Neutral Salt Action. I. The Effect of Neutral Salts on the Velocity of the Reaction $2Fe(CN)_6^= + 3I^- \longrightarrow 2Fe(CN)_6^\equiv + I_3^-$

By HAROLD B. FRIEDMAN AND BERNARDE E. ANDERSON[1]

1. Introduction

Various papers have appeared on the kinetics and equilibrium of the reaction between potassium ferricyanide and potassium iodide.[2] La Mer and Friedman studied the variation of the equilibrium constants with and without the presence of excess neutral salts, in the event that the cations be changed from potassium to sodium, and the anions were chloride, nitrate, and sulfate. They showed that the constants were larger in every case for the potassium than for the corresponding sodium salt, and larger for chloride than for nitrate.

The purpose of the present work was to determine the effect on the velocity of the reaction of the same neutral salts as were used by La Mer and Friedman in the equilibrium studies.

Fig. 1.

2. Methods and Materials

The experimental procedure was the same as that followed by La Mer and Sandved and by

La Mer and Friedman. It involved titration of the reacting solution with standard thiosulfate at intervals to determine the amount of free iodine formed. In all cases the ferricyanide concentration was initially 0.075 M, the iodide (either from potassium or sodium) 0.2 M, and neutral salts added in 1, 2, or 3 M concentration.

Preparation of Materials.—0.05 N sodium thiosulfate needed in determining reaction rates was standardized against potassium permanganate.

Potassium Ferricyanide.—Twice recrystallized from water and dried.

Potassium and Sodium Iodides, and Neutral Salts.—Good c. p. grades, thoroughly dried.

3. Experimental Data and Discussion

The data are presented in graphical form in Figs. 1 to 4. As the reaction proceeds, more iodine forms in the sample and requires a larger amount of thiosulfate, corresponding to a continuously decreasing ratio until equilibrium is
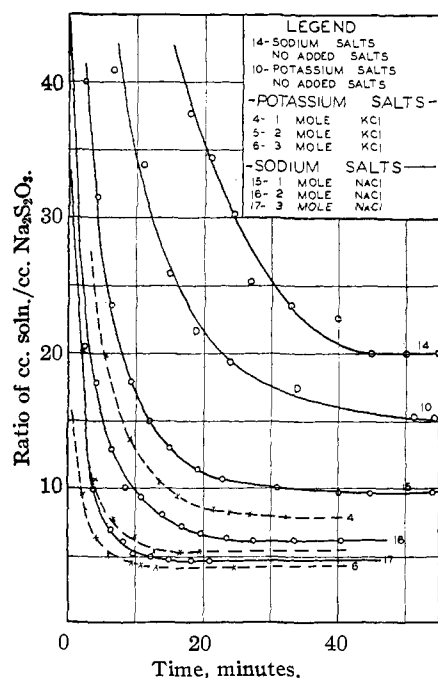

Fig. 2.

(1) Present address: Krebs Pigment Co., Wilmington, Del.

(2) (a) Donnan and LeRossignol, J. Chem. Soc., 83, 703 (1903); (b) Just, Z. physik. Chem., 63, 513 (1908); (c) Wagner, ibid., 113, 261 (1924); (d) La Mer and Sandved, THIS JOURNAL, 50, 2656 (1928); (e) La Mer and Friedman, ibid., 52, 876 (1930),

Fig. 3.

is made between the effect of nitrate and chloride, using potassium salts (Fig. 3) and sodium salts (Fig. 4). In both cases, chloride accelerates the reaction more than nitrate of like concentration.
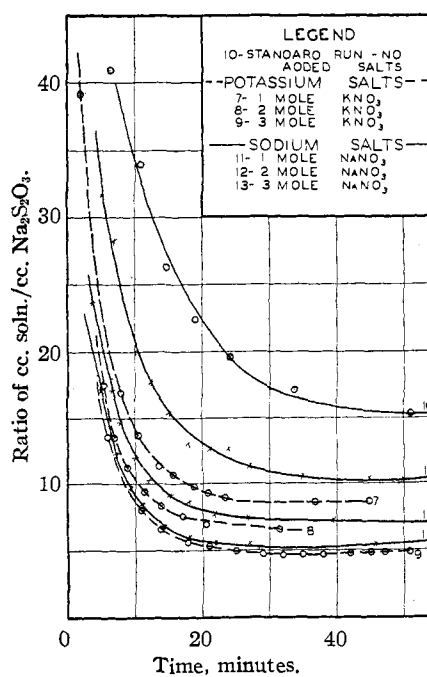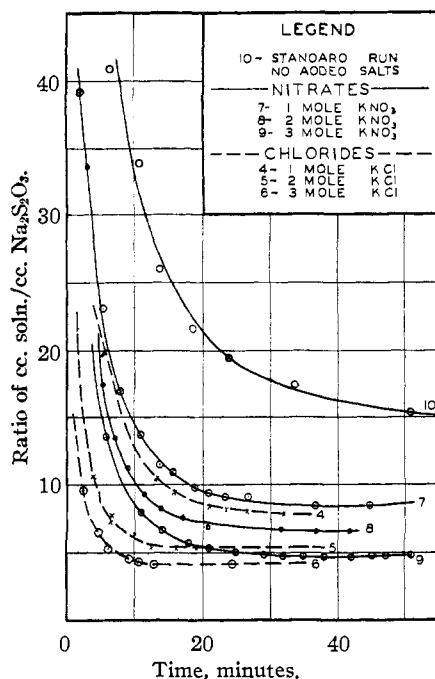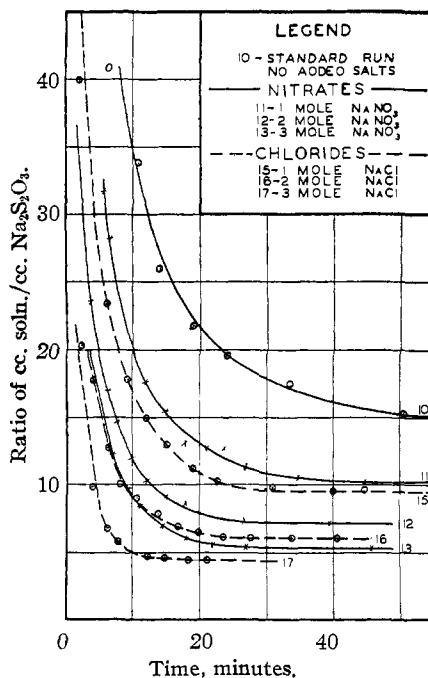

Fig. 4.

reached. A curve which lies below and to the left of another corresponds to a faster reaction.

In all cases, the initial concentration of potassium ferricyanide was 0.075 M and potassium iodide (or sodium iodide in the case of the sodium studies) was 0.2 M. The neutral salts were the nitrates and chlorides of potassium and sodium, with runs for each of the 1, 2, and 3 molar additions. If the neutral salt contained potassium, the system was set up entirely with potassium salts, but when sodium salts were used, the small amount of K^+ (from the 0.075 M potassium ferricyanide) remained, since the ferricyanide of potassium was used throughout. It has been shown[2e] (p. 878) that for all practical purposes the cation may be regarded as entirely sodium.

The curves in Fig. 1 represent the normal systems uncatalyzed by neutral salt (curve 10 in potassium salts; curve 14 in sodium salts), along with a comparison of the effect of changing the thermodynamic environment from potassium chloride to sodium chloride. In each case it is seen that (1) the shift for the added salt is proportional to the salt concentration, and (2) the velocity with potassium salts is always greater than with like concentrations of sodium salts.

In Fig. 2, the catalyzing anion is nitrate. The effect is the same as the chloride. Comparison

As was pointed out by La Mer and Friedman, if the velocity constant for the reverse reaction is independent of the environment, then the velocity of the forward reaction should be proportional to the free energy. This is qualitatively demonstrated by our curves in which it is to be noted that the further a reaction must proceed in each case, the greater is its velocity in its early course, and the shorter the time required to reach equilibrium. That this is probably the case in the oxidation of hydroquinone in presence of manganous ion was noted by Temple.[3]

Summary

1. The velocity of the reaction between ferricyanide and iodide ions has been studied in systems of potassium and sodium salts, with and without addition of the neutral salts, potassium chloride, sodium chloride, potassium nitrate, sodium nitrate in 1, 2, and 3 molar solutions.

2. Potassium salts accelerate the reaction more than sodium salts, and the chlorides more

(3) J. W. Temple, thesis, Columbia University, 1928.

than nitrates. This is in accord with the measurements of Just and the equilibrium measurements of La Mer and Friedman.

Neutral Salt Action. II. The Effect of Neutral Salts on the Hydrolysis of Copper Sulfate[1]

BY HAROLD B. FRIEDMAN AND JEFFERSON A. STOKES, JR.[2]

1. Introduction

The effect of neutral salts on various types of chemical equilibria has been studied by many investigators. However, little work has been devoted to the salt effect on hydrolysis. In those few cases, the investigations have been limited to esters.[3] An electrometric method readily permits the determination of the low concentration of hydrogen ions existing in solutions of copper sulfate.

2. Historical

Denham[4] using an electrometric method with a hydrogen electrode determined the degree of hydrolysis of a number of different salts and obtained excellent results in many cases. He did not investigate the effect of neutral salts since he thought that they "interfered with the measurement of hydrolysis."

Poma and Albonico[5] studied the effect of neutral salts on the hydrolysis of methyl acetate and found that neutral salts accelerated the rate and increased the degree of hydrolysis. The increase was in the order of potassium, sodium, lithium, and iodides, nitrates, bromides, and chlorides.

O'Sullivan[6] determined the hydrolysis of 0.1 N copper sulfate by an electrometric method in which he used a quinhydrone electrode. The results which he obtained are not to be relied upon, as his measurements on four solutions of identical concentration vary as much as 3.5 mv. An increase of e. m. f. with time is also noted.

These erratic results may be due to the possible oxidation of the quinhydrone, since the measurements extend over a period of two days. Also, there is a possibility of diffusion of potassium chloride from the salt bridge into the solution in this prolonged measurement, resulting in an increase of e. m. f. O'Sullivan attributes "it, therefore, to gradual coagulation of the colloidal particles of cupric hydroxide, produced by hydrolysis, whereby adsorbed acid would be set free."

O'Sullivan did not investigate the neutral salt effect on the hydrolysis of copper sulfate.

3. Preparation and Purification of Materials

All salts used in this investigation were of c. p. grade and were purified very carefully by recrystallizations from water. In all operations, freshly distilled water was used. The water was boiled immediately before use to expel the dissolved gases.

The purified salts were dried in an oven at 110° for a period of twelve hours. The dry salts were put into glass-stoppered bottles and kept in a desiccator over concentrated sulfuric acid.

Copper Sulfate.—C. p. $CuSO_4 \cdot 5H_2O$ was three times recrystallized. Solutions were prepared from this purified salt, standardized by thiosulfate and checked by electrolysis. The two methods agreed to one part in one thousand.

Potassium Chloride, Potassium Sulfate, Sodium Chloride, and Sodium Sulfate.—These neutral salts were recrystallized twice from water, except the potassium chloride for use in the calomel electrodes which was recrystallized three times. The sodium chloride was precipitated from a saturated solution by means of hydrogen chloride gas. This necessitated longer drying at about 140° to free the salt from hydrogen chloride incorporated in the crystals.

Quinhydrone.—The quinhydrone was the standard Eastman product and was not further purified.

4. Apparatus and Method.—The pH measurements were made with a Leeds and Northrup students' potentiometer, using a quinhydrone electrode and a saturated calomel reference electrode. The cells were immersed in a water thermostat at 25 ± 0.01°. The degree of hydrolysis was calculated from pH by the equations

$$- \log C_{\mathrm{H}} = p\mathrm{H}, \quad x = \frac{C_{\mathrm{H}}}{2M},$$ where M = molar concn.

The liquid junction potentials were cut down by salt bridges of saturated potassium chloride in agar gel.

(1) Constructed from a thesis presented to the Department of Chemistry, Georgia School of Technology, in partial fulfilment of the requirements of the degree of Master of Science in Chemistry.

(2) Present address, E. I. du Pont de Nemours & Company, Inc., Richmond, Virginia.

(3) Thomas and Whitehead, *J. Am. Leather Chemists Assn.*, **25**, 127 (1930), have some measurements on SO_4^- and Cl^- on solutions of aluminum salts, but they varied the ratios of their concentrations in a manner that makes direct comparison difficult. However, their results will be discussed in a subsequent paper in which one of us has studied aluminum sulfate as a hydrolyzing salt.

(4) Denham, *J. Chem. Soc.*, **93**, 41–63 (1908).

(5) Poma and Albonico, *Atti Accad. Lincei*, **24**, 1, 747 (1915).

(6) O'Sullivan, *Trans. Faraday Soc.*, **21**, 319 (1925).