution into a beaker using four 100cm^3 pipettes
4. Add the methyl orange solution to the sulphuric acid solution in a 1000cm^3 volumetric flask using a funnel
5. Wash out the beakers used with deionised water at least three times, pouring the washings into the volumetric flask
6. Fill the volumetric flask up to the mark with deionised water, using a dropping pipette to add the last few drops
7. Stopper the flask, label it and invert it ten times to ensure the concentration is the same in the whole solution

Solution D requires 0.40M potassium bromide solution. Using the equations above, this means that I will require 48g of potassium bromide when I make up 1000cm^3 of solution D. This is the method that I will use to make up solution D:

1. Put on safety goggles
2. Measure out 48g of potassium bromide into a beaker using a balance
3. Add some deionised water to the beaker and dissolve the potassium bromide in the water using a glass rod

4. Measure out 20cm^3 of methyl orange solution (5 g dm^{-3}) using a pipette into a beaker
5. Add the methyl orange solution and the potassium bromide solution into a 1000cm^3 volumetric flask using a funnel
6. Wash out the beakers and the glass rod used with deionised water at least three times into the volumetric flask
7. Fill the volumetric flask up to the mark with deionised water, using a dropping pipette to add the last few drops
8. Stopper the flask, label it and invert it ten times to ensure the concentration is the same in the whole solution

2.4 – Method for Varying the Concentration of a Reactant[xi]

This is the general method that I will use to obtain results when varying the concentration of the potassium bromide solution, the potassium bromate solution or the sulphuric acid.

1. Put on safety goggles
2. Measure out using a burette the volumes of solutions required into beaker X and beaker Y (see tables 2.4.1 to 2.4.3 below method giving details of what volumes of each solution are required when varying the concentration of each reaction)
3. Pour the contents of beaker X into beaker Y and start the stop-watch
4. Mix the solutions by pouring the mixture back into beaker X and then back into beaker Y
5. When the pink colour has disappeared, stop the stop-watch and record the time in the results table, as shown below
6. Measure the temperature of the solution and record this in the results table
7. Rinse out both beakers with deionised water and dry them
8. Repeat the experiment with the same concentrations until there are three results with times within 10% of the average time
9. Repeat steps 1-8 with each set of volumes of solutions as shown in the table below.

Volumes of solutions required when varying the concentration of bromide solution:

Beaker X		**Beaker Y**		
Volume of 0.01M KBr /cm^3	**Volume of deionised water /cm^3**	**Volume of 0.005M $KBrO_3$ /cm^3**	**Volume of solution C /cm^3**	**Volume of 0.0001M phenol /cm^3**
10.0	0.0	10.0	15.0	5.0
8.0	2.0	10.0	15.0	5.0

6.0	4.0	10.0	15.0	5.0
4.0	6.0	10.0	15.0	5.0
2.0	8.0	10.0	15.0	5.0

(Table 2.4.1)

Volumes of solutions required when varying the concentration of bromate solution:

Beaker X		Beaker Y		
Volume of 0.005M $KBrO_3$ /cm³	**Volume of deionised water /cm³**	**Volume of 0.01M KBr /cm³**	**Volume of solution C /cm³**	**Volume of 0.0001M phenol /cm³**
10.0	0.0	10.0	15.0	5.0
8.0	2.0	10.0	15.0	5.0
6.0	4.0	10.0	15.0	5.0
4.0	6.0	10.0	15.0	5.0
2.0	8.0	10.0	15.0	5.0

(Table 2.4.2)

Volumes of solutions required when varying the concentration of sulphuric acid:

Beaker X		Beaker Y		
Volume of 0.01M H_2SO_4 /cm³	**Volume of deionised water /cm³**	**Volume of 0.20M $KBrO_3$ /cm³**	**Volume of solution D /cm³**	**Volume of 0.0001M phenol /cm³**
10.0	0.0	10.0	15.0	5.0
8.0	2.0	10.0	15.0	5.0
6.0	4.0	10.0	15.0	5.0
4.0	6.0	10.0	15.0	5.0
2.0	8.0	10.0	15.0	5.0

(Table 2.4.3)

Results table for varying the concentration of each reactant (I will draw up three of these, one for each reactant):

[Reactant] /mol dm³	**Repeat 1**		**Repeat 2**		**Repeat 3**		**Repeat 4**		**Repeat 5**	
	Time/s	**Temp/ K**	**Time/s**	**Temp/ K**	**Time/s**	**Temp/ K**	**Time/s**	**Temp/ K**	**Time/s**	**Temp/ K**

(Table 2.4.4)

2.5 – Method for Varying the Temperature of the Reaction

Following experiments varying the concentration of reactants, I will investigate the effect of varying the temperature of the reaction. I will choose one set of concentrations from my previous experiment and will use these concentrations for all further reactions. I will choose a set of concentrations that take approximately five

minutes to change colour, as increasing the temperature will cause the reaction to speed up, so any shorter time than five minutes would mean that reactions taking place at higher temperatures would change colour too quickly to accurately measure.

I will carry out the reaction at five different temperatures, as well as at room temperature. So as to remove the necessity to use extremely high temperatures (greater than around 330K), I will increase the intended temperature by 8 degrees in each experiment.

Having chosen a set of concentrations, this is the method that I will use:

1. Put on safety goggles
2. Measure out the correct volumes of reactants given by the chosen concentrations (set chosen from table 2.4.1, table 2.4.2 or table 2.4.3) into two boiling tubes, labelled X and Y. Measure the volumes using a burette
3. Carry out the reaction at room temperature. Pour boiling tube X into boiling tube Y and start the stop-watch
4. Pour the contents now in boiling tube Y back into boiling tube X, to ensure that the reactants are fully mixed
5. When the pink colour has disappeared, stop the stop-watch and record the time taken in the table shown below (table 2.5.1)
6. Measure the temperature throughout the reaction and record the final temperature in the table shown below (table 2.5.1)
7. Repeat the reaction at room temperature until there are three concordant results, which are results with times within 10% of the average time of each other and temperatures within 1 degree Kelvin of each other
8. Set up a Bunsen burner with a water bath (see figure 2.5.1)
9. Wash out boiling tubes X and Y with deionised water, then re-fill them both with the correct volumes of reactants, as above
10. Heat up the water to 303K
11. Place boiling tubes X and Y in the water bath and monitor their temperatures
12. When the temperatures in both boiling tubes reaches 303K, pour the contents of boiling tube X into boiling tube Y and start the stop-watch
13. Pour the contents now in boiling tube Y back into boiling tube X, to ensure that the reactants are fully mixed, and place boiling tube X back into the water bath
14. When the pink colour has disappeared, stop the stop-watch and record the time taken in the table shown below (table 2.5.1)
15. Measure the temperature throughout the reaction and record the final temperature in the table shown below (table 2.5.1)
16. Repeat steps 9-15 until there are three concordant results, which are results with times within 10% of the average time of each other and temperatures within 1 degree Kelvin of each other and that do not deviate more than 1 Kelvin during the course of the reaction

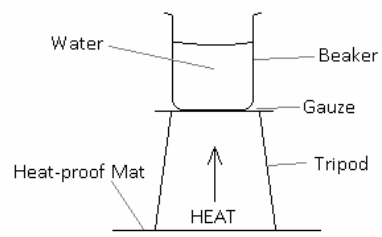


Figure 2.5.1 Diagram of water bath

17. Repeat steps 9-16 at all of the temperatures shown in the table below (table 2.5.1)

Results table for varying the temperature of the reaction:

Intended Temp. / K	Repeat 1		Repeat 2		Repeat 3		Repeat 4		Repeat 5	
	Time/s	Temp/ K	Time/s	Temp/ K	Time/s	Temp/ K	Time/s	Temp/ K	Time/s	Temp/ K
298										
303										
309										
315										
321										
327										

(Table 2.5.1)

2.6 – Method for Testing Different Catalysts

Using the same choice of concentrations of solutions in beakers X and Y as were used when varying the temperature, this is the method I will use when testing the effect of one of the five catalysts I will be testing (solutions of Mn^{2+}, Co^{2+}, Fe^{3+}, Cu^{2+} and Ni^{2+}):

1. Put on safety goggles
2. Measure out using a burette the volumes of solutions chosen (as above when varying the temperature) into beaker X and beaker Y
3. Add 10 drops of one of the catalyst solutions into beaker X
4. Pour the contents of beaker X into beaker Y and start the stop-watch
5. Mix the solutions by pouring the mixture back into beaker X and then back into beaker Y; then place beaker Y on a white tile
6. When the pink colour has disappeared, stop the stop-watch and record the time in the results table, as shown below (table 2.6.1)
7. Measure the temperature of the solution and record this in the results table (table 2.6.1)
8. Rinse out both beakers with deionised water and dry them
9. Repeat the experiment with the same catalyst until there are three results with times within 10% of the average time
10. Repeat steps 1-9 using 10 drops of each catalyst solution as well as one set of results without a catalyst

Results table for testing different catalysts:

Catalyst	Repeat 1		Repeat 2		Repeat 3		Repeat 4		Repeat 5	
	Time/s	Temp/ K	Time/s	Temp/ K	Time/s	Temp/ K	Time/s	Temp/ K	Time/s	Temp/ K

None										
Cu^{2+}										
Co^{2+}										
Ni^{2+}										
Fe^{3+}										
Mn^{2+}										

(Table 2.6.)

Method for Varying the Temperature with a Catalyst

The method that I will use to vary the temperature with a catalyst will be exactly the same as the method used to vary the temperature written above, except that I will add 10 drops of one of the catalyst solutions (a catalyst which gives a reaction time of between three and four minutes) to boiling tube X in every experiment. I will record the results in a table exactly like the one shown above for varying the temperature without a catalyst. (table 2.5.1)

2.7 – Analysing the Results

When all the data has been collected, I will use the data to establish certain facts about the rate of the reaction. Firstly, using the results for varying the concentration of a reactant, I will take an average of the three times that are within the 10% boundary (ignoring outlying results). I will then draw up a table for each of the varied reactants ([reactant] means the concentration of that reactant):

[reactant] /mol dm^{-3}	**Average time (t) /s**	**$^1/_t$ /s^{-1}**

(Table 2.7.)

The rate of the reaction is proportional to $^1/_t$, so a graph of $^1/_t$ against concentration will produce the same result as a rate/concentration graph. Plotting the graph will give me the order of the reaction with respect to that reactant, which then leads to the rate equation for the reaction (see above). Using a computer spreadsheet, I can calculate a value for the Pearson's Product Moment Correlation Coefficient (PMCC) for $^1/_t$ against the concentration of each reactant, which is a number between -1 and 1 to indicate the level of linear correlation between two variables. If the value is close to 1, it suggests strong linear correlation, so in this context this would suggest that there is strong evidence that a reaction is first order.[xii]

I can then use the results for varying the temperature to find the activation enthalpy of the reaction. Taking averages of the times and temperatures of the three concordant results I have found, I will then find a value for the rate constant k at each temperature. Since the rate equation will be of the form:

$$\mathbf{rate} = \mathbf{k}[\mathbf{Br}^-]^x[\mathbf{BrO_3}^-]^y[\mathbf{H}^+]^z$$

(Equation 2.7.)

I can rearrange this to find a value for k at each temperature:

$$k = \frac{\text{rate}}{[Br^-]^x[BrO_3^-]^y[H^+]^z}$$ *(Equation 2.7.2)*

So to find k I will have to divide the rate of reaction by the product of the concentrations, each to their respective powers x, y and z, that I have chosen to use when varying the temperature. I will then take the natural logarithm of each value of k and write these in a table (The unit of k depends upon the rate equation and hence the order of the reaction with respect to each reactant):

Average Time (t) / s	$^1/_t$ / s^{-1}	k	**ln k**	**Average Temperature (T) / K**	$^1/_T$ / K^{-1}

(Table 2.7.2)

I will then plot a graph of $\ln k$ against $^1/_T$ to find the value of the Activation Enthalpy (see above).

The results of adding different transition metal ion solutions to the reaction will allow me to find out if any of the solutions I tested catalyse the reaction. I will draw up a table showing the average time (t) and $^1/_t$ for each transition metal ion:

Catalyst	**Average Time (t) / s**	$^1/_t$ / s^{-1}
None		
Copper (II)		
Cobalt (II)		
Nickel (II)		
Iron (III)		
Manganese (II)		

(Table 2.7.3)

I can compare the rates of reaction with each catalyst by comparing the values of $^1/_t$, since this is proportional to rate. The higher the value of $^1/_t$, the faster the rate of reaction.

I will analyse the results of varying the temperature using a catalyst in exactly the same way as I analysed the results of varying the temperature without a catalyst. The small volume of catalyst used will have negligible affect on the calculation of k, so all calculations can be the same. This will allow me to find the value of the activation enthalpy for the reaction with a catalyst.

2.8 – Why this Method will produce Reliable Results

I believe that this method should produce precise and reliable results. Firstly, I will carry out the experiments enough times to ensure results are accurate. By repeating experiments until I have results which are within 10% of the average result, I should be able to identify any anomalous results and discount them from my analysis.

I have taken steps to ensure that measurements I take are accurate. For example, I will measure out quantities of solutions required using burettes, which have a lower tolerance than a measuring cylinder. Also, all the measurements I will have to take should be sufficiently large to minimise the percentage error on the measurement.

I am confident that the concentrations of all solutions made will be accurate, which is important when investigating how concentration affects the rate of the reaction. When solutions are made up, several washings will be carried out to ensure that all of the required chemical is in the solution.

2.9 – Modifications made to the Method during the Investigation

Whilst I was carrying out the practical part of the investigation, I made one change to the method described above. I placed beakers of solution on a white tile to ensure that I could see accurately the point at which the colour changed.

3) Results and Analysis

Having completed the practical part of my investigation, I will now analyse my results to draw conclusions about the rate of the reaction.

3.1 Concentration of Solutions

Since all the reactants were in a mixture together, their actual concentrations differ from the concentrations that they were made up to, like so:

Take a reactant X; the number of moles of X in the reacting mixture is given by: [xiii]

$$\textbf{moles X} = \frac{\textbf{initial concentration X} \times \textbf{volume X added}}{1000}$$ (Equation 3.1.1)

if concentration is measured in mol dm^{-3} and volume is measured in cm^3. The total volume of the reacting mixture is $40cm^3$, so the actual concentration of X (in mol dm^{-3}) is given by:

$$\textbf{concentration X} = \frac{1000 \times \textbf{moles X}}{40}$$ (Equation 3.1.2)

Putting together equations 3.1.1 and 3.1.2, we get the relationship:

$$\textbf{concentration X} = \frac{\textbf{initial concentration X} \times \textbf{volume X added}}{40}$$ (Equation 3.1.3)

I have used this equation to get the concentration of all the reactants for all the reactions I completed. The only more complicated concentration is that of the acid solution when solution C was used (when the concentration of bromide and bromate ions was varied): In the making-up of solution C, $400cm^3$ of 1M sulphuric acid was used. Therefore:

$$\text{Moles } H_2SO_4 = \frac{1 \times 400}{1000} = 0.40 \text{ moles}$$

Since there are two moles of H^+ ion for every one mole of H_2SO_4, this means that there were 0.80 moles of H^+ ions in solution C. This solution was made up with deionised water to $1000cm^3$, meaning that the concentration of H^+ ions in solution C was given by:

$$\text{Concentration } H^+ = \frac{1000 \times 0.8}{1000} = 0.80 \text{ mol dm}^{-3}$$

Since I used 15cm^3 of solution C in each reacting mixture (of total volume 40cm^3), the concentration of H^+ ions in the reacting solution was given by:

$$\text{Concentration } H^+ = \frac{0.8 \times 15}{40} = 0.30 \text{ mol dm}^{-3}$$

Firstly, when varying the concentration of bromide ion solution:

- $[BrO_3^-] = \frac{0.005 \times 10}{40} = 1.25 \times 10^{-3} \text{mol dm}^{-3}$
- $[H^+] = 0.30 \text{ mol dm}^{-3}$

The volume of bromide ions was varied, so this table shows the results of the calculations for the concentration of bromide ions for each volume of 0.01M KBr solution added:

Volume KBr added / cm^3	Concentration Br^- solution at this volume / 10^{-3} mol dm^{-3}
10.0	2.50
8.00	2.00
6.00	1.50
4.00	1.00
2.00	0.50

(Table 3.1.1)

Next, when varying the concentration of bromate ion solution:

- $[Br^-] = \frac{0.01 \times 10}{40} = 2.50 \times 10^{-3} \text{mol dm}^{-3}$
- $[H^+] = 0.30 \text{ mol dm}^{-3}$

Table 3.1.2 shows the concentrations of bromate ions for each different volume of 0.005M $KBrO_3$ added:

Volume $KBrO_3$ added / cm^3	Concentration BrO_3^- solution at this volume / 10^{-3} mol dm^{-3}
10.0	1.25
8.00	1.00
6.00	0.75
4.00	0.50
2.00	0.25

(Table 3.1.2)

Next, when varying the concentration of acid solution:

- $[Br^-] = \frac{0.4 \times 15}{40} = 0.15 \text{ mol dm}^{-3}$
- $[BrO_3^-] = \frac{0.2 \times 10}{40} = 0.05 \text{ mol dm}^{-3}$

Table 3.1.3 shows the concentrations of acid for each different volume of 0.01M H_2SO_4 added:

Volume H_2SO_4 added / cm^3	Concentration H^+ ions at this volume / 10^{-3} mol dm^{-3}

10.0	5.00
8.00	4.00
6.00	3.00
4.00	2.00
2.00	1.00

(Table 3.3)

Finally, these are the concentrations used for all the reactants when I varied the temperature, tested catalyst solutions and varied the temperature with a catalyst:

- $[Br^-] = \frac{0.4 \times 15}{40} = 0.15 \text{ mol dm}^{-3}$
- $[BrO_3^-] = \frac{0.2 \times 10}{40} = 0.05 \text{ mol dm}^{-3}$
- $[H^+] = \frac{0.02 \times 6}{40} = 3.00 \times 10^{-3} \text{ mol dm}^{-3}$

3.2 – Results: Varying the Concentration of each Reactant

Below are detailed the results I found when varying the concentration of each reactant in turn. All times are shown to the nearest second (which was the greatest degree of accuracy that I could use when judging the time that the reaction changed colour). Anomalous results are highlighted. Firstly, the results when I varied the concentration of bromide ions:

$[Br^-]$ /mol dm^{-3}	Repeat 1		Repeat 2		Repeat 3		Repeat 4		Repeat 5	
	Time/s	Temp/ K	Time/s	Temp/ K	Time/s	Temp/ K	Time/s	Temp/ K	Time/s	Temp/ K
2.50×10^{-3}	113	296.5	115	296	110	296	116	296		
2.00×10^{-3}	167	295	151	295.5	148	295.5	144	295		
1.50×10^{-3}	190	295	216	295	219	294.5	171	295	182	295
1.00×10^{-3}	344	295	329	294	321	294.5				
5.00×10^{-4}	660	294.5	609	295	610	294.5				

(Table 3.2.1)

Next, the results when I varied the concentration of bromate ions:

$[BrO_3^-]$ /mol dm^{-3}	Repeat 1		Repeat 2		Repeat 3		Repeat 4		Repeat 5	
	Time/s	Temp/ K	Time/s	Temp/ K	Time/s	Temp/ K	Time/s	Temp/ K	Time/s	Temp/ K
1.25×10^{-3}	132	295.5	130	296	130	294.5				
1.00×10^{-3}	165	296	136	295	145	296	141	296		
7.50×10^{-4}	170	296	170	296	169	296				
5.00×10^{-4}	242	296	239	296	230	296				
2.50×10^{-4}	449	295	413	296.5	301	293	427	293		

(Table 3.2.2)

Next, the results when I varied the concentration of acid (H^+ ions):

$[H^+]$ /mol dm^{-3}	Repeat 1		Repeat 2		Repeat 3		Repeat 4		Repeat 5	
	Time/s	Temp/ K	Time/s	Temp/ K	Time/s	Temp/ K	Time/s	Temp/ K	Time/s	Temp/ K
5.00×10^{-3}	128	290.5	137	290	139	290.5	139	290		
4.00×10^{-3}	201	293	195	293	197	293				
3.00×10^{-3}	336	293	308	293.5	235	294	251	294	316	293.5
2.00×10^{-3}	764	292	675	292	732	293				

1.00×10^{-3}	2967	293	3243	292.5	3199	292.5				

(Table 3.2.3)

3.3 – Results: Varying the Temperature of the Reaction

When I had carried out the experiment with different concentrations of all of the reactants, I moved on to vary the temperature. I had to choose a set of concentrations to use for all subsequent experiments, which took around 5 minutes to change colour. This is the set of volumes I chose to use:

Beaker X		**Beaker Y**		
Volume of 0.01M H_2SO_4 /cm³	**Volume of deionised water /cm³**	**Volume of 0.20M $KBrO_3$ /cm³**	**Volume of solution D /cm³**	**Volume of 0.0001M phenol /cm³**
6.0	4.0	10.0	15.0	5.0

(Table 3.3.1)

Table 3.3.2 below shows the results I obtained at different temperatures. All times are given to the nearest second, all temperatures are given to the nearest half a second and anomalous results are highlighted:

Intended Temp. / K	**Repeat 1**		**Repeat 2**		**Repeat 3**		**Repeat 4**		**Repeat 5**	
	Time/s	**Temp/ K**	**Time/s**	**Temp/ K**	**Time/s**	**Temp/ K**	**Time/s**	**Temp/ K**	**Time/s**	**Temp/ K**
298	271	296	275	296.5	262	297				
303	189	303.5	194	302.5	200	302.5				
309	109	309.5	113	310	157	311	111	309.5		
315	75	315.5	71	316	74	316				
321	51	321	62	322	53	321.5	50	321.5		
327	38	327	37	327.5	38	327				

(Table 3.3.2)

3.4 – Results: Using different Transition Metal Ions as Catalysts

Using the same reaction as I used to vary the temperature, I repeated the experiment, this time adding a small amount of solution of five different transition metal ions. The results are shown in the table below. Times are to the nearest second and anomalous results are highlighted:

Catalyst	**Repeat 1**		**Repeat 2**		**Repeat 3**		**Repeat 4**		**Repeat 5**	
	Time/s	**Temp/ K**	**Time/s**	**Temp/ K**	**Time/s**	**Temp/ K**	**Time/s**	**Temp/ K**	**Time/s**	**Temp/ K**
None	265	294.5	275	295.5	287	296				
Cu^{2+}	281	296	282	296.5	287	296				
Co^{2+}	273	295.5	296	293.5	290	294.5				
Ni^{2+}	261	296.5	274	296	265	296.5				
Fe^{3+}	190	293.5	163	293.5	162	294.5	157	294.5		
Mn^{2+}	313	294.5	298	295.5	202	295	308	295		

(Table 3.4.1)

Since the only solution which appeared to have a noticeable effect was the Iron (III) solution, I had to use this as the catalyst for the next, experiments, in which I varied the temperature of the reaction again, with the addition of a catalyst. Since this

catalyst was slightly faster than I had hoped to use to vary the temperature with a catalyst, I adjusted the intended temperatures accordingly, making them slightly lower so that I would still be able to measure the point at which the colour changed accurately. The results I obtained are shown below in table 3.4.2 (all times are to the nearest second, all temperatures are to the nearest half a degree and anomalous results are highlighted):

Intended Temp. / K	Repeat 1		Repeat 2		Repeat 3		Repeat 4		Repeat 5	
	Time/s	Temp/ K	Time/s	Temp/ K	Time/s	Temp/ K	Time/s	Temp/ K	Time/s	Temp/ K
298	137	297	136	297	135	297				
303	82	303	77	304	81	303.5				
306	71	306	55	306	69	306.5	69	307		
311	62	309	55	310.5	53	311	53	310		
316	44	314	43	314.5	45	314				
321	32	323	31	322	24	323	29	323		

(Table 3.4.2)

3.5 – Analysis of Results of Varying the Concentration of the Reactants

From varying the concentration of each reactant in turn, I can determine the order of the reaction with respect to each reactant, the overall order of the reaction. Firstly, the results of varying the concentration of the bromide ions. I have calculated an average time for the three concurrent results, as shown in the table below (All results to 2 decimal places):

$[Br^-]$ /10^{-3} mol dm^{-3}	Average time (t) /s	$^1/_t$ /10^{-3} s^{-1}
2.50	114.67	8.72
2.00	147.67	6.77
1.50	181.00	5.53
1.00	331.33	3.02
0.50	626.33	1.60
0.00	-	0.00

(Table 3.5.1)

I have plotted a graph of $^1/_t$ against concentration (graph 3.5.1), which is on page 34. This shows a clear linear correlation between concentration and initial rate (since rate is proportional to $^1/_t$), which suggests that the reaction is first order with respect to the concentration of bromide ions. I have calculated the value of the Pearson's Product Moment Correlation Coefficient for these results, which gives a value of 0.997, suggesting very strong positive linear correlation. Therefore, the first conclusion of my investigation is that:

CONCLUSION 1: $\mathbf{rate} \propto [\mathbf{Br^-}]$ *(Section 3.5.1)*

Table 3.5.2 below shows the values of the average time (t) and $^{1}/_{t}$ when the concentration of bromate ions was varied (all results to 2 decimal places):

$[BrO_3^-]$ /10^{-3} mol dm^{-3}	Average time (t) /s	$^{1}/_{t}$ /10^{-3} s^{-1}
1.25	130.67	7.65
1.00	140.67	7.11
0.75	169.67	5.89
0.50	237.00	4.22
0.25	429.67	2.33
0.00	-	0.00

(Table 3.5.2)

The graph of $^{1}/_{t}$ against concentration of bromate ions (graph 3.5.2) is on page 35. It also shows clearly a linear correlation exists between the initial rate of the reaction and the concentration of bromate ions. The value of Pearson's Product Moment Correlation Coefficient for these results is 0.981, again suggesting strong positive linear correlation. This leads me to the conclusion that the reaction is first order with respect to the concentration of bromate ions.

CONCLUSION 2: $\mathbf{rate} \propto [\mathbf{BrO_3}^-]$ *(Section 3.5.2)*

Table 3.5.3 shows the values of average time (t) and $^{1}/_{t}$ when the concentration of the acid solution was varied (all results to two decimal places):

$[H^+]$ /10^{-3} mol dm^{-3}	Average time (t) /s	$^{1}/_{t}$ /10^{-3} s^{-1}
5.00	138.33	7.23
4.00	197.67	5.06
3.00	320.00	3.13
2.00	723.67	1.38
1.00	3136.33	0.32
0.00	-	0.00

(Table 3.5.3)

Page 37 shows the graph (graph 3.5.3) of $^{1}/_{t}$ against concentration for hydrogen ions. It is clear from the graph that the correlation is not linear, so the reaction is not first order with respect to hydrogen ions. I suspect that the reaction is second order with respect to hydrogen ions. To test this, I will look at the correlation between $^{1}/_{t}$ and the values for concentration squared. If the reaction is second order with respect to hydrogen ions, then this graph will be linear.

$[H^+]^2$ /10^{-6} mol^2 dm^{-6}	Average time (t) /s	$^{1}/_{t}$ /10^{-3} s^{-1}
25.00	138.33	7.23
16.00	197.67	5.06
9.00	320.00	3.13
4.00	723.67	1.38

1.00	3136.33	0.32
0.00	-	0.00

(Table 3.5.4)

The graph (graph 3.5.4) of these results is shown on page 38, which shows clear positive linear correlation between $^1/_t$ and concentration squared, which is backed up with the high value of the Pearson Product Moment Correlation Coefficient of this data, which is 0.997. Therefore the reaction is second order with respect to hydrogen ions.

CONCLUSION 3: $$\mathbf{rate} \propto [\mathbf{H}^+]^2$$ *(Equation 3.5.3)*

Now that I know the order of the reaction with respect to all of the reactants, I can come up with the rate equation for the reaction and the overall order of the reaction. The overall order of the reaction is the sum of the orders of all the reactants, which is equal to **4**. The overall rate equation is given by:

CONCLUSION 4: $$\mathbf{rate} = \mathbf{k}[\mathbf{Br}^-][\mathbf{BrO_3}^-][\mathbf{H}^+]^2$$ *(Equation 3.5.4)*

3.6 – Analysis of the Results of Varying the Temperature

These results will allow me to calculate a value for the activation enthalpy of the reaction. My results for varying the concentration of the reactants have shown me that the rate equation for the reaction is:

$$\mathbf{rate} = \mathbf{k}[\mathbf{Br}^-][\mathbf{BrO_3}^-][\mathbf{H}^+]^2$$ *(Equation 3.6.1)*

So the value of k, the rate constant is given by:

$$\mathbf{k} = \frac{\mathbf{rate}}{[\mathbf{Br}^-][\mathbf{BrO_3}^-][\mathbf{H}^+]^2}$$ *(Equation 3.6.2)*

Since rate is proportional to $^1/_t$ (where t is average time taken to change colour), k can be shown as:

$$\mathbf{k} \propto \frac{1}{\mathbf{t}[\mathbf{Br}^-][\mathbf{BrO_3}^-][\mathbf{H}^+]^2}$$ *(Equation 3.6.3)*

Since I will be drawing a graph of the natural logarithm of k, I can use equation 3.6.3 to find values of k (since $\ln ab = \ln a + \ln b$, the constant of proportionality does not affect the gradient of the graph, which is all I need to find the activation enthalpy for the reaction). Hence I need to know the value of $[\mathrm{Br}^-][\mathrm{BrO_3}^-][\mathrm{H}^+]^2$ for the reaction for which I varied the temperatures. These are the concentrations of reactants I used in this experiment:

- $[Br^-]$ = 0.15 mol dm^{-3}
- $[BrO_3^-]$ = 0.05 mol dm^{-3}
- $[H^+]$ = 3.00x10^{-3} mol dm^{-3}

Therefore:

$$[\mathrm{Br}^-][\mathrm{BrO_3}^-][\mathrm{H}^+]^2 = 6.75 \times 10^{-8}$$

We then get, for k:

$$\mathbf{k} \propto \frac{1.48\times10^{7}}{\mathbf{t}} \qquad \text{(Equation 3.6.3)}$$

The values for average time (t), k, $\ln k$, average temperature (T) and $^1/_T$ for the reactions taking place at different temperatures are shown in table 3.6.1 below (all results are to 2 decimal places):

Average Time (t) /s	k / 10^5 mol^{-4} dm^{-12} s^{-1}	ln k	Average Temperature (T) /K	$^1/_T$ /10^{-3} K^{-1}
269.33	0.55	10.92	296.50	3.37
194.33	7.62	11.24	302.83	3.30
111.00	13.35	11.80	309.67	3.23
73.33	20.20	12.22	315.83	3.17
51.33	28.86	12.57	321.50	3.11
37.67	39.33	12.88	327.00	3.06

(Table 3.6.1)

A graph of ln k against $^1/_T$ (graph 3.6.1) is plotted on page 40. The graph is a straight line, as expected, and the spreadsheet gives the equation of the graph as:

$$y = -6442.9x + 32.60$$ (Equation 3.6.4)

Where $y = \ln k$ and $x = {}^1/_T$. Therefore the gradient of the line is -6.442.9. By the Arrhenius equation, the activation enthalpy of a reaction is given by $E_a = -mR$, where m is the gradient and R is the molar gas constant, equal to 8.31.Therefore the activation enthalpy of the reaction between bromide ions and bromate ions in acid solution is equal to $-(-6442.9) \times 8.31 = 53540$.

CONCLUSION 5: $\mathbf{E_a = 53.54\ kJ\ mol^{-1}\ (to\ 2\ d.p.)}$ (Equation 3.6.5)

3.7 – Analysis of the Results of Using different Transition Metal Ions as Catalysts

These results allow me to compare the catalytic affect of different transition metal ions on the reaction. Table 3.7.1 shows the values of the average time (t) and $^1/_t$ for the different transition metal ion solutions tested (All values are to two decimal places):

Catalyst	Average Time (t) / s	$^1/_t$ / 10^{-3} s^{-1}
None	275.67	3.63
Copper (II)	283.33	3.53
Cobalt (II)	286.33	3.49
Nickel (II)	266.67	3.75
Iron (III)	160.67	6.22
Manganese (II)	306.33	3.26

(Table 3.7.1)

To clarify these results, I have drawn a bar chart showing the value of $^{1}/_{t}$ for each different transition metal ion solution added, which is graph 3.7.1 on page 42.

Unfortunately, these results are rather inconclusive. Only one of the metal ions (Iron (III)) appears to have had any affect on the reaction, causing the rate to almost double. None of the other solutions

have caused any noticeable change in the rate of the reaction at all. Whilst I was not expecting all of the solutions to have a catalytic affect, the fact that only one of them has made the remotest amount of difference suggests that there was a problem in my experiment. Potential causes of this problem will be discussed in the evaluation (4.1, page 47).

The results I obtained from varying the temperature with the addition of Iron (III) solution will give me the activation enthalpy of the reaction with Iron (III) solution. I will have to find a value for the rate constant, k, for the reaction time at each temperature. Since the volume of catalyst solution is relatively small, its affect on the rate equation is negligible, so I can use the same equation as I did when varying the temperature without a catalyst (page 39) to find k.

$$\mathbf{k} \propto \frac{1.48\times10^{7}}{\mathbf{t}}$$ *(Equation 3.7.1)*

The values for average time (t), k, $\ln k$, average temperature (T) and $^{1}/_{T}$ for the reactions taking place at different temperatures with Iron (III) solution acting as a catalyst are shown in table 3.7.2 below (all results are to 2 decimal places):

Average Time (t) /s	**k / 10^5 mol^{-4} dm^{-12} s^{-1}**	**ln k**	**Average Temperature (T) /K**	**$^{1}/_{T}$ /10^{-3} K^{-1}**
136.00	1.09	11.60	297.00	3.37
80.00	1.85	12.13	303.50	3.30
69.67	2.13	12.27	306.50	3.26
53.67	2.76	12.53	310.50	3.22
44.00	3.37	12.73	314.17	3.18
30.67	4.83	13.09	322.67	3.10

(Table 3.7.2)

A graph of ln k against $^{1}/_{T}$ (graph 3.7.2) is plotted on page 44. The graph is a straight line, as expected, and the spreadsheet gives the equation of the graph as:

$$y = -5519.5x + 30.26$$ *(Equation 3.7.2)*

Where $y = \ln k$ and $x = {}^{1}/_{T}$. Therefore the gradient of the line is -5519.5. By the Arrhenius equation, the activation enthalpy of a reaction is given by $\mathrm{E_a} = -\mathrm{mR}$, where m is the gradient and R is the molar gas constant, equal to 8.31.Therefore the activation enthalpy of the reaction between bromide ions and bromate ions in acid solution with a catalyst of Iron (III) ions is equal to $-(-5519.5) \times 8.31 = 45867$.

CONCLUSION 5: $\mathbf{E_a\ (with\ catalyst) = 45.87\ kJ\ mol^{-1}\ (to\ 2\ d.p.)}$ *(Equation 3.7.3)*

3.8 – Suggesting a Reaction Mechanism

As explained on page 9, the rate equation can suggest a possible rate determining step for a reaction. As I have determined above, the rate equation for this reaction is:

$$\mathbf{rate} = [\mathbf{Br^-}][\mathbf{BrO_3}^-][\mathbf{H^+}]^2 \qquad \text{(Section 3.8.7)}$$

This suggests that the rate determining step for the reaction could involve one Br^- ion, one BrO_3^- ion and two H^+ ions. Since reaction steps with a molecularity of more than two are very rare, it is likely that the rate determining step is preceded by faster reactions. The overall equation for the reaction is:

$$5Br^-_{(aq)} + BrO_3^-{}_{(aq)} + 6H^+_{(aq)} \rightarrow 3Br_{2\,(aq)} + 3H_2O_{(l)} \qquad \text{(Equation 3.8.2)}$$

It is possible that the first two steps of the reaction are:[xiv]

Step 1 (fast): $$Br^-_{(aq)} + H^+_{(aq)} \rightarrow HBr_{(aq)} \qquad \text{(Equation 3.8.3)}$$

Step 2 (fast): $$BrO_3^-{}_{(aq)} + H^+_{(aq)} \rightarrow HBrO_{3\,(aq)} \qquad \text{(Equation 3.8.4)}$$

These two products, hydrogen bromide and hydrogen bromate, then react together in the rate determining step:

Step 3 (slow): $$HBr_{(aq)} + HBrO_{3\,(aq)} \rightarrow HBrO_{(aq)} + HBrO_{2\,(aq)} \qquad \text{(Equation 3.8.5)}$$

This corresponds with the rate equation, since there are two moles of hydrogen and one mole of bromide and bromate involved in this step. The products of this step can then react with more hydrogen bromide to form the final products of the reaction:

Step 4 (fast): $$HBrO_{2\,(aq)} + HBr_{(aq)} \rightarrow HBrO_{(aq)} \qquad \text{(Equation 3.8.6)}$$

Step 5 (fast): $$HBrO_{(aq)} + HBr_{(aq)} \rightarrow Br_{2\,(aq)} + H_2O_{(l)\,(aq)} \qquad \text{(Equation 3.8.7)}$$

3.9 – Summary of Conclusions

The aims of my investigation, as stated in the introduction, were to find the rate equation for the reaction, find a suitable catalyst, and find a value for the activation enthalpy with and without a catalyst. I successfully found the rate equation to be:

$$\mathbf{rate = k[Br^-][BrO_3^-][H^+]^2} \qquad \text{(Equation 3.9.1)}$$

This equation shows that the overall order of the reaction is 4. In finding a catalyst, my results were rather inconclusive, although they showed that Iron (III) ions caused the rate of reaction to increase. The activation enthalpy without a catalyst was found to be:

$$\mathbf{E_a = 53.54\ kJ\ mol^{-1}\ (to\ 2\ d.p.)} \qquad \text{(Equation 3.9.2)}$$

The activation enthalpy using Iron (III) ions as a catalyst was found to be:

$$\mathbf{E_a\ (with\ catalyst) = 45.87\ kJ\ mol^{-1}\ (to\ 2\ d.p.)} \qquad \text{(Equation 3.9.3)}$$

4) Evaluation

In this section I will evaluate my investigation and discuss whether the conclusions I made were reliable. I will look at the potential for error in my investigation, and evaluate whether my method could have been improved.

4.1 Evaluation of Method

Overall, I believe that the majority of the method that I used was successful.

I believe I took the correct steps to ensure that my results were accurate. For example, I ensured that I had three concordant results for each experiment, of which I took the average result, to ensure that no anomalous results were used in the calculations. This was useful, as I did obtain some anomalous results, which are discussed below (4.4, page 48).

I also believe that the method was successful in ensuring that concentrations of reactants were accurate. My method for making up solutions included multiple washings of glassware used, to ensure that all the solid reactant ended up in the solution. I also used burettes as opposed to measuring cylinders to measure out volumes of reactants, which gives a lower percentage error than a measuring cylinder would have.

However, it is possible that my method led to errors. These procedural errors are discussed below (4.2, page 47).

The only major problem in my investigation was the identification of a suitable catalyst for the reaction. This experiment only identified one of the potential catalysts (iron (III)) as having a catalytic effect on the reaction, when expected results suggest that other transition metal ions could affect the rate of reaction, either increasing it or decreasing the rate. I believe that this may have been caused by the failure in differentiating in the method between which set of concentrations were used when varying the temperature and the catalyst. The concentrations of bromide and bromate ions in the first sets of concentrations (when solution C was used) were significantly higher than in the sets of concentrations when solution D was used. However, the method for adding potential catalysts did not take this into account; the instruction was simply to add 10 drops of catalyst. I believe that at the higher concentrations that I used when varying the catalyst, there was not enough catalyst solution in the reacting mixture to have a significant effect, in all the cases except for iron (III).

4.2 Procedural Errors

In this section I will examine some of the greatest procedural errors that could have affected the results of my investigation.

In my opinion, the greatest source of error in my experiment will have come from the judgement of the point of the colour change. This was totally down to human judgement, so was completely subjective. It relied upon memory, since the colour of the reacting mixture continued to change colour after the major colour change had occurred, so a reference solution could not be kept to compare with the reacting solution. If I stopped the stopwatch slightly after the colour change had occurred, this would have made the value of higher, and hence the value of $^1/_t$ would have been lower. Since is proportional to $^1/_t$, this means that that value of and $\ln k$ would have been lower. This would have reduced the gradient of my graph and made the value of the activation enthalpy lower.

To try and reduce the problems that this caused, I carried out repeats of all my experiments. I did enough repeats to ensure that I had three results for each experiment with times all within 10% of the average time of each other. I believe that this is sufficiently accurate to ensure that the results I have obtained are reliable.

Another possible source of error was variations in room temperature whilst I carried out my experiment. Since I carried out the practical part of my investigation at different times of day over a period of three weeks, there were variations in the room temperature throughout this time. I recorded the temperature at the end of each reaction I did, as is shown in my results tables. From these I can see that the largest range of temperatures for any of the sets of results (results of varying concentrations of bromide ions, bromate ions and hydrogen ions, results of testing different catalysts) was 3.5K. This is 1.17% of the standard room temperature, 298K. This suggests that the temperature remained constant enough throughout the course of the experiment to produce reliable results.

To reduce the effect of this problem, I could carry out all the reactions at the same time of day, over a shorter time period, but timetabling problems make this impractical.

Another example of a possible procedural error in my experiment is the mixing of reactants. To ensure the reaction could occur fully, the reactants needed to be completely mixed. I poured the contents of beaker X back into beaker Y twice to reduce this error, however when boiling tubes were used as opposed to beakers, this was harder to do to make the reactants fully mixed. Also, when the time for the colour change was at its shortest, the time it takes for the reactants to mix represents a significant proportion of the overall reaction time. This could have skewed these results, making the rate appear slower than it was.

4.3 Anomalous Results

During my investigation I obtained several anomalous results, the causes of which I will attempt to explain. For my experiments, I defined an anomalous result as a result for

which the time was more than 10% of the average time apart from the other times under the same conditions. When temperature was varied, results for which the temperature was more than 1K apart from the other temperatures was also anomalous. I did not include any anomalous results in my subsequent calculations.

Overall, I obtained 16 anomalous results in the course of my investigation, which represents 13.9% of all the reactions that took place, which is a significant proportion. However, to ensure that my results were reliable, I placed strict limits on what results could be deemed concurrent, so I expected to obtain some anomalous results.

I believe the most likely cause of the majority of these anomalous results is the limited accuracy with which it is possible to judge the point of the colour change for the reaction, as discussed above (4.2, page 47). It is my opinion that this could lead to results with a range greater than 10%, therefore some anomalies were inevitable. However, since I ensured that I had three concordant results for each experiment, I believe I successfully negated this problem.

Another possible cause of the anomalous results could have been slight variations in the concentrations of the reactants, due to errors in measuring out the volume of solutions. A slight difference in concentration of a reactant could lead to a difference in the rate. This could have been particularly noticeable if the concentration of hydrogen ions was not as it should have been, since this would have had a disproportionate effect on the rate, as shown by the rate equation that I derived. Similarly for the phenol; since the experiment measures the amount of time for all the phenol to have reacted, if there was slightly too much phenol in the reacting mixture, the reaction could have taken longer to change colour, leading to an anomaly. Using a burette should have reduced the potential for this error, since a burette is more accurate than a measuring cylinder, but the occasional error still could have occurred.

It is perhaps significant that more anomalies occurred towards the start of my investigation. I obtained four anomalous results when varying the concentration of bromide ions, which I carried out first, compared with no more than three for any of the other sets of results. This is probably due to becoming more practised at carrying out the experiment over time, so I was less likely to make errors with the point of colour change the further into the practical that I got.

The majority of my anomalous results do not lie that far from the limits I imposed on my results for concurrence. However I obtained six anomalous results which are significantly different to the other results obtained under the same conditions, which are shown below (anomalies are the highlighted results):

When I varied the concentration of bromide ions:

$[Br^-]$ /mol dm^3	Repeat 1		Repeat 2		Repeat 3		Repeat 4		Repeat 5	
	Time/s	Temp/ K	Time/s	Temp/ K	Time/s	Temp/ K	Time/s	Temp/ K	Time/s	Temp/ K
1.50×10^{-3}	190	295	216	295	219	294.5	171	295	182	295

(Page 4.3.)

When I varied the concentration of bromate ions:

$[BrO_3^-]$ /mol dm³	Repeat 1		Repeat 2		Repeat 3		Repeat 4		Repeat 5	
	Time/s	Temp/ K	Time/s	Temp/ K	Time/s	Temp/ K	Time/s	Temp/ K	Time/s	Temp/ K
2.50×10^{-4}	449	295	413	296.5	301	293	427	293		

(Table 4.3.2)

When I varied the concentration of acid:

$[H^+]$ /mol dm³	Repeat 1		Repeat 2		Repeat 3		Repeat 4		Repeat 5	
	Time/s	Temp/ K	Time/s	Temp/ K	Time/s	Temp/ K	Time/s	Temp/ K	Time/s	Temp/ K
3.00×10^{-3}	336	293	308	293.5	235	294	251	294	316	293.5

(Table 4.3.3)

When I varied the catalyst:

Catalyst	Repeat 1		Repeat 2		Repeat 3		Repeat 4		Repeat 5	
	Time/s	Temp/ K	Time/s	Temp/ K	Time/s	Temp/ K	Time/s	Temp/ K	Time/s	Temp/ K
Mn^{2+}	313	294.5	298	295.5	202	295	308	295		

(Table 4.3.3)

These results are so different from the other results that they suggest something serious went wrong. In tables 4.3.3 and 4.3.1, there are two anomalous results that are concordant with each other, suggesting that there was the same problem with both experiments. These could have been caused by contamination of the burettes – there were two instances of burettes becoming contaminated by other solutions over the course of the practical, so this could have led to a significant effect on the results before it was noticed.

4.4 Equipment Errors

In this section I will quantitatively evaluate the margin of error in the equipment that I used. I shall use this formula to calculate the percentage error on different procedures in my investigation:

$$\% \text{ error} = \frac{\text{tolerance}}{\text{amount measured}} \times 100$$

(Equation 4.5.1)

The tolerance of a piece of apparatus is the greatest degree of accuracy to which it can measure, that is, the smallest value that it can measure. For volumetric flasks and pipettes, the tolerance is given on the apparatus. For burettes, the tolerance is doubled to account for errors in both the initial and final readings on the burette.

I have not calculated any errors for the stopwatch, since the procedural error for the stopwatch is large enough to make the equipment error negligible (the stopwatch can measure times to the nearest hundredth of a second, whereas I could only accurately give a time for the colour change to the nearest second).

I have examined the equipment errors associated with the making up of each solution to work out a total percentage error for the volume of each solution made up, as shown below (all values to 2 decimal places):

Making up 0.01M potassium bromide solution

- Error on balance: $\% \text{ error} = \frac{0.01}{2.38} \times 100 = 0.42\%$
- Error on volumetric flask: $\% \text{ error} = \frac{0.60}{2000} \times 100 = 0.03\%$
- Total error: **0.45%**

Making up 0.005M potassium bromate solution

- Error on balance: $\% \text{ error} = \frac{0.01}{1.67} \times 100 = 0.60\%$
- Error on volumetric flask: $\% \text{ error} = \frac{0.60}{2000} \times 100 = 0.03\%$
- Total error: **0.63%**

Making up 0.2M potassium bromate solution

- Error on balance: $\% \text{ error} = \frac{0.01}{66.8} \times 100 = 0.01\%$
- Error on volumetric flask: $\% \text{ error} = \frac{0.60}{2000} \times 100 = 0.03\%$
- Total error: **0.04%**

Making up 0.01M phenol solution

- Error on balance: $\% \text{ error} = \frac{0.01}{0.94} \times 100 = 1.06\%$
- Error on volumetric flask: $\% \text{ error} = \frac{0.40}{1000} \times 100 = 0.04\%$
- Total error: **1.10%**

Making up 0.0001M phenol solution

- Error on pipette: $\% \text{ error} = \frac{0.04}{10} \times 100 = 0.004\%$
- Error on volumetric flask: $\% \text{ error} = \frac{0.40}{1000} \times 100 = 0.04\%$
- Total error: **0.04%**

Making up solution C

- Error on 20cm^3 pipette: $\% \text{ error} = \frac{0.06}{20} \times 100 = 0.30\%$
- Error on 100cm^3 pipette (x4, since was used 4 times to obtain 400cm^3 of H_2SO_4): $\% \text{ error} = 4 \times \frac{0.15}{100} \times 100 = 0.60\%$
- Error on volumetric flask: $\% \text{ error} = \frac{0.40}{1000} \times 100 = 0.04\%$
- Total error: **0.94%**

Making up solution D

- Error on 20cm^3 pipette: $\% \text{ error} = \frac{0.06}{20} \times 100 = 0.30\%$
- Error on balance: $\% \text{ error} = \frac{0.01}{48} \times 100 = 0.02\%$
- Error on volumetric flask: $\% \text{ error} = \frac{0.40}{1000} \times 100 = 0.04\%$
- Total error: **0.36%**

Making up copper (II) sulphate solution

- Error on balance: $\% \text{ error} = \frac{0.01}{4.99} \times 100 = 0.20\%$
- Error on volumetric flask: $\% \text{ error} = \frac{0.10}{100} \times 100 = 0.10\%$
- Total error: **0.30%**

Making up cobalt (II) nitrate solution

- Error on balance: $\% \text{ error} = \frac{0.01}{5.82} \times 100 = 0.17\%$
- Error on volumetric flask: $\% \text{ error} = \frac{0.10}{100} \times 100 = 0.10\%$
- Total error: **0.27%**

Making up nickel (II) chloride solution

- Error on balance: $\% \text{ error} = \frac{0.01}{4.75} \times 100 = 0.21\%$
- Error on volumetric flask: $\% \text{ error} = \frac{0.10}{100} \times 100 = 0.10\%$
- Total error: **0.31%**

Making up iron (III) sulphate solution

- Error on balance: $\% \text{ error} = \frac{0.01}{8.00} \times 100 = 0.12\%$
- Error on volumetric flask: $\% \text{ error} = \frac{0.10}{100} \times 100 = 0.10\%$
- Total error: **0.22%**

Making up manganese (II) sulphate solution

- Error on balance: $\% \text{ error} = \frac{0.01}{4.46} \times 100 = 0.22\%$
- Error on volumetric flask: $\% \text{ error} = \frac{0.10}{100} \times 100 = 0.10\%$
- Total error: **0.32%**

If I consider any of the runs I did of the bromine clock, the equipment errors directly related to the run are those of measuring out the volume of the solutions required using a burette (errors from the stopwatch and thermometer are small enough to be

negligible). I measured out 5 volumes for each experiment, which had an average titre of 8cm^3. Therefore the error for the measuring out of volumes is $5 \times \frac{0.1}{8} \times 100 = 6.25\%$.

I can now work out the overall error on the value I calculated for the activation enthalpy of the reaction. The solutions I used to work this out were 0.2M potassium bromate solution, 0.0001M phenol solution and solution D. Therefore the total percentage error is equal to the sum of these percentage errors plus the percentage errors on the burettes $= 0.04 + 1.10 + 0.04 + 0.36 + 6.25 = \mathbf{7.79\%}$. Applying this value to my value for the activation enthalpy, I can conclude that:

$$\mathbf{E_A = 53.54\ kJ\ mol^{-1}\ (\pm 4.17\ kJ\ mol^{-1})}$$

I can do the same for the activation enthalpy with a catalyst. This required 0.2M potassium bromate solution, 0.0001M phenol solution, solution D and iron (III) sulphate solution. The total percentage error is equal to $0.04 + 1.10 + 0.04 + 0.36 + 0.22 + 6.25 = \mathbf{8.01\%}$. This gives me, for the activation enthalpy with a catalyst:

$$\mathbf{E_A\ (with\ catalyst) = 45.87\ kJ\ mol^{-1} (\pm 3.67\ kJ\ mol^{-1})}$$

4.5 Overall Reliability of Results

Overall, I believe that, with the exception of the results for finding a catalyst, my results are reliable enough to support the conclusions I have made about the rate equation and the activation enthalpy of the reaction.

Firstly, the rate equation. I calculated values for the Pearson's Product Moment Correlation Coefficient (PMCC) of the rate against concentration for the reactions where I varied the concentration. This gives a value between -1 and 1 to suggest the strength of linear correlation for the results. For varying the concentration of bromide ions and bromate ions, the values for the PMCC were 0.997 and 0.981 respectively, so the results very strongly suggest that the reaction is first order with respect to these reactants. Similarly for varying the acid concentration, the value of the PMCC against the concentration of H^+ ions squared is 0.997, which suggests that there is little doubt that the reaction is second order with respect to the concentration of hydrogen ions.

As was calculated above (4.5, page 52), the percentage errors on my results for the activation enthalpy of the reaction with and without a catalyst are 7.79% and 8.01% respectively. This suggests that my method was sufficient to calculate the value of the activation enthalpy to at least the nearest 10 kJ mol^{-1}. I would also expect the activation enthalpy to be around 50 kJ mol^{-1}, since the majority of reactions that take place at room temperature do.

The only part of my investigation that I do not believe produced sufficiently good results was the testing for catalysts, as has been explained above. Whilst I can conclude that iron (III) acts as a catalyst for the reaction, I cannot conclude anything about the

affect of the other transition metal ion solutions that I tested, since they did not affect the reaction, whereas I expected more than one of them to have a catalytic effect.

4.6 – Suggestions for Improvements to the Method

Whilst my method produced reliable results, there are still ways in which it could be improved to reduce the possibility of error in the investigation. As has been discussed above, the greatest source of error in my investigation was probably the determination of the point at which the colour of the solution changed. To improve this I could have taken a high resolution photograph of my solution at the point of colour change during a preliminary experiment, and used this to determine the end point in all subsequent experiments, ensuring that the end point was exactly the same in all experiments.

If I had more resources available to me, there are many ways in which I could have reduced the errors. To reduce the problems of temperature fluctuation, I could have carried out all experiments in a laboratory with a controlled temperature. This would also have allowed me to better control the temperature in the experiments in which I varied the temperature. I could also have used pipettes instead of burettes to measure out the solutions required for each experiment. This would have slightly reduced the error, but would have been unfeasible given the extra time it would have taken.

In summary, I believe that my investigation has been a success. I have fulfilled the aims of my investigation and I can be confident that the results are reliable.

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