Chemical Kinetics: The Iodine-Clock Reaction:

\[
S_{2}O_{8}^{2-} (aq) + 2 I^{-} (aq) \rightarrow I_{2}(aq) + 2 SO_{4}^{2-} (aq)
\]

To measure the rate of this reaction we must measure the rate of concentration change of one of the reactants or products. Here, it is convenient to carry out a clock reaction involving the product I\(_{2}\). To do this, you will include (to the reacting \(S_{2}O_{8}^{2-}\) and \(I^{-}\))

\(i)\) a small (but accurately known) amount of sodium thiosulfate, \(Na_{2}S_{2}O_{3}\), and

\(ii)\) some starch indicator.

The added \(Na_{2}S_{2}O_{3}\) does not interfere with the rate of above reaction, but it does consume the \(I_{2}\) as soon as it is formed (see below):

\[
2 S_{2}O_{3}^{2-} (aq) + I_{2}(aq) \rightarrow S_{4}O_{6}^{2-} (aq) + 2 I^{-} (aq)
\]

This reaction is much faster than the previous, so the conversion of \(I_{2}\) back to \(I^{-}\) is essentially instantaneous.

In a typical experiment, known concentrations of \(S_{2}O_{8}^{2-}\) and \(I^{-}\) are mixed with a small amount of \(S_{2}O_{3}^{2-}\) and starch. As reaction the first proceeds, \(S_{2}O_{8}^{2-}\) and \(I^{-}\) react to produce \(I_{2}\), but nothing appears to be happening because the second reaction is consuming the \(I_{2}\) as quickly as it is formed.

The important moment is when the \(S_{2}O_{3}^{2-}\) runs out, for then the \(I_{2}\) is no longer consumed (see the second reaction), and the dark blue starch–\(I_{2}\) complex forms. The stoichiometry of the second reaction indicates that one \(I_{2}\) molecule must have been generated for every 2 ions of \(S_{2}O_{3}^{2-}\) initially present in the solution.

\[\text{[I}_2\text{]} \text{ generated(from first reaction)} = \text{[I}_2\text{]} \text{ consumed(in second reaction)} = \{1/2[S_2O_3^{2-}] \text{ initially present}\}\]

Note that the change in concentration of \(I_{2}\) (before the blue complex forms) is fixed by amount of \(S_{2}O_{3}^{2-}\) included in the initial reaction mixture.

\[rate = \frac{d[I_{2}]}{dt} = \frac{1}{2} \frac{[S_{2}O_{3}^{2-}]}{t}\]

Where \(t\) = time for blue color to appear.

In this experiment you will:

A. Determine Rate Law and Rate Constant
   \(\{k\text{ is constant at constant temperature}\}\)

B. Vary temperature and estimate \(E_A\)
   \(\{\text{Using the Arrhenius Equation}\}\)

A. Determining the rate constant (\(k\)) and the rate law for the iodine-clock reaction:
We know \([S_2O_8^{2-}]\) and [I], because we know initial volume and concentration of each solution and the final volume for each solution, (Remember \(M_1V_1 = M_2V_2\))

e.g for \([S_2O_8^{2-}]\) in trial 1: \([S_2O_8^{2-}] = (0.100 \text{ M})(0.00100 \text{L})/(0.0100 \text{L}) = 0.0100 \text{ M}\)

and we know the general rate law for the iodine-clock reaction:

\[
\text{rate} = k[S_2O_8^{2-}]^\alpha [I]^\beta
\]

So we will:

1. Experimentally determine rate of the reaction (stopwatch, color change, \([S_2O_3^{2-}]\)).

\[
\text{rate} = \frac{d[I_2]}{dt} = \frac{1}{2}\frac{[S_2O_3^{2-}]}{t}
\]

2. Empirically determine \(\alpha\) and \(\beta\).

\[
\log(\text{rate}) = \log(k) + \alpha\log[S_2O_8^{2-}] + \beta\log[I]
\]

a. If temperature is constant, \(k\) is constant.

If [I] is constant, log[I] is constant

\[
\log(\text{rate}) = \alpha\log[S_2O_8^{2-}] + C \quad \text{(Where } C = \log(k) + \beta\log[I]\text{)}
\]

\[
y = mx + b
\]

For trials 1 -5, you should plot log(rate) vs \(\alpha\log[S_2O_8^{2-}]\)
slope (rounded to the nearest integer) = \(\alpha\)
b. If temperature is constant, k is constant.
   If \([S_2O_8^{2-}]\) is constant, \(\log[S_2O_8^{2-}]\)
   \[
   \log(\text{rate}) = \beta \log[I^-] + C \quad \text{(Where } C = \log(k) + \alpha \log[S_2O_8^{2-}])
   \]
   \[\text{y} = \text{m x} + b\]

For trials 6 - 10, you should plot \(\log(\text{rate})\) vs \(\beta \log[I^-]\):

![Log-rate vs log(I^-) graph](image)

slope (rounded to the nearest integer) = \(\beta\)

After \(\alpha\) and \(\beta\) have been determined:

3. Solve for \(k\) @ constant temperature (°K) for trials 1 - 10 using the rates and \(\alpha\) and \(\beta\) that you have determined from trials 1 - 10. (Find mean \(k\), don't forget units units for \(k\): M\(^{-1}\)s\(^{-1}\))

4. Determine the rate law for the iodine-clock reaction (use mean \(k\) from #3: \(k\))
   \[
   \text{rate} = k[S_2O_8^{2-}]^\alpha [I^-]^\beta
   \]
B. Varying the temperature, measure rate of reaction, calculate k and estimate $E_A$

5. Vary the temperature and solve for k (@ each temp).

6. Using k and T, construct an Arrhenius plot and solve for $E_A$.

Arrhenius Equation: $\ln k = \frac{-E_A}{R} \left( \frac{1}{T} \right) + A$

- $k$ = rate constant
- $E_A$ = activation energy
- $T$ = temperature (°K)
- $R$ = Ideal Gas Constant (8.314 J•mol$^{-1}$•°K$^{-1}$)
- $A$ = reaction specific constant

For trials 8, 11 - 14 you should plot ln(k) vs 1/T

In this example: $-E_A = (R)(-6227.7$ °K)

$E_A = (8.314$ J•mol$^{-1}$•°K$^{-1}$)( 6227.7 °K)

$E_A = 51777$ J/mol or 51.777 kJ/mol