

The iodine clock reaction

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Chemical Kinetics: The Iodine-Clock Reaction: $\text{S}_2\text{O}_8^{2-}(\text{aq}) + 2 \text{I}^{-}(\text{aq}) \rightarrow \text{I}_2(\text{aq}) + 2 \text{SO}_4^{2-}(\text{aq})$ 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 $\text{S}_2\text{O}_8^{2-}$ and I^{-}) i) a small (but accurately known) amount of sodium thiosulfate, $\text{Na}_2\text{S}_2\text{O}_3$, and ii) some starch indicator. The added $\text{Na}_2\text{S}_2\text{O}_3$ does not interfere with the rate of above reaction, but it does consume the I_2 as soon as it is formed (see below): $2 \text{S}_2\text{O}_3^{2-}(\text{aq}) + \text{I}_2(\text{aq}) \rightarrow \text{S}_4\text{O}_6^{2-}(\text{aq}) + 2 \text{I}^{-}(\text{aq})$ 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 $\text{S}_2\text{O}_8^{2-}$ and I^{-} are mixed with a small amount of $\text{S}_2\text{O}_3^{2-}$ and starch. As reaction the first proceeds, $\text{S}_2\text{O}_8^{2-}$ 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 $\text{S}_2\text{O}_3^{2-}$ 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 $\text{S}_2\text{O}_3^{2-}$ initially present in the solution. $[\text{I}_2]_{\text{generated}}(\text{from first reaction}) = [\text{I}_2]_{\text{consumed}}(\text{in second reaction}) = \{1/2[\text{S}_2\text{O}_3^{2-}]_{\text{initially present}}\}$ Note that the change in concentration of I_2 (before the blue complex forms) is fixed by amount of $\text{S}_2\text{O}_3^{2-}$ included in the initial reaction mixture. $-\frac{1}{2} \frac{d[\text{S}_2\text{O}_3^{2-}]}{dt} = \frac{d[\text{I}_2]}{dt}$ Where t = time for blue color to appear. In this experiment you will: A. Determine Rate Law and Rate Constant { k is constant at constant temperature} B. Vary temperature and

estimate EA {Using the Arrhenius Equation} A. Determining the rate constant (k) and the rate law for the iodine-clock reaction: We know [S₂O₈²⁻] and [I⁻], because we know initial volume and concentration of each solution and the final volume for each solution, (Remember M₁V₁ = M₂V₂) e. g for [S₂O₈²⁻] in trial 1: [S₂O₈²⁻] = (0.100 M)(0.00100L)/(0.0100L) = 0.0100 M and we know the general rate law for the iodine-clock reaction: rate = k[S₂O₈²⁻]^m [I⁻]ⁿ So we will:

- Experimentally determine rate of the reaction (stopwatch, color change, [S₂O₃²⁻]). $\frac{1}{t} \left[\frac{S_2O_8^{2-}}{I_2} \right] \frac{d[I_2]}{dt}$ rate = = dt t
- Empirically determine ^m and ⁿ. $\log(\text{rate}) = \log(k) + m \log[S_2O_8^{2-}] + n \log[I^-]$
 - If temperature is constant, k is constant. If [I⁻] is constant, log[I⁻] is constant $\log(\text{rate}) = m \log[S_2O_8^{2-}] + C$ $y = m x + b$ -4.50 -5.00 -5.50 -6.00 -2.20 (Where C = log(k) + ⁿlog[I⁻]) $y = 1.1704x - 3.3137$ R² = 0.995 -2.00 -1.80 -1.60 log[S₂O₈²⁻] -1.40 For trials 1 -5, you should plot log(rate) vs ^mlog[S₂O₈²⁻] slope (rounded to the nearest integer) = ^m b. If temperature is constant, k is constant. If [S₂O₈²⁻] is constant, log[S₂O₈²⁻] log(rate) = ⁿlog[I⁻] + C $y = m x + b$ (Where C = log(k) + ^mlog[S₂O₈²⁻]) For trials 6 - 10, you should plot log(rate) vs ⁿlog[I⁻]: -4.50 -5.00 -5.50 -6.00 -1.80 $y = 0.9707x - 3.9334$ R² = 0.9835 -1.60 -1.40 log[I⁻] -1.20 -1.00 slope (rounded to the nearest integer) = ⁿ After ^m and ⁿ have been determined:
 - Solve for k @ constant temperature (°K) for trials 1 - 10 using the rates and ^m and ⁿ that you have determined from trials 1 - 10. (Find mean k, don't forget units units for k: M⁻¹s⁻¹)
 - Determine the rate law for the iodine-clock reaction (use mean k from #3: k) rate = k[S₂O₈²⁻]^m [I⁻]ⁿ
- Varying the temperature, measure rate of reaction, calculate k and estimate EA
- Vary the temperature and solve for k (@ each temp).
- Using k and T, construct

an Arrhenius plot and solve for EA. Arrhenius Equation: $\ln k = \hat{A} - \frac{E_a}{RT}$

k = rate constant E_a = activation energy T = temperature ($^{\circ}\text{K}$) R = Ideal Gas Constant ($8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$) A = reaction specific constant

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

$1/T$	$\ln k$
0.0031	-3.5
0.0032	-4.5
0.0033	-5.5
0.0034	-6.5
0.0035	-7.5
0.0036	-8.5
0.0037	-9.5

$y = -6227.7x + 15.576$ $R = 0.9965$

slope = $-E_a/R$ In this example : $-E_a = (R)(-6227.7 \text{ }^{\circ}\text{K})$

$E_a = (8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})(6227.7 \text{ }^{\circ}\text{K})$ $E_a = 51777 \text{ J/mol}$ or 51.777 kJ/mol