**Kenneth W. Watkins
and June A. Olson**
Colorado State University
Fort Collins, CO 80523

# Ionic Strength Effect on the Rate of Reduction of Hexacyanoferrate(III) by Ascorbic Acid

## *A physical chemistry laboratory experiment*

There are several experiments designed for physical chemistry laboratory that allow students to test the effect of ionic strength on the rates of reactions in solution. However, examination of physical chemistry laboratory manuals reveals that the only reaction suggested for this purpose is the oxidation of iodide ion by persulfate ion in the iodine clock reaction. Students who study kinetics of clock reactions can be left with the erroneous conclusion that all reaction rates are followed by this means. This situation may be especially true for those who previously examined kinetic principles by using clock reactions in general chemistry laboratory.

In the experiment below we describe a reaction which is suitable for physical chemistry students to use to examine the influence of ionic strength on the rate of a reaction between ions. During the past two years we have found that the reduction of hexacyanoferrate III by ascorbic acid yields reliable data for kinetic studies. The rate of reaction displays second order behavior and can be easily followed colorimetrically by a uv-visible spectrophotometer. The reaction is rapid enough that one kinetic run can be carried out in about 20 min. A single 4-hr laboratory period was found to be sufficient for preparation and completion of the measurements.
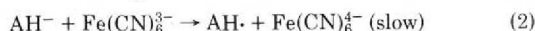
### The Reaction

The experiment described here involves an easily followed reaction in which ascorbic acid ($C_6H_8O_6$) is oxidized to dehydroascorbic acid ($C_6H_6O_6$) by hexacyanoferrate(III). The reaction has been studied



Ascorbic acid ($C_6H_8O_6$)   Dehydroascorbic acid ($C_6H_6O_6$)
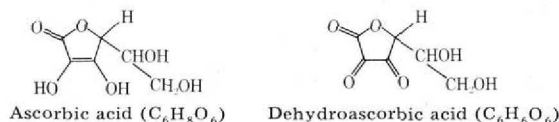
by Mehrotra, Angrawal, and Mushran[1], and it was found to have the following stoichiometry.

$$2Fe(CN)_6^{3-} + C_6H_8O_6 \rightarrow 2Fe(CN)_6^{4-} + C_6H_6O_6 + 2H^+$$
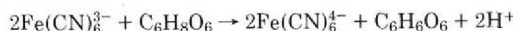
A mechanism has been proposed which involves the formation of an intermediate ascorbate anion ($AH^-$) by ionization of ascorbic acid ($AH_2$). The ascorbate anion transfers one electron to hexacyanoferrate(III) in a slow, rate determining step.

$$AH_2 \rightleftharpoons AH^- + H^+ \text{ (fast)} \qquad (1)$$

$$AH^- + Fe(CN)_6^{3-} \rightarrow AH\cdot + Fe(CN)_6^{4-} \text{ (slow)} \qquad (2)$$

Step two is followed by a fast step in which the ascorbate free radical ($AH\cdot$) transfers an electron to hexacyanoferrate(III) to give the end product dehydroascorbic acid (A).

$$AH\cdot + Fe(CN)_6^{3-} \rightarrow A + Fe(CN)_6^{4-} + H^+ \qquad (3)$$
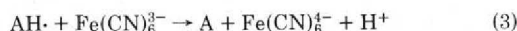
The kinetics of the oxidation of ascorbic acid can be followed by determining the concentration of unreacted $Fe(CN)_6^{3-}$ with time. Aqueous solutions of hexacyanoferrate(III) are yellow having an absorption maximum at 418 nm with an absorption coefficient of 1012 $M^{-1}$ cm$^{-1}$ [2]. Hexacyanoferrate(II), ascorbic acid, and dehydroascorbic acid are

colorless, and therefore they do not interfere with determinations based on Beer's Law at 418 nm. The fraction of $Fe(CN)_6^{3-}$ remaining at any time $t$ is just $A/A_0$ where $A$ is the absorbance due to $Fe(CN)_6^{3-}$ at time $t$, and $A_0$ is the absorbance at zero time. The concentration of $Fe(CN)_6^{3-}$ at time $t$, therefore, is given by

$$[Fe(CN)_6^{3-}] = \frac{A}{A_0}[Fe(CN)_6^{3-}]_0$$

where $[Fe(CN)_6^{3-}]_0$ is the initial hexacyanoferrate(III) concentration. The concentration of ascorbic acid at time $t$ is given

$$[AH_2] = [AH_2]_0 - \frac{1}{2}\{[Fe(CN)_6^{3-}]_0 - [Fe(CN)_6^{3-}]\}$$

### Experimental

Students can prepare four $K_3Fe(CN)_6$—$NaNO_3$ solutions of 100 ml each. Each solution should be approximately $1 \times 10^{-3}$ $M$ $K_3Fe(CN)_6$. Four $NaNO_3$ concentrations are used in order to vary the ionic strength. The recommended $NaNO_3$ concentrations are 0.02, 0.05, 0.1, and 0.2 $M$. Next 100 ml of ascorbic acid solution is prepared. It should be approximately 0.010 $M$ $HNO_3$, $2.5 \times 10^{-4}$ $M$ $C_6H_8O_6$, and 0.001% disodium EDTA dihydrate. The concentration of $HNO_3$ must be known accurately. Of the three ingredients the ascorbic acid should be added last. These solutions should be allowed to come to room temperature. It is not necessary to use a constant temperature bath if all solutions are within ±1°. Since ascorbic acid reacts slowly with dissolved $O_2$, the solution should be made up and used within the same laboratory period. No effect of $O_2$ is noticeable when this procedure is followed.

When ready to start, 25 ml of one of the $K_3Fe(CN)_6$—$NaNO_3$ solutions is pipeted into an Erlenmeyer flask, and 25 ml of $C_6H_8O_6$—
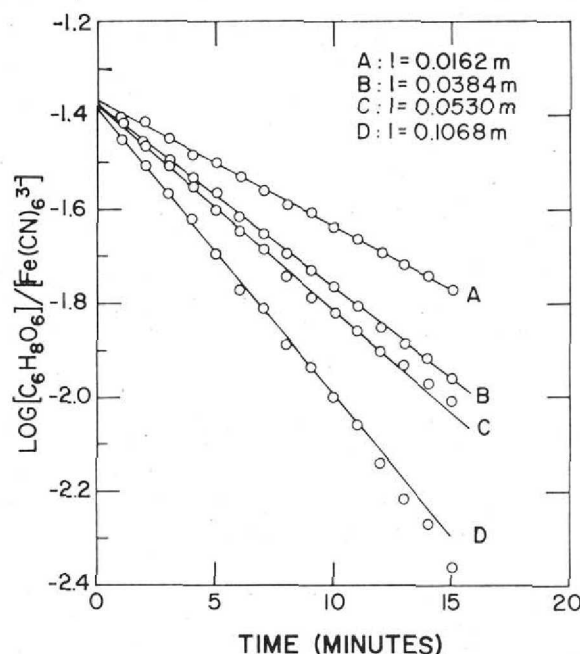


Figure 1. A second-order plot of the data.

[1] Mehrotra, U. S., Agrawal, M. C., and Mushran, S. P., *J. Phys. Chem.*, **73**, 1996 (1969).
[2] Aziz, F. and Mirza, G. A. *Talanta*, **11**, 889 (1964).

$HNO_3$ solution is pipeted into a beaker. The solution from the beaker is poured into the Erlenmeyer and the timer started. Swirling the solution of reactants for a few seconds improves mixing. Then the solution is introduced into the absorption cell, placed in the spectrophotometer, and the absorbance is recorded at 1.0 min intervals for about 20 min. $A_\infty$ readings can be taken after several hours. To obtain an absorbance reading corresponding to zero time, $A_0$, 25 ml of distilled water is mixed with 25 ml of $K_3Fe(CN)_6$—$NaNO_3$. The procedure is repeated for each of the $NaNO_3$ concentrations.

## Treatment of Data

The rate constants for the reaction at different ionic strengths are calculated from the integrated rate equation[3] for a second order reaction of the type

$$aA + bB \rightarrow products$$

which is

$$kt = \frac{a}{[b(A)_0 - a(B)_0]} \ln \frac{(A)(B)_0}{(A)_0(B)}$$

A more suitable form for graphical presentation is

$$\ln \frac{(A)}{(B)} = \frac{[b(A)_0 - a(B)_0]}{a} kt + \ln \frac{(A)_0}{(B)_0}$$

A plot of ln (A)/(B) versus time yields a straight line with a slope of $[b(A)_0 - a(B)_0]k/a$ from which the value of $k$ can be calculated if the initial concentrations are known. Note that the slope may be either positive or negative depending on whether the quantity $b(A)_0 - a(B)_0$ is positive or negative. Figure 1 shows typical data obtained by students in our physical chemistry laboratory.

The measured effect of ionic strength on the rate constant is compared with two theoretical equations that predict ionic strength effects. The first is based on the Debye-Hückel limiting law for activity coefficients.

$$\log k = \log k_0 + 1.02 \, Z_A Z_B I^{1/2}$$

where $k$ is the rate constant at ionic strength, I and $Z_A$ and $Z_B$ are charges on the two reacting species. The second equation applies to more concentrated solutions.
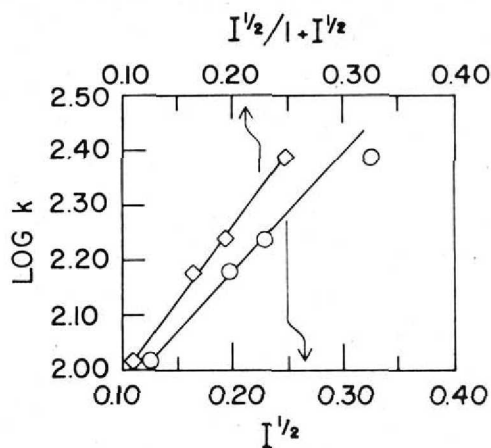


Figure 2. The effect of ionic strength on the rate of reaction.
O log $k$ versus $I^{1/2}$
□ log $k$ versus $I^{1/2}/1 + I^{1/2}$

$$\log k = \log k_0 + 1.02 \, Z_A Z_B \frac{I^{1/2}}{1 + I^{1/2}}$$

The values of $Z_A Z_B$ obtained from graphs as shown in Figure 2 can be compared to the theoretical value of 3.0 and reasons for differences can be discussed.

## Acknowledgment

[3] Benson, S. W., "The Foundations of Chemical Kinetics," McGraw-Hill, New York, 1980, p. 18.