Chemical Kinetics of Photographic Development

This is actually two experiments that you will do in one lab period. In Experiment I the rate law for the chemical reaction occurring in photographic development will be determined, and in Experiment II, the effect of temperature on this reaction will be investigated.

Experiment I: Determining the Rate Law of the Development Reaction

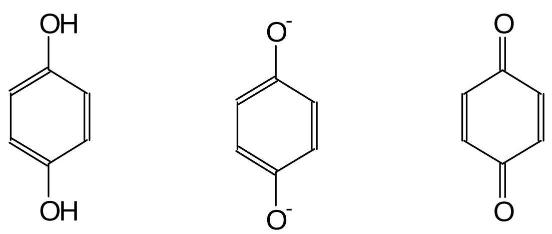
One possible mechanism for photographic development is:

$$2OH^- + H_2Q \rightarrow Q^{2-} + 2H_2O \qquad (1)$$

$$Q^{2-} + \text{emulsion} \rightarrow Q^{2-}{}_{(em)} \qquad (2)$$

$$Q^{2-}{}_{(em)} + 2Ag^+ \rightarrow 2Ag + Q_{(em)} \qquad (3)$$

Q^{2-}(em) and Q(em) represent the hydroquinone ion and hydroquinone, each dissolved in the photographic emulsion. Reaction (2) in the above mechanism represents the diffusion of the anion



hydroquinone, H_2Q — $C_6H_6O_2$ quinone anion, Q^{2-} — $C_6H_4O_2$ quinone, Q — $C_6H_4O_2$

into the emulsion. The overall reaction can be written as:

$$2OH^- + H_2Q + 2Ag^+ \rightarrow Q + 2H_2O + 2Ag$$

and the rate law is:

$$\text{Rate} = \frac{\Delta(Ag)}{\Delta t} = k(H_2Q)^m(OH^-)^n \qquad (4)$$

The purpose of this experiment will be experimentally to determine m, the order of the reaction with respect to H_2Q.

Method: In the development reaction, silver ion is reduced to tiny grains of silver metal which appear as the black portions of a black and white photographic print. In this experiment you will measure Δt, the development time required to give a constant degree of blackness in a contact print. This degree of blackness is a measure of Δ(Ag), the silver metal concentration. Thus, Δ(Ag) will be a constant for all of the trials, and the reaction rate is:

$$\text{Rate} = \frac{\Delta(Ag)}{\Delta t} = \frac{\text{Constant}}{\Delta t} = \frac{C}{\Delta t}$$

As a result, the reaction rate will be inversely proportional to the development time (Δt).

Equation (4) may then be rewritten as:

$$\frac{C}{\Delta t} = k(H_2Q)^m(OH^-)^n \quad (5)$$

$$\text{and} \quad \frac{1}{\Delta t} = \frac{k}{C}(H_2Q)^m(OH\text{-})^n \quad (6)$$

In part A, (OH^-) will be kept constant and (H_2Q) will be varied. In this case, equation (6) becomes:

$$\frac{1}{\Delta t} = \frac{k(OH\text{-})^n\,(H_2Q)^m}{C} = k'(H_2Q)^m \quad (7)$$

where k' is a constant.

Thus, if m = 1, a plot of $1/\Delta t$ vs. (H_2Q) will be linear.
If m = 2, a plot of $1/\Delta t$ vs. $(H_2Q)^2$ will be linear. Such plots will be used to determine m.

Part A - Determining the order with respect to hydroquinone

Procedure

The various developer solutions to be used in this experiment are summarized in Table 1. The method of preparation will be described in a following section.

The concentrations of the stock solutions are:
Na_2SO_3 = .635 mole/L (80 g/L)
(You must prepare this stock solution of Na_2SO_3 by dissolving 40 g Na_2SO_3 in 500 ml distilled water.)
NaBr = 1.68 mole/L (173 g/L)
NaOH = 3.13 mole/L (125 g/L)
(The sodium bromide and sodium hydroxide solutions have been prepared for you.)

Table 1. Developer Solutions to be Prepared

Developer solution	Na_2SO_3(ml)	NaBr(ml)	H_2O (ml)	g of H_2Q	NaOH(ml)
1	75	10	95	3.0	20
2	75	10	95	1.5	20
3	75	10	95	1.0	20
4	75	10	95	0.5	20

Developer solutions 1 - 4 in Table 1 differ only in their concentrations of hydroquinone (H_2Q), and they will be used to determine the order with respect to H_2Q. This will be done by making contact prints with each of these solutions and measuring the development time required to produce a "good" print. Make sure that all prints are of the same degree of darkness.

Developer Preparation: Prepare Solution 1 in Table 1 by adding 75 ml of Na_2SO_3 stock solution, 10 ml of NaBr stock solution, 95 ml distilled H_2O, 3.0 g of H_2Q, and 20 ml of NaOH stock solution in to a 200 ml beaker. **Be sure to add the chemicals in the above order**. Mix thoroughly. Label the beaker. If you forget the sodium hydroxide or hydroquinone, the experiment will not work at all. If you leave out the sodium bromide or sodium sulfite, your results will be affected. Don't forget anything. Make sure you communicate with your partner!

(Spilled H_2Q or Na_2SO_3 can be wiped up with a wet paper towel and discarded. Excess solutions can be put down the drain with running water. **Be careful with the NaOH solution**).

Repeat the above procedure to prepare the other developer solutions, except use 1.50, 1.00 and 0.50 g of H_2Q, respectively. Label each beaker. Mix the solutions.

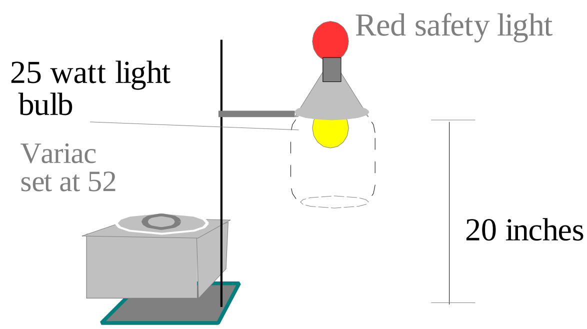
Before proceeding to the next section, make sure that all three developer solutions are at the same temperature. Place them in a tub of room temperature water and stir periodically until they are within one degree or so from each other. Record the temperature. When everyone has their solutions made the lights will be turned out for the next step of the experiment.

<u>Determining the effect of hydroquinone concentration on development time</u>

Step 1: Obtain several sheets of photographic paper. Caution: this paper is very sensitive to light--be certain it never sees the "light of day."

Step 2: Place approximately 100 ml each of stop bath, fixer and distilled water into 400-ml beakers; label each beaker. (Excess and used stop bath can be put down the drain with running water. The fixer solution should be put in the used fixer container because it contains silver).

Step 3: Set up the exposing light as shown in the figure below.



Step 4: Using only safety lights, remove a piece of photographic paper from its storage space and place it directly under the light with the emulsion (glossy) side up. Place the negative on top of the paper and a piece of glass on top of the negative.

Step 5: Turn on the light for 30 seconds to expose the paper.

Step 6: Develop the print (still under safety lights) by placing it in the beaker containing developer solution 1. Use tongs to handle the print and agitate it slightly during development. Continue the development until a "good" print is obtained. Determine the development time with a stopwatch or the second hand on your wristwatch, and record it. If you have trouble getting a good print after two attempts, see your instructor. Place the print in the stop bath for 60 seconds and then into the fixer for 5 minutes. Finally, place it in the wash water for 5 minutes. During the fixing and washing steps you can move on to Step 7. The print obtained in this step will be your "standard print," and it represents a fixed amount of reduced silver. Mount the print with your data in your notebook. [See the sample data table below for recording your data].

Step 7: Make a second print, again using Solution 1. Develop the print until it looks just like your standard print in Step 6.

Using the procedure above, prepare **two** prints with each of the other developers: Solutions 2, 3 and 4. Use the same stop bath and fixer as before. In each case, develop the print until it looks just like the standard print obtained with Solution 1. Record the development times (Δt) and mount all prints in your notebook.

A3. Calculations: Calculate the concentration of hydroquinone (moles/L) in each of the developer solutions and 1/Δt, and enter the values in your notebook. Prepare a graph of 1/Δt on the y axis vs. $[H_2Q]$ on the x axis **using Excell** and include it in your writeup. Prepare a second plot of 1/Δt vs. $[H_2Q]^2$ (1/Δt on y-axis).

Be sure to answer this question in your conclusion: what is the value of m in equation (4)?

EXPERIMENT II -- The Effect of Temperature on the Rate of Development

The purpose of this experiment will be to investigate the effect of temperature on the rate of photographic development.

In general, the rate of a chemical reaction increases with temperature. Theoretically, this temperature dependence is due to the temperature dependence of the rate constant which can be written as

$$\log k = \log A - \frac{Ea}{2.303\,RT} \qquad (1)$$

This is a form of the Arrhenius Equation, where A is the pre-exponential factor; Ea is the activation energy in Joules; T is the temperature in K, and R = 8.314 J/K.

In this experiment the rate is given by:

$$\text{Rate} = k(H_2Q)^m(OH\text{-})^n \qquad (2)$$

$$k = \frac{\text{Rate}}{(H_2Q)^m(OH\text{-})^n} \qquad (3)$$

Substitution into equation (1) gives

$$\log(\text{Rate}) = -\frac{Ea}{2.303RT} + \log A + \log[(H_2Q)^m(OH^-)^n] \qquad (4)$$

If a series of trials is carried out in which the concentrations of all reactants are held constant, Then, since log A is a constant:

$$\log A + \log[(H_2Q)^m(OH^-)^n] = \text{a constant} = c'$$

Equation (4) can be rewritten as

$$\log(\text{Rate}) = -\frac{Ea}{2.303R}\left(1/T\right) + c' \qquad (5)$$

For this series of experiments a graph of log(Rate) on the y axis vs. 1/T on the x axis should give a straight line with the slope given by:

$$\text{slope} = -\frac{Ea}{2.303R} \qquad (6)$$

The activation energy can then be calculated from the slope by solving Equation (6) for Ea

$$Ea = -(2.303R)(\text{slope}) \qquad (7)$$

In this experiment you will measure the time required to develop a Standard Print (one that looks like the "Standard Print" of Part A. 1 of Experiment I) at three different temperatures. The reactant concentrations will be kept constant. As before,

$$\text{Rate} = \frac{c}{\Delta t} \text{ where}$$

Δt = time of development

Then from Equation (5) a graph of log(Rate) vs. 1/T can be used to calculate Ea, the activation energy for the reaction.

Procedure:

Prepare Developer Solution 1, as described in Part A. 1, and use the same stop bath and fixer as used in Experiment I. Assemble a controlled temperature bath by placing your developer solution in a copper bath (or large beaker) of water.

Next, using the same negative as in Experiment I, expose three pieces of photographic paper for 30 seconds each. Be sure to protect these from light before and after exposure. Adjust the temperature of the developer in the inner beaker to 25°C by adding warm water or ice to the outer beaker. Stir well. Prepare one contact print using the procedure in Experiment I. Agitate the print in the developer during development. Develop the print until it looks like your Standard Print from Part A-2 of Experiment I. Record the development time in your data table.

Adjust the temperature of the developer solution to 15°C by adding ice to the outer beaker. Stir solution in both beakers to insure uniformity of temperature. Prepare another contact print, again developing until the print looks like the Standard Print. Record the development time. Be sure that the temperature does not vary by more than 1°C during development. Finally, adjust the temperature of the developer to 35°C and repeat the process above.

Calculations:

Complete your data table by converting the temperatures to K, calculating 1/T, 1/Δt, and log(1/Δt). As mentioned previously,

$$\text{Rate} = \frac{c}{\Delta t}$$

hence, according to Equation (5) a graph of log(1/Δt) vs. 1/T should give a straight line. Use **Excel** to graph your data. Calculate Ea. Remember that Δt is the amount of time that it takes to develop a good print.