

The following experiment highlights a method of determining the rate constant and the order of a reaction. It uses the reaction between household bleach and blue food colouring.

We came across the article [1] recently when seeking materials to address the lack of suggested activities in some parts of the Advanced Higher Chemistry syllabus [2] on Pages 33-34.

In these experiments the household bleach decolourises the solution of blue food dye within about ten minutes.

The overall rate equation is:

$$\text{Rate} = k [\text{blue dye}]^a [\text{bleach}]^b$$

The rate of dye decolouration can be followed using a colorimeter, and by applying the Beer-Lambert Law the concentrations of dye can be calculated.

From these results, the rate constant for the reaction (k), and the orders of reaction (a and b) can be determined with respect to dye and bleach concentration.

Exemplar Results		
Time / min	Absorbance at wavelength 590 nm	
	0.50 cm ³ bleach	0.25 cm ³ bleach
0	0.84	0.84
1	0.68	0.75
2	0.58	0.67
3	0.46	0.62
4	0.37	0.56
5	0.30	0.50
6	0.25	0.45
7	0.20	0.41
8	0.16	0.36
9	0.13	0.33
10	0.10	0.30

These absorbance values are used to calculate the concentrations of the dye. The calculation uses the molar absorptivity value of the blue dye which is quoted as being $1.38 \times 10^5 \text{ cm}^{-1} \text{ mol}^{-1} \text{ litre}$ at 630 nm.



Figure 1: Most blue food colourants used in cookery contain the dye E133 (brilliant blue) which is oxidised to a colourless form by NaOCl.



Figure 2: Household bleach is an aqueous solution of sodium chlorate(I) (sodium hypochlorite - NaOCl).

We used a WPA CO 7500 and the closest wavelength to 630 nm which could be selected was 590 nm. These results were obtained using this. If you happen to have 630 nm filter, then it should be used.

Firstly, calculate the dye concentrations using the Beer-Lambert Law:

$$\text{Absorbance (A)} = l \times c \times \epsilon$$

where:

l is the distance that the light passes through the solution – path length (1 cm)

c is the concentration of dye

ϵ is the molar absorption for the blue dye ($1.38 \times 10^5 \text{ cm}^{-1} \text{ mol}^{-1} \text{ litre}$ at 630 nm)

Time / min	Concentration of dye ($\times 10^{-7}$ moles l^{-1})	
	0.50 cm^3 bleach	0.25 cm^3 bleach
0	61	61
1	49	54
2	42	49
3	33	45
4	27	41
5	22	36
6	18	33
7	14	30
8	12	26
9	9.4	24
10	7.2	22

Secondly, calculate the values of $\ln[\text{blue dye}]$ and $1/[\text{blue dye}]$ for both bleach concentrations.

Time / min	0.50 cm^3 bleach		0.25 cm^3 bleach	
	$\ln[\text{dye}]$	$1/[\text{dye}] \times 10^5$	$\ln[\text{dye}]$	$1/[\text{dye}] \times 10^5$
0	-12.01	1.6	-12.01	1.6
1	-12.22	2.0	-12.12	1.8
2	-12.38	2.4	-12.24	2.1
3	-12.61	3.0	-12.31	2.2
4	-12.83	3.7	-12.41	2.5
5	-13.04	4.6	-12.53	2.8
6	-13.22	5.5	-12.63	3.1
7	-13.44	6.9	-12.73	3.4
8	-13.67	8.6	-12.86	3.8
9	-13.88	11	-12.94	4.2
10	-14.14	14	-13.04	4.6

Finally, plot $\ln[\text{blue dye}]$ versus time, and $1/[\text{blue dye}]$ versus time for both bleach concentrations to find the order of reaction with respect to the blue dye.

If the reaction is **first order** with respect to the blue dye, then

$$\text{Rate} = k_{obs} [\text{blue dye}]^1$$

where k_{obs} is the observed rate constant.

The integrated form of this equation is

$$\ln[\text{blue dye}] = -k_{obs}t + \ln[\text{blue dye}]_0$$

where t = time, and $[\text{blue dye}]_0$ is the initial concentration of blue dye.

The integrated form of the equation can be compared to the equation of a straight line ($y = mx + c$)

So plotting $\ln[\text{blue dye}]$ versus time will give a straight line with a gradient of $-k_{obs}$ if it is a first order reaction with respect to the blue dye.

If the reaction is **second order** with respect to the blue dye, then

$$\text{Rate} = k_{obs} [\text{blue dye}]^2$$

where k_{obs} is the observed rate constant.

The integrated form of this equation is

$$1/[\text{blue dye}] = k_{obs}t + 1/[\text{blue dye}]_0$$

where t = time, and $[\text{blue dye}]_0$ is the initial concentration of blue dye.

This integrated form of the equation can once again be compared to the equation of a straight line ($y = mx + c$)

So plotting $1/[\text{blue dye}]$ versus time will give a straight line with a gradient of $+k_{obs}$ if it is a second order reaction with respect to the blue dye.

Calculation of Values

From your graphs you now know if the reaction is first order or second order with respect to the blue dye. You can also calculate k_{obs} for each linear graph.

The overall rate equation for the reaction between bleach and the blue dye is:

$$\text{Rate} = k [\text{dye}]^a [\text{bleach}]^b$$

In the two experiments the initial (or starting) concentration of dye was kept constant, but the concentration of bleach was changed.

Here we have used household bleach with a stated value of 5.25% (m/v) sodium hypochlorite, giving a concentration of 0.705 mol l^{-1} . So 0.5 ml of bleach in 10 ml blue dye solution gives a concentration of 0.035(3) mol l^{-1} . Its exact concentration can, of course, be obtained by iodometric titration.

The order of the reaction with respect to the bleach can be determined by observation of the experimental data obtained.

The value of k can now be calculated for each experiment and averaged to provide a final value. With the necessity of using the 590 nm filter instead of the 630 nm one, the value of k will obviously be slightly inaccurate. However, the process of its calculation holds true.

The complete experimental procedure, treatment of results, and how the reaction can be used to calculate Activation Energies by using the Arrhenius Equation, will be posted on the SSERC Website in the near future.

References

- [1] Department of Chemistry,
University of Waterloo, Ontario, Canada
Published in Chem 13 News/October 2007
- [2] <http://www.sqa.org.uk/files/nq/ChemistryAH.pdf>