Alternative Rate Calculations

At the end of the "From Pressure to Moles" subsection in Section 5.2, we state that we will use the larger of the two H_2O_2 mole amounts in the paper's remaining calculations. This supplementary document runs the same calculations as those run in the "From Moles to Rates" subsection in Section 5.2, except they are run using the smaller value.

As calculated in Section 5.2, this smaller value is 1.45 x 10^{-4} mol, the amount of H_2O_2 which had reacted after 400 seconds in the "internal volume only" model. We proceed with the same calculation route, beginning with finding the difference of initial moles H_2O_2 and the moles reacted after 400 seconds: 0.0264 − 1.45 x 10^{-4} = **0.02626 mol**. (This is a value rounded to four significant figures – the raw number is 0.026255 mol.)

Continuing on, we again treat the volume of the solution as a constant, which remains at 60 mL (**0.06 L**) over the course of the reaction. Thus, we calculate the concentration of H_2O_2 at t = 400 as follows (once again using the formula $C = n/V$):

$$\frac{0.02626 \; mol}{0.06 \; L} = \mathbf{0.438 \; M}$$

As before, we use the first order integrated rate law equation to solve for k as follows:

$$k = -\left(\frac{\ln(0.438) - \ln(0.44)}{400 \; s}\right) = \frac{\mathbf{1.14 \times 10^{-5}}}{\mathbf{s}}$$

Therefore, the integrated rate law equation (using the internal volume only model) for iodide-catalyzed H_2O_2 breakdown at an ambient laboratory temperature of ~296 K is

$$\ln[\boldsymbol{H_2O_2}]_t - \ln[\boldsymbol{H_2O_2}]_0 = -\frac{\mathbf{1.14 \times 10^{-5}}}{\boldsymbol{s}} \times \boldsymbol{t}$$

Finally, this smaller *k* value can also be used to calculate half-life in an identical way:

$$t_{\frac{1}{2}} = \frac{0.693}{\dfrac{1.14 \times 10^{-5}}{s}} = 60789\ s = 1013\ min = \mathbf{16.9\ hr}$$

The internal volume only model gives a massively different result for the reaction half-life than the more inclusive approach detailed in Section 5.2, which results in a half-life of less than 20 minutes. By comparison, the half-life obtained here is above half a day!