Treat ‘em to

Background

Clock reactions are amongst the most dramatic and visually pleasing chemical demonstrations [1]. Typically after a clock reaction has been started there is a period during which no noticeable change takes place and then a change (often in colour) occurs. This sudden and unexpected nature of the change gives clock reactions their charm and visual appeal.

The activity described here is based on the so-called iodine clock reaction. When a solution of hydrogensulfite (or bisulfite) ions (HSO_3^-) is mixed with a solution of iodate (IO_3^-) ions and a starch solution, the mixture remains colourless for a time and then suddenly turns blue. The clock period (the time from mixing to colour change) can be changed by varying the concentrations of the reactants. Whilst the chemistry of the iodine clock reaction is quite complex the effect of concentration on the rate can be readily shown and appreciated.

It might at first glance seem strange to have a chemistry article in the SSERC Bulletin with a title such as the one used here and so some explanation is in order. The activities which follow are based on an article of the same name by Mark Whitman which was published in the Journal of Chemical Education [2].

Figure 1 *- Mark Whitman. (Image: http://www.k12tlc.net/mark/mark.htm).*

In his article Whitman [2] states:

‘The beauty of the activity is that it has yet to work as predicted. Always, one or two flasks turn out of sequence, or a student spills the contents of their test tube on the floor and often the last flask doesn’t turn until two minutes or so after the demonstration has been completed. It is my belief that the mistakes are the heart of the activity’s success. Class discussion of what might have gone wrong reinforces students’ understanding. The whole procedure requires 40 minutes, but on the next quarterly exam no area receives as many correct student responses...’

It is possible to use this activity at a number of points across the chemistry curriculum (see Appendix 1). At its heart lies the premise that changing the concentration of one or more reactants can lead to a change in the rate of a chemical reaction.

The reactions - oxidation of hydrogensulfite by iodate

The overall process can be represented (detail taken from [1]) by the following sequence of reactions shown in Table 1 below.

In reaction (1) hydrogensulfite ions reduce iodate ions to iodide ions and in reaction (2) these iodide ions are oxidised by iodate ions to triiodide ions. At this point the solution contains, amongst other things, triiodide and starch which are the components of the blue starch-iodine complex whose formation co-occurs in reaction 4. However, reaction 3 is so rapid that the formation of the blue complex is prevented. Once all of the hydrogensulfite has been consumed then reaction 4 is no longer suppressed and the blue complex forms. So, the solution remains colourless whilst there is still hydrogensulfite present. Once the hydrogensulfite is gone the blue colour appears. Under the conditions detailed below the reaction time is reasonably linear with respect to water volume (see Figure 2).

The activity

There are a number of ways in which one might set up the iodine clock reaction but we believe that the method described below offers opportunity for wide-ranging discussion about potential sources of error, opportunities for improvement etc.

Preparation of solutions

In broad terms we adopt the solutions recommended by Whitman [2]. The following stock solutions are prepared:

- Soluble starch solution - approximately 10 g of starch in 250 cm^3 distilled water - warmed to dissolve.
- H_2SO_3 solution prepared by adding 250 cm^3 of 0.2 mol l^{-1} $NaHSO_3$ to 250 cm^3 of H_2SO_4 (0.1 mol l^{-1}).
- Iodic acid solution (0.038 mol l^{-1}).

1	$IO_3^-(aq) + 3\,HSO_3^-(aq)$ →	$I^-(aq) + 3\,SO_4^{2-}(aq) + 3\,H^+(aq)$
2	$IO_3^-(aq) + 8\,I^-(aq) + 6\,H^+(aq)$ →	$3\,I_3^-(aq) + 3\,H_2O(aq)$
3	$I_3^-(aq) + 3\,HSO_3^-(aq) + H_2O(l)$ →	$3\,I^-(aq) + SO_4^{2-}(aq) + 3\,H^+(aq)$
4	$2\,I_3^-(aq)$ + starch ⇄	(blue) starch-I_5^- complex + $I^-(aq)$

Table 1 *- Sequence of reactions.*

Tchaikovsky!

Volume of water in flask, cm^3	Reaction time, s	Volume of water in flask, cm^3	Reaction time, s
125	81	145	120
130	90	150	127
135	98	155	138
140	105		

Table 2 *- Typical reaction times post mixing.*

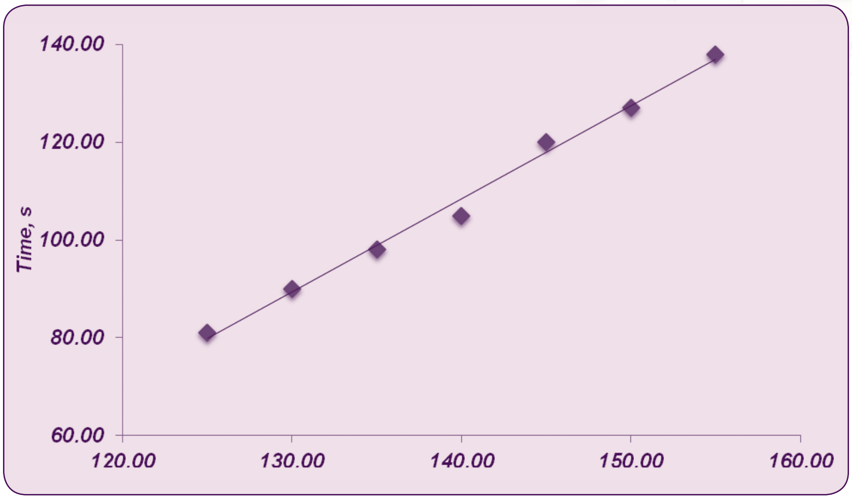

Figure 2 *- Time taken, as a function of volume of water, for the appearance of the characteristic bue colour of iodine-starch complex. Experimental details in the text.*

Whitman [2] acknowledges that the idea of linking the iodine clock to a musical performance was not new having its origins at by an anonymous individual at Virginia Tech.

The music of the 1812 Overture by Tchaikovsky will be familiar to most of us. A key feature of the overture itself is the series of cannons which are fired during the performance. It is possible, with careful solution preparation, and a fair wind, to arrange conditions such that the solutions in the conical flasks change as the cannons are heard in the music. The timings will of course vary with the recording of the 1812 Overture which you use. For reasons of convenience (i.e. it was the one available) we use the version conducted by Antal Doráti featuring the Minneapolis Symphony Orchestra.

'Construction of the clock'

1) Prepare 7 conical flasks (250 cm^3) containing 125, 130, 135, 140, 145, 150 and 155 cm^3 of distilled water. (Measuring the mass of water in the flask and assuming that 1 cm^3 of water has a mass of 1.0 g is probably the most accurate way of approaching this).
2) Prepare 7 test tubes each containing 8 cm^3 of the iodic acid solution.
3) To each conical flask add 1 cm^3 of soluble starch solution.
4) To each conical flask add 3 cm^3 of the H_2SO_3 solution.
5) Add the iodic acid solution to the flask and measure the length of time taken for the appearance of the blue colour.

Table 2 shows typical reaction times post mixing with the data being plotted in Figure 2.

As can be seen (Figure 2), under the conditions used the reaction time is reasonably linear with respect to water volume. Typically at volumes below about 110 cm^3 the reaction time is non-linear. As can be seen from the data, quite modest increases in the volume of water present can have a significant impact on the time taken for the reaction to go to completion.

So what about Tchaikovsky?

We pick a point in the music some 2 minutes before its end. It is at that point that 15 volunteers are invited to mix the contents of a test tube containing iodic acid solution (8.0 cm^3) into a conical flask which contains soluble starch, H_2SO_3 solution (3 cm^3) and the 'correct' volume of water as predicted/ calculated from a plot such as that shown in Figure 2. The timings we 'aim for' are shown in table 3.

In our version there are about 12 cannons in the final 2 minutes of the music and we add an extra couple of flasks in the hope that at least one will 'go off' at the right time. The final solution is set to change colour as the music ends. The overall effect of 15 participants lined up willing their solutions to

Figure 3 *- 'The music'!*

Flask Nº	Time, s	Flask Nº	Time, s	Flask Nº	Time, s
1	75	6	84	11	90
2	77	7	85	12	92
3	79	8	86	13	93
4	81	9	87	14	95
5	82	10	88	15	120

Table 3 *- Timings.*

change in time with the cannons can be exciting and memorable. One teacher several years ago said to us '*I shall never listen to that music again without that image coming into my mind!*'

We agree with Whitman [2] that '*....it has yet to work as predicted.*' We have on one occasion had as many as 11 solutions change at exactly the correct moment in time but a full set is yet to be accomplished (now there's a challenge...). Discussion as to why not all solutions 'behave' can lead to the identification of a number of possible reasons including (but not limited to):

- Incorrect mixing technique.
- Temperature effects – participants should be encouraged to hold their flasks at the top to avoid warming the solution.
- Incorrect measurement of solutions – have all volumes of water been measured using the same glassware/balance etc?
- Is all the iodic acid transferred from the test tube?
- Are the iodic acid and H_2SO_3 stock solutions stable?

In our experience the first 2 items on the above list are the ones most likely to cause problems.

References

[1] Shakhashiri, B.Z. (1992), Clock Reactions in Chemical Demonstrations: A Handbook for Teachers of Chemistry Volume 4, pp 3-89, University of Wisconsin Press, Madison.

[2] Whitman, M. (1983), Treat 'Em to Tchaikovsky. J. Chem. Educ., 60, 229.

Suppliers of materials

We have used the following sources for our reagents but others could be used:

- Soluble starch from Scientific and Chemical (product code ST015).
- Sodium bisulfite ($NaHSO_3$) from Sigma-Aldrich (marketed as an ACS reagent mixture of $NaHSO_3$ and $Na_2S_2O_5$; product code 243973).
- Iodic acid (HIO_3) from Sigma-Aldrich (product code 58060).
- Sulfuric acid from Scientific and Chemical (product code SU045/1).

Health and safety considerations

1) A risk assessment should be carried out particularly in respect of stock solution preparation.
2) The H_2SO_3 solution is sufficiently dilute so as to not merit any warning labels; however, those suffering from asthma should avoid breathing in the vapour.

APPENDIX 1
Additional information

Curriculum links

1) CfE

Chemical change

Through experimentation, I can identify indicators of chemical reactions having occurred. I can describe ways of controlling the rate of reactions and can relate my findings to the world around me - *SCN 3-19a.*

I can collect and analyse experimental data on chemical reactions that result in an obvious change in energy. I can apply my findings to explain the significance of the energy changes associated with chemical reactions - *SCN 4-19a.*

2) NATIONAL 3

Key Area – Rates of reaction

There are 4 factors that affect the rate of reaction: temperature, concentration, catalyst and surface area. Increasing the temperature, concentration and surface area will speed up a reaction, decreasing them slows reactions down.

3) NATIONAL 4

Key Area – Rates of reaction

Reactions monitored and graphs interpreted.

A working knowledge of the factors affecting rates of reaction is required for this Course. To compare rates of chemical reactions, changes in mass, volume and other quantities can be measured. Graphs can then be drawn to help this comparison.

4) HIGHER

Key Area – Controlling the rate

Learners can investigate the effect of temperature by using the reaction between sodium thiosulfate and acid in which a sulfur precipitate forms, or the reaction of potassium iodate and bisulfite/starch solution.

Key Area – Getting the most from reactants

Chemical 'egg race' activities can be used to provide opportunities to practise or consolidate the mathematical skills being developed. In the Chemical Egg Timer, teams are given a graph showing how the concentration of potassium iodide affects the time taken for the blue-black colour to appear in a hydrogen peroxide/iodide clock reaction.