Iodine clock reaction

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The **iodine clock reaction** is a classical chemical clock demonstration experiment to display chemical kinetics in action; it was discovered by Hans Heinrich Landolt in 1886. [1] The iodine clock reaction exists in several variations, which each involve iodine species (iodide ion, free iodine, or iodate ion) and redox reagents in the presence of starch. Two colourless solutions are mixed and at first there is no visible reaction. After a short time delay, the liquid suddenly turns to a shade of dark blue due to the formation of a triiodide-starch complex. In some variations, the solution will repeatedly cycle from colorless to blue and back to colorless, until the reagents are depleted.



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Hydrogen peroxide variation [edit]

This reaction starts from a solution of hydrogen peroxide with sulfuric acid. To this is added a solution containing potassium iodide, sodium thiosulfate, and starch. There are two reactions occurring in the solution.

In the first, slow reaction, iodine is produced:

$${\rm H_2O_2} \, + \, 2{\rm I}^- \, + \, 2{\rm H}^+ \, {\rightarrow} \, {\rm I_2} \, + \, 2{\rm H_2O}$$

In the second, fast reaction, iodine is reconverted to 2 iodide ions by the thiosulfate:

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

After some time the solution always changes color to a very dark blue, almost black.

When the solutions are mixed, the second reaction causes the triiodide ion to be consumed much faster than it is generated, and only a small amount of triiodide is present in the dynamic equilibrium. Once the thiosulfate ion has been exhausted, this reaction stops and the blue colour caused by the triiodide – starch complex appears.

Anything that accelerates the first reaction will shorten the time until the solution changes color. Decreasing the pH (increasing H⁺ concentration), or increasing the concentration of iodide or hydrogen peroxide will shorten the time. Adding more thiosulfate will have the opposite effect; it will take longer for the blue colour to appear.

Iodate variation [edit]

An alternative protocol uses a solution of iodate ion (for instance potassium iodate) to which an acidified solution (again with sulfuric acid) of sodium bisulfite is added.

In this protocol, iodide ion is generated by the following slow reaction between the iodate and bisulfite:

$$IO_3^- + 3 HSO_3^- \rightarrow I^- + 3 HSO_4^-$$

This is the rate determining step. The iodate in excess will oxidize the iodide generated above to form iodine:

$${\rm IO_3}^-$$
 + 5 ${\rm I}^-$ + 6 ${\rm H}^+$ \rightarrow 3 ${\rm I_2}$ + 3 ${\rm H_2O}$

However, the iodine is reduced immediately back to iodide by the bisulfite:

$$I_2 + HSO_3^- + H_2O \rightarrow 2 I^- + HSO_4^- + 2 H^+$$

When the bisulfite is fully consumed, the iodine will survive (i.e., no reduction by the bisulfite) to form the dark blue complex with starch.

Persulfate variation [edit]

This clock reaction uses sodium, potassium or ammonium persulfate to oxidize iodide ions to iodine. Sodium thiosulfate is used to reduce iodine back to iodide before the iodine can complex with the starch to form the characteristic blue-black color.

lodine is generated:

$$2 I^{-} + S_{2}O_{8}^{2-} \rightarrow I_{2} + 2 SO_{4}^{2-}$$

And is then removed:

$$I_2 + 2 S_2 O_3^{2-} \rightarrow 2 I^- + S_4 O_6^{2-}$$

Once all the thiosulfate is consumed the iodine may form a complex with the starch. Potassium persulfate is less soluble (cfr. Salters website) while ammonium persulfate has a higher solubility and is used instead in the reaction described in examples from Oxford University. [2]

Chlorate variation [edit]

An experimental iodine clock sequence has also been established for a system consisting of iodine potassium-iodide, sodium chlorate and perchloric acid that takes place through the following reactions. [3]

Triiodide is present in equilibrium with iodide anion and molecular iodine:

$$I_3^- I^- + I_2$$

Chlorate ion oxidizes iodide ion to hypoiodous acid and chlorous acid in the slow and rate-determining step:

$$\text{ClO}_3^- + \text{I}^- + 2 \text{ H}^+ \rightarrow \text{HOI} + \text{HClO}_2$$

Chlorate consumption is accelerated by reaction of hypoiodous acid to iodous acid and more chlorous acid:

$$ClO_3^- + HOI + H^+ \rightarrow HIO_2 + HClO_2$$

More autocatalysis when newly generated iodous acid also converts chlorate in the fastest reaction step:

$$ClO_3^- + HIO_2 \rightarrow IO_3^- + HClO_2$$

In this clock the induction period is the time it takes for autocatalytic process to start after which the concentration of free iodine falls rapidly as observed by UV/VIS spectroscopy.

See also [edit]

- Clock reaction
- Old Nassau reaction

References [edit]

- 1. ^ See:
 - Landolt, H. (1886). "Ueber die Zeitdauer der Reaction zwischen Jodsäure und schwefliger Säure" [On the duration of the reaction between iodic acid and sulfurous acid]. Berichte der Deutschen Chemischen Gesellschaft (in German). 19: 1317–1365.
 - Landolt, H. (1887). "Ueber die Zeitdauer der Reaction zwischen Jodsäure und schwefliger Säure [Part 2] [On the duration of the reaction between iodic acid and sulfurous acid]. Berichte der Deutschen Chemischen Gesellschaft (in German). 20: 745–760. doi:10.1002/cber.188702001173].
- 2. ^ Hugh Cartwright (2006). "Kinetics of the Persulfate-iodide Clock Reaction" (PDF). 2nd/3rd Year Physical Chemistry Practical Course. Oxford University. Retrieved 25 March 2018.
- 3. ^ André P. Oliveira and Roberto B. Faria (2005). "The chlorate-iodine clock reaction". *J. Am. Chem. Soc.* **127** (51): 18022–18023. doi:10.1021/ja0570537 ₽. PMID 16366551 ₽.

External links [edit]

- Hydrogen peroxide variation
- Sodium bisulfite variation with a high-speed camera

Categories: Chemical kinetics | Chemical reactions | Iodine | Thiosulfates