Lecture Demonstration #2:  
Dependence of Reaction Rate on Temperature

We consider the same reaction as in the first (Clock Reaction) demonstration:

\[
I^- + S_2O_8^{2-} + 2 S_2O_3^{2-} \rightarrow 2 SO_4^{2-} + S_4O_6^{2-}
\]

We have shown that this reaction has the following DRL:

\[
\text{Rate} = k [S_2O_8^{2-}] [I^-] \approx k [S_2O_8^{2-}]_0 [I^-]_0
\]

Solving for \(k\) gives:

\[
k \approx \frac{\text{Rate}}{[S_2O_8^{2-}]_0 [I^-]_0}
\]

We showed in the first demo that the rate can be obtained experimentally as:

\[
\text{Rate} = \frac{[S_2O_3^{2-}]_0}{2t_{\text{blue}}}
\]

where \(t_{\text{blue}}\) is the time to the color change. Therefore:

\[
k \approx \frac{1}{2t_{\text{blue}}} \frac{[S_2O_3^{2-}]_0}{[S_2O_8^{2-}]_0 [I^-]_0}
\]

In Experiment "B" (see the first demo handout) the values of the concentrations were

\[
[S_2O_3^{2-}]_0 = 0.0016M \\
[S_2O_8^{2-}]_0 = 0.040M \\
[I^-]_0 = 0.080M
\]

Thus, \(k \approx [0.25 \text{ M}^{-1}] t_{\text{blue}}^{-1}\).

Arrhenius theory predicts \(k = A \exp\{-E_a/RT\}\), or equivalently,

\[
\ln k = \ln A + \{-E_a/R\} (1/T)
\]

If the Arrhenius law is valid for this reaction, we expect a plot of \(\ln k\) against \(1/T\) to give a straight line. At the y-intercept \((1/T = 0)\) \(\ln k = \ln A\), and since the slope is \(-E_a/R\), we can solve for \(A\) and for \(E_a\). The data obtained in class are analyzed on the back of this sheet.
Data obtained in class:

<table>
<thead>
<tr>
<th>$T$ (°C)</th>
<th>$1/T$ (K)</th>
<th>$t_{\text{blue}}$ (sec)</th>
<th>$\ln(k)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>0.003624</td>
<td>313±1</td>
<td>-7.115</td>
</tr>
<tr>
<td>20</td>
<td>0.003411</td>
<td>81±1</td>
<td>-5.787</td>
</tr>
<tr>
<td>22</td>
<td>0.003388</td>
<td>68±1</td>
<td>-5.643</td>
</tr>
<tr>
<td>37</td>
<td>0.003224</td>
<td>26±1</td>
<td>-4.619</td>
</tr>
</tbody>
</table>

Results:

Best fit: slope = -6244 K \ y-intercept = 15.51

Activation energy $E_a = R \times 6244$ K = 8.314 J K$^{-1}$ mol$^{-1}$ (6244 K) = 51.9 kJ mol$^{-1}$

$A = e^{15.51} = 5.4 \times 10^6$ M$^{-1}$s$^{-1}$ (note: same units as k)