Kinetics: Temperature Effect

In this experiment, you will measure the average rate of a redox reaction at several different temperatures, and then analyze the data to find the Arrhenius activation energy, E_a. The reaction is that between permanganate ion (MnO_4^-) and oxalate ion ($C_2O_4^{2-}$), where manganese is reduced from its purple +7 oxidation state to the pale pink +2 state. The progress of the reaction will be monitored by watching the color change.

$$2\ MnO_4^-\ (aq) + 5\ C_2O_4^{2-}\ (aq) + 16\ H^+\ (aq) \rightarrow 2\ Mn^{2+}\ (aq) + 10\ CO_2\ (g) + 8\ H_2O\ (l)$$

The average reaction rate will be ($-\frac{1}{2}\ \Delta[MnO_4^-]/\Delta t$). The time taken for all of the permanganate ion to react is Δt and, since all of the permanganate has been used up when that time has elapsed, $\Delta[MnO_4^-]$ is equal to the initial permanganate concentration. A complication is that the reaction proceeds by way of a yellow intermediate, so the end point (the point at which the final time reading is made) will be when the purple color of the permanganate ion has just disappeared and the solution is pale yellow. When the average rate has been found for six different temperatures, a plot of the linear form of the Arrhenius equation will yield the activation energy:

$$\ln(\text{rate}) = -\ (E_a/R) \times (1/T) + \ln(\text{constant})$$

Here the gas constant R is equal to 8.314 J K^{-1} mol^{-1}. Note that the Arrhenius equation is:

$$k = A\ \exp(-E_a/RT)$$

However, we won't actually measure rate constant k. Instead we will assume that since the concentration of reactants is the same in each trial, the measured rate is equal to k times some constant. Thus the ln(constant) term above includes the concentrations and the Arrhenius pre-exponential factor (A). You don't need to know the value of ln(constant) in order to find the slope and evaluate E_a.

The temperatures used are **initial** temperatures, since we are not keeping the reaction mixtures in the water bath after mixing the reactants. Obviously the mixtures, other than the room temperature one, will cool some during the course of the reaction. For the purposes of this experiment, this factor is not critical, other than being aware of it.

Procedure:
Work in partners. Obtain a thermometer from the designated point in the lab.

1. Obtain 35 mL (and only 35 ml) of each of the reagents required, 0.0050 M $KMnO_4$ and saturated oxalic acid, in *labeled* 50-mL beakers.

2. Determine the room temperature by examining the thermometer.

3. Use the graduated cylinder to measure 5.0 mL of 0.0050 M $KMnO_4$ solution into two of your large test tubes. Similarly measure 5.0 mL of saturated oxalic acid solution into two other large test tubes.

4. Set up a water bath in your 800 mL beaker. The beaker need be only about one-third full of water. Place your thermometer in the water. Place one test tube of each solution in the bath.

5. Begin *slowly* heating the bath to about 8-9°C above room temperature.

6. Meanwhile, watching the time, pour the room-temperature tube of oxalic acid into the room-temperature test tube of potassium permanganate solution. Pour the solution back and forth twice to mix the solutions.

7. Note the exact time that the oxalic acid contacts the potassium permanganate solution. Use this as the initial time.

8. When the test tube has become yellow note the time. This value is the final time.

9. Place the test tube of reacted solutions in a 250 mL beaker so that you may observe any additional color change (Remember to record any observations in your notebook!)

10. Thoroughly rinse out the empty tube from the room temperature trial. Measure 5.0 mL of 0.0050M $KMnO_4$ solution into the tube. Measure 5.0 mL of oxalic acid solution into your remaining large test tube.

11. When the temperature of the water bath reaches about 8-9°C above room temperature, record the temperature, remove the two tubes from the bath, mix and record the initial time as before. Place the newly filled test tubes in the water bath and continue *slowly* heating to 16-18°C above room temperature; the temperature does not need to be exactly 20°C above room temperature, but record the experimental value.

12. Repeat the procedure, measuring times to disappearance of the purple MnO_4^- color at 24-27°C, 32-36°C, and 40-45°C degrees above room temperature. (You will have to reuse your test tubes. Rinse them thoroughly.)

13. Note any trend or pattern in your data; record this in your lab notebook. If one run does not fit the pattern, decide whether to repeat it or not.

14. Clean up.

After completing the procedure but before leaving lab, write in your notebook a brief statement (two to three sentences) on the quality and reasonableness of the data you collected. Note what you might do differently if you performed the lab again.