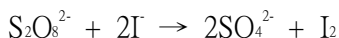# Determining activation energy (Ea) of a reaction

Objective

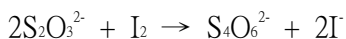To determine the activation energy for the reduction of peroxodisulphate(VI) ions. $S_2O_8^{2-}$, by iodide ions I^-, using a 'clock' reaction.

Principle

The equation for reduction of $S_2O_8^{2-}$ by I^- is:

$$S_2O_8^{2-} + 2I^- \rightarrow 2SO_4^{2-} + I_2$$

The formation of iodine is 'monitored' by small & known amount of thiosulphate ions, $S_2O_3^{2-}$:

$$2S_2O_3^{2-} + I_2 \rightarrow S_4O_6^{2-} + 2I^-$$

Once the reactants are mixed, the stop-watch is started. At the time when all of the thiosulphate is reacted, any free iodine produced will turn starch solution (added before) into dark-blue, the time is then recorded. The amount of thiosulphate added monitors the time in which starch turns blue and the reaction rate is directly proportional to $1 \div$ time taken for starch changes to dark blue.

By plotting a graph of $\log_{10}(1/t)$ against $1/T$ (T=absolute temperature), activation energy (E_a) can be found.

Chemicals

0.020M $K_2S_2O_8$, 0.50M KI, 0.010M $Na_2S_2O_3$, 0.2% starch solution

Apparatus

400 cm^3 beaker, boiling tubes x2, pipettes (10ml), thermometer x2, water bath, stop-watch

Procedure

1.> Half-fill the beaker with hot water at temperature between 49 - 51$°C$ (as water bath).

2.> Pipette 10 cm^3 of 0.020M $K_2S_2O_8$ solution into the first boiling tube, place a thermometer in this solution and keep this in the water bath.

3.> Pipette 5 cm^3 of both 0.50M KI and 0.010M $Na_2S_2O_3$ and 2.5 cm^3 of starch solution into the second boiling tube. Place another thermometer in this solution and stand it in the water bath.

4.> When the temperatures of the two solutions are equal and constant (to within $\pm 1°C$), pour the contents of the second boiling tube into the first, shake to mix, and start the stop-watch.

5.>When the blue colour of the starch-iodine complex appears, stop the stop-watch and record the time.

6.>Repeat the experiment at temperatures at $50℃$, $45℃$, $40℃$, $35℃$, $30℃$.

7.>Plot a graph of $\log_{10}(1/t)$ against $1/T$ to calculate the E_a.

Data Analysis

Temperature / ℃	50	45	40	35	30
Temperature (T) /K	323	318	313	308	303
Time (t) /sec	52	62	95	135	182
$\log_{10}(1/t)$	- 1.72	- 1.79	- 1.98	- 2.13	- 2.26
$1/T$ /K^{-1}	3.10×10^{-3}	3.14×10^{-3}	3.19×10^{-3}	3.25×10^{-3}	3.30×10^{-3}

● Plot $\log_{10}(1/t)$ against $1/T$:

Let the rate equation be: Rate = $k[S_2O_8^{2-}]^a[I^-]^b$

From Arrhenius equation, we have $k = Ae^{-E_a/RT}$, where A is Arrhenius constant.

By taking logarithm of above equation, we have $\log_{10}k = \log_{10}A - E_a \div (2.303RT)$ [1]

∵ All concentration terms have been kept constant

∴ Rate only varies as k (rate constant)

∵ Rate is directly proportional to $1/t$ & varies as k in the rate equation

∴ We can substitute k by $1/t$ in **[1]**:

$\log_{10}(1/t) = \log_{10}A - E_a \div (2.303RT)$, which is the equation of the previous graph

From the graph, the slope is,

$-E_a \div (2.303R) = [-1.75 - (-1.98)] \div [(3.12 - 3.20) \times 10^{-3}] = -2875$

∴ E_a (activation energy of reduction of $S_2O_8^{2-}$ by I^-)

$= (-2875)(-2.303)(R)$

$= (2875)(2.303)(8.314)$ $Jmol^{-1}$

$= 55.05$ $kJmol^{-1}$

Precaution

1.> The amount of $S_2O_8^{2-}$, I^- and $S_2O_3^{2-}$ must keep constant at the start of each experiment, so it's better to use a pipette to transfer these chemicals instead of measuring cylinder.

2.> The temperature measured should be the temperature of the mixtures inside two

boiling tubes, not the water-bath. It's because boiling tubes have
their own heat capacities, they will absorb part of heat from water-bath. Hence, the temperature inside boiling tubes are slightly lower than that of
water-bath.

3.> It is necessary to cover the reagent bottle containing $Na_2S_2O_3$ immediately after use because it can be easily oxidized by oxygen in air.

Discussion

In this experiment, known amount of thiosulphate is added. Some thiosulphate can reduce I_2 produced. When all thiosulphate is used up, any excess I_2 produced will turn starch to dark blue. Hence, the reaction is monitored by thiosulphate ion. Without adding thiosulphate, the starch will turn dark blue immediately.

Reaction rate is directly proportional to temperature and inversely proportional to activation energy. Higher the temperature, higher the rate of reaction whereas higher the activation energy, lower the reaction rate. However, a rise in temperature has a more significant effect on the reactions with high activation energy.

For peroxodisulphate(VI) ion, $S_2O_8^{2-}$, we may expect the oxidation number of S should be +7. However, oxidation number of S only exists from -2 to +6. This interesting phenomenon can be explained by its structure:
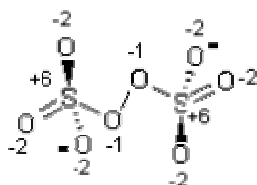
There are actually two oxidation numbers of oxygen, one with oxidation number -1 and another one -2. Oxygen has oxidation number -2 if attached only to less electronegative than itself (e.g. sulphur) whereas when attached to itself, is -1. Hence, oxidation number of S must be +6, not +7.

Conclusion

By using a 'clock' reaction, the experimental value of activation energy of reduction of $S_2O_8^{2-}$ by I^- can be easily obtained by measuring the slope of Arrhenius plot of $\log_0(1/t)$ against $1/T$.