[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF WISCONSIN]

Some Aspects of the Oxidation of Thiosulfate Ion by Peroxydisulfate Ion[1,2]

BY C. H. SORUM AND JOHN O. EDWARDS

The oxidation of thiosulfate ion by peroxydisulfate ion has been reinvestigated. The rate is first order in oxidant concentration and zero order in thiosulfate concentration. A small amount of catalytic material such as copper ions has been shown to account for the largest share of the reaction velocity. The presence of side reactions has been demonstrated and their rate laws deduced. Inert salts exert large and specific influences on the rate constant. Free radical chain mechanisms have been proposed and these explain most of the observed anomalies.

Introduction

The polymerization of vinyl monomers is often initiated by free radicals resulting from peroxide decomposition. At present, peroxydisulfate (hereafter designated persulfate) ion is commonly employed in emulsion polymerization as the peroxide catalyst and thiosulfate ion has been used as a reducing agent to promote peroxide decomposition. The mechanism of the reaction between these two anions in water was studied by King and Steinbach[3] who demonstrated that several unusual phenomena existed in their studies. The rate was first order in persulfate concentration and almost zero order in thiosulfate concentration; there was a marked irreproducibility in the rate constant and a sizable positive salt effect was noticed when potassium chloride was added. Morgan[4] studied this reaction in connection with the polymerization of acrylonitrile and found that the rate of reduction of monomer concentration is not dependent on the thiosulfate concentration.

It was decided to reinvestigate the kinetics and mechanism of the oxidation of thiosulfate by persulfate in conjunction with studies of *p*H changes in various reactions.[5]

Materials and Procedures

The chemicals were Reagent Grade or best grade available and were employed without further purification. Distilled water was used, although comparison experiments were carried out with water redistilled from alkaline permanganate.

Solutions of thiosulfate were standardized by the dichromate method. Iodine solutions, made with a 50–50 ethanol–water solvent containing about 0.02 *M* iodide, were standardized by the thiosulfate and were kept tightly stoppered to prevent evaporation. Solutions of persulfate and inert salts were made up by weight in volumetric flasks for each group of experiments.

Aliquots were quenched into a 250-ml. glass-stoppered bottle containing 100 ml. of distilled water, 5 ml. of starch solution and just under the expected titer of iodine solution. The final titer could thus be obtained in about 20 seconds after the quenching. The results obtained by this rapid titration procedure were generally good to ±0.2%.

The *p*H change was observed during the reaction by means of a Beckman model G *p*H meter which was standardized with Beckman buffer solutions.

The reaction mixtures were made up with marked pipets to ensure reproducibility. The temperature of the large water-bath containing the reagent and reaction vessels was held constant at 25.0 ± 0.1°, unless otherwise noted.

Several factors were quickly observed. If identical solutions were used, the reaction rate was reproducible to ±5%. If the distilled water used in dilution of the reaction mixture to the desired concentration was varied, large changes (about 100%) were found in some cases. For this reason, groups of experiments were carried out with one series of reactant and inert salt solutions, all made up from the same bottle of distilled water. In the evaluation of the kinetics, further care had to be used since large, specific salt effects were found.

In the equations and formulas, the symbol $P^=$ will be used for persulfate and the symbol $T^=$ for thiosulfate. Brackets will be employed to denote concentrations.

Stoichiometry and Kinetics

At room temperature, the reaction was reported to be essentially quantitative in formation of tetrathionate from thiosulfate[3]; our investigations showed that this is a reasonably correct result. The stoichiometry is

$$S_2O_8^= + 2S_2O_3^= \longrightarrow S_4O_6^= + 2SO_4^=$$

The rate is first order with respect to persulfate concentration. Using potassium sulfate as the inert salt to keep the ionic strength constant, first order constants for 0.0058, 0.0115, 0.0230 and 0.0460 *M* potassium persulfate were 0.00352, 0.00352, 0.00359 and 0.00380 min.$^{-1}$, respectively. With an excess of thiosulfate, good first order rate plots were obtained for about two half-lives in persulfate concentration.

The rate of change of thiosulfate concentration with respect to its own concentration is zero order. With sodium sulfate as the replacement salt, no serious deviation (greater than 10%) was detected as the thiosulfate concentration was varied over a fourfold range. When a large excess of persulfate was present, the rate remained independent of the thiosulfate concentration until only 4% of the original amount remained. Figure 1 demonstrates this zero order rate. In similar fashion, it was found that the rate does not depend on the hydrogen ion concentration in the *p*H range from 4 to 10.5.

No significant variation from first order kinetics was found in better than 125 experiments so the observed rate law is

$$-\frac{d[T^=]}{dt} = k_x[P^=]$$

in which k_x is the experimental rate constant which had values from 3.0×10^{-4} to 1.28×10^{-2} min.$^{-1}$.

Side Reactions

This oxidation–reduction reaction is unusual in that no change in *p*H would be expected during its course. The reactants and products are identical in charge type and in number, and, further, all are ions from strong acids so there should be no buffer action in the stated *p*H range. Thus, any change in the observed *p*H as the reaction proceeds will result from side reactions. In Fig. 1, results for one experiment are shown. The presence of side reactions which do not influence the main reaction to any large degree is demonstrated.

In Fig. 2, the change in shape of the *p*H–time curve when industrial oxygen is bubbled through the reaction vessel is shown. For these two otherwise identical runs, comparative rate plots for the main reaction are also given. While the oxygen causes a large change in *p*H, it does not change the reaction rate.

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(1) Presented at the 118th National Meeting of the American Chemical Society on Sept. 7, 1950, at Chicago, Illinois.

(2) Taken in part from the Ph.D. thesis of John O. Edwards. Further details and rate constants may be found in this thesis which is filed at the Library of the University of Wisconsin in Madison, Wisconsin.

(3) C. V. King and O. F. Steinbach, THIS JOURNAL, **52**, 4779 (1930).

(4) L. B. Morgan, *Trans. Faraday Soc.*, **42**, 169 (1946).

(5) C. H. Sorum, F. S. Charlton, J. A. Neptune and J. O. Edwards, paper presented at the Symposium on Kinetics of Oxidation–Reduction Reactions, American Chemical Society Meeting at Detroit, Michigan; April 18, 1950; THIS JOURNAL, **74**, 219 (1952).

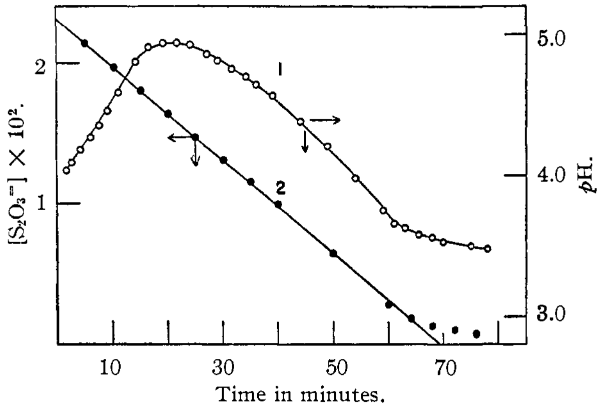

Fig. 1.—Change in thiosulfate ion concentration with time using an excess of persulfate ion (Curve 2) and the pH variation for the same experiment (Curve 1).

The maximum found in most of the pH–time curves seems to result from two competing reactions; one uses up and the other releases protons. With this concept in mind, correlations made from the position of the pH maximum with time as a function of the variables in the system give information as to the nature of the two side reactions.

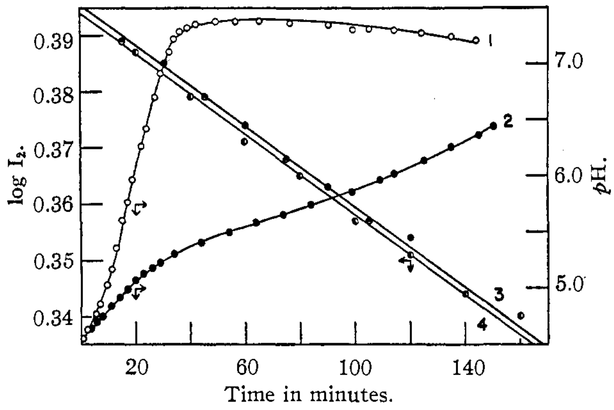

Fig. 2.—Effect of oxygen on pH–time curve and rate plot: Curves 1 and 4 with bubbling oxygen; $[S_2O_3^=] = [S_2O_8^=] = 0.0368$ N.

Oxygen causes the pH to rise rapidly in acid ranges and to form a flat maximum. Increasing the ionic strength or the concentration of persulfate (at constant ionic strength) causes the maximum to arrive sooner. Increases in the concentration of either thiosulfate or hydrogen ion move the maximum to the right on the time axis; that is to say, the pH reaches its greatest value later. It was also found that the side reaction which lowers the pH is particularly prevalent when the ratio of persulfate concentration to thiosulfate concentration is larger than one. This side reaction seems to exert a small catalytic effect on the main reaction.

Rate equations based on these data and on the kinetic laws for the main reaction will be presented in the discussion section of this paper.

Effect of Inert Salts

The most interesting aspect of this reaction lies in the pronounced specificity of salt effects on the rate constants. That the rate is increased at all is somewhat surprising at first sight since a salt effect is not generally found with a unimolecular reaction, particularly at low salt concentrations.

When the orders were evaluated, it was necessary to replace potassium persulfate with potassium sulfate and to replace sodium thiosulfate with sodium sulfate. Comparative runs showed that the effect of potassium sulfate is about twice as large as that of the sodium salt. Ammonium sulfate had an intermediate effect on the rate constant. Figure 3 shows how four univalent chlorides affect the rate constant. The lithium salt is lower than the other three chlorides, which have the same relative influence as the sulfates of these cations. Although the experimental results are best fitted by plotting the rates as functions of the square root of the positive ion concentration, the reaction is too complex to allow theoretical interpretation at this time.

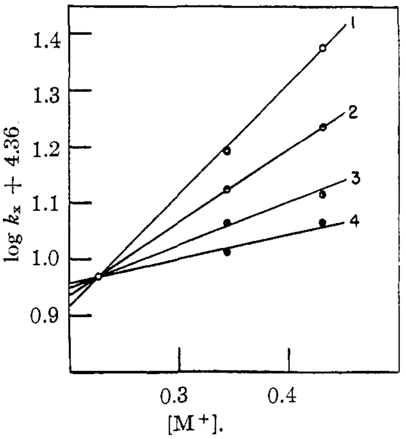

Fig. 3.—Influence of four univalent cations on rate: potassium 1, ammonium 2, sodium 3, and lithium 4; as the chloride salts; $[S_2O_3^=] = [S_2O_8^=] = 0.0171$ N.

The polyvalent cations studied, with the exception of cadmium, caused large increases in the rate constant. Their influences, as the chloride and sulfate salts, fall in the following order: Al > Ca > Zn > Mg. Cadmium salts cause an initial fast drop in the thiosulfate concentration; the rate then levels off and decreases very slowly thereafter.

It was found that some anions have specific influences on the rate. Three groups of runs, embracing 28 salts, were carried out. The salts of the first group contained potassium ion, those of the second contained ammonium ion and the final group (run at 29.95°) was made up of sodium salts.

Salts of the strong mineral acids, containing a particular cation, exert an identical effect on the rate constant (within the experimental error), when calculated on the basis of positive ion concentration. It seems probable, therefore, that the effects of strong anions can be ignored, which condition would be expected if the rate steps contain no positive ions.[6] Anions which fall in this group are sulfate, thiosulfate, persulfate, chloride, bromide, nitrate, perchlorate and presumably tetrathionate. Acetate and benzoate salts exert an influence of the same magnitude as the salts of the mineral acids.

We wished to find out the relative rates of the reactions in the presence of different weak anions so a means to eliminate the specific influences of the three cations was devised. To make the relative rate have a value of 1.00 when strong anions were present, the average value of the rate constant for several runs was multiplied by a normalization factor. This factor, which was different for each cation, was then multiplied by the rate constant for each salt in order to obtain comparative values for the weaker anions.

In every case, the relative rate was near or significantly below 1.00. One group of relative values between 0.69 and 0.87 embraced seven salts of which three contained the dihydrogen phosphate ion and the three different cations. The other salts were ammonium dihydrogen citrate, potassium hydrogen phthalate, sodium fluoride and $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$. Although an accurate comparison cannot be made, the relative rates in solutions where no inert salt was present were in the same general range as that for the above seven salts. Relative rates below 0.65 denote a significant inhibition. Disodium hydrogen phosphate had a value of 0.47 and that for sodium hydrogen carbonate was 0.29. Sodium carbonate and sodium tungstate were at 0.08 and 0.15 on the relative scale. Potassium carbonate was at 0.22.

Since we have shown that there is little probability of a positive ion present in the rate law, the relative rate values below 1.00 demonstrate that these anions are exerting a

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[6] A. R. Olsen and T. R. Simonsen, *J. Chem. Phys.*, **17**, 1167 (1949).

strong influence on the rate in an unusual fashion. An explanation for this specificity will be given in the next section.

Discussion

Consider the observed rate law as the sum of two rate laws, both of which are first order in persulfate concentration. One of these rate terms contains a catalytic influence which we shall designate X. We have, therefore

$$-\frac{\mathrm{d}[\mathrm{T}^{=}]}{\mathrm{d}t} = \{k_a + k_b[\mathrm{X}]\}[\mathrm{P}^{=}]$$

in which

$$k_a + k_b[\mathrm{X}] = k_x$$

It seems probable that this reaction proceeds through a free radical chain mechanism for several reasons: namely, (1) the effect of oxygen on the *p*H–time curve, (2) the initiation of vinyl polymerization by this reaction, (3) the presence of well-defined induction periods in about one-fourth of the runs, (4) the absence of any order in thiosulfate concentration while the rate constant k_x is many orders of magnitude greater than that of the persulfate decomposition alone, and (5) the catalysis of the main reaction by the second side reaction. With these facts in mind, it is possible to devise several free radical chain mechanisms for the uncatalyzed rate law. Of these, the most reasonable is

$$\mathrm{P}^{=} = \xrightarrow{k_{1a}} 2\mathrm{SO}_4^{\underset{\cdot}{-}}$$

$$\mathrm{SO}_4^{\underset{\cdot}{-}} + \mathrm{H_2O} \xrightarrow{k_{2a}} \mathrm{HSO}_4^{-} + \mathrm{OH}\cdot$$

$$\mathrm{OH}\cdot + \mathrm{S_2O_3}^{=} \xrightarrow{\text{fast}} \mathrm{OH}^{-} + \mathrm{S_2O_3}^{\underset{\cdot}{-}}$$

$$\mathrm{S_2O_3}^{\underset{\cdot}{-}} + \mathrm{P}^{=} \xrightarrow{k_{3a}} \mathrm{SO_4 \cdot S_2O_3}^{=} + \mathrm{SO}_4^{\underset{\cdot}{-}}$$

$$\mathrm{S_2O_3}^{\underset{\cdot}{-}} + \mathrm{SO}_4^{\underset{\cdot}{-}} \xrightarrow{k_{4a}} \mathrm{SO_4 \cdot S_2O_3}^{=}$$

$$\mathrm{SO_4 \cdot S_2O_3}^{=} + \mathrm{S_2O_3}^{=} \xrightarrow{\text{fast}} \mathrm{S_4O_6}^{=} + \mathrm{SO_4}^{=}$$

Making the usual steady-state approximations that the concentration of free radicals is constant and that k_{1a} is slow, the rate law

$$-\frac{\mathrm{d}[\mathrm{T}^{=}]}{\mathrm{d}t} = \left(\frac{k_{1a}k_{2a}k_{3a}}{k_{4a}}\right)^{1/2}[\mathrm{P}^{=}]$$

is obtained. This agrees with the experimentally observed rate equation. Other free radical chain mechanisms which can satisfy the kinetics have a disadvantage in that they require a termolecular chain termination step. The propagation step k_{2a} and the subsequent fast reaction seem a bit unusual; however a step like k_{2a} probably takes place in the decomposition of persulfate in water.[7,8] King and Steinbach[3] showed that this reaction is extremely sensitive to trace amounts of copper, less sensitive to iron salts and hardly affected by silver ion. (Needless to say, it is virtually impossible to remove all of the copper and iron from water and from salts.) They found that over a fifty-fold range in added copper sulfate, the reaction is first order in copper ion concentration as well as first order in persulfate. They observed that the bimolecular rate constant was about 500 and that it was increased by the addition of inert salt.

A free radical mechanism for the copper-ion catalyzed oxidation of thiosulfate would be in agreement with the findings of Morgan.[4] He observed that copper ion in small traces causes tremendous increases in the rate of polymerization by the persulfate–thiosulfate catalyst. Presumably the persulfate oxidizes a complex of cuprous ion and thiosulfate, since cupric ion is rapidly reduced to a colorless, soluble complex by thiosulfate,[9] the rate is increased by addition of inert salt,[2,3] and no positive ions are involved in the rate steps. Whether the steps after the first one in the catalyzed mechanism make up a chain cannot be said at this time,[10] for mechanisms with or without chains can be postulated and all of these mechanisms can fit the experimental rate law.

The catalysis by iron and silver salts can be explained by other oxidation–reduction cycles employing the different valence states of these metals. This hypothesis is substantiated by the observed effect of specific anions on the rate. The retardation can be attributed to their complexing and precipitation reactions which stabilize certain valences of the metals.

Since the rate of the uncatalyzed mechanism should not be changed to any large extent by inert salts, an upper limit can be established for k_a. Our lowest value of k_x was 3.0×10^{-4} min.$^{-1}$, obtained in a solution containing 0.067 *M* sodium carbonate. The lowest value reported by King and Steinbach was 1.77×10^{-4} min.$^{-1}$. This is the upper limit for k_a.[11] It is our opinion that k_a, the uncatalyzed mechanism, is not a factor in the oxidation of thiosulfate by persulfate, however, we cannot give a definite answer to the problem at this time. One can say that X, the catalytic factor, is most probably one or more complex ions containing cations and thiosulfate and that k_b is the important term in reaction mixtures employed in polymerization catalysis.

The kinetics of the side reactions can now be deduced from the postulated mechanism for the main reaction. The rise in *p*H during the first few minutes of the reaction is a result of the uptake of dissolved oxygen by the reducing free radical. From the shape of the *p*H–time curve and the influence of the initial *p*H, it is reasonable to assume that this reaction is dependent on the *p*H. The rate law for the first side reaction appears to be

$$-\frac{\mathrm{d}[\mathrm{H}^+]}{\mathrm{d}t} = k_5[\mathrm{S_2O_3}^{\underset{\cdot}{-}}][\mathrm{O_2}][\mathrm{H}^+]$$

and the stoichiometry is

$$\mathrm{O_2} + 4\mathrm{H}^+ + 4\mathrm{S_2O_3}^{=} \longrightarrow 2\mathrm{H_2O} + 2\mathrm{S_4O_6}^{=}$$

as we know that free radicals are neither given off or used up in the stoichiometry since k_x is not affected by k_5.

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(7) P. D. Bartlett and J. D. Cotman, Jr., THIS JOURNAL, **71**, 1419 (1949).

(8) I. M. Kolthoff and I. K. Miller, *ibid.*, **73**, 3055 (1949).

(9) D. I. Ryabchikov and V. G. Sil'nichenko, *Bull. acad. sci. U. R. S. S., Classe sci. chim.*, 19 (1947); *C. A.*, **42**, 4477 (1948).

(10) The referee suggested that a mechanism proceeding by way of Cu^{+3} could fit the rate law. Previously, we had considered the Cu^{+1}; Cu^{+2} pair.

(11) Using the bimolecular rate constant of 500 for copper ion catalysis,[3] this corresponds to about 4×10^{-7} *M* copper ion.

The side reaction which generates hydrogen ion must be the oxidation of a sulfur compound to a valence higher than tetrathionate. From considerations of the *p*H maximum and the kinetics of k_a, it is believed that this reaction has the rate law

$$+\frac{\mathrm{d}[\mathrm{H}^+]}{\mathrm{d}t} = k_6[\mathrm{SO}_4^{-}][\mathrm{SO}_4\cdot\mathrm{S}_2\mathrm{O}_3^{-}]$$

where the ion $\mathrm{SO}_4\cdot\mathrm{S}_2\mathrm{O}_3^{=}$ is the kinetic intermediate postulated in the mechanism. It is known that the particle $\mathrm{S}_2\mathrm{O}_3^0$ forms complexes with bases of the Lewis type,[12] therefore we prefer this form to that of the isolated particle $\mathrm{S}_2\mathrm{O}_3^0$. Assuming that a steady state concentration of this complex is present, the rate law

$$+\frac{\mathrm{d}[\mathrm{H}^+]}{\mathrm{d}t} = k_6\,\frac{[\mathrm{P}^-]^2[\mathrm{CuT}_2^{-3}]}{[\mathrm{T}^-]}$$

is obtained. So far, it has not been possible to find a means of testing the rate laws for the side reactions since the concentration of dissolved oxygen is not known.

The stoichiometry of the second side reaction is complex so no attempt will be made here to discuss the many possibilities. It was found that some hydrogen sulfide was formed in the course of the experiments. Small amounts of this material were detected by the insoluble sulfides of zinc, cadmium and silver and by its typical odor. There was no trace of colloidal sulfur in any of our experiments.

The specificity of salt effects is easily explained in the case of the anions, but the marked influence of cations is another matter. It is possible that there are small amounts of catalytic impurities in the salts, but this is hardly a satisfactory postulate since it does not explain why one sodium salt of a mineral acid can replace another without specific effects nor does it explain the inhibition by carbonate and other similar ions. In their work on the acid hydrolysis of the lactones, McDevit and Long[13] demonstrated that the ionic polarizability (or ionic volume) of inert ions has a tremendous influence on the reaction rate. The polarizability increases as one goes from lithium to sodium to potassium. Ammonium ion has a larger polarizability than potassium, but it also has a different electronic structure which could explain the observed discrepancy. A similar discrepancy was found for the relationship between perchlorate ion and the halogenide ions.[13]

A search of the literature showed that this order for specific effects of cations is not new. Seven reactions[14] of varying type have rates whose constants were affected by all or part of the following series:

$$\mathrm{Cs}^+ > \mathrm{Rb}^+ > \mathrm{K}^+ > \mathrm{NH}_4^+ > \mathrm{Na}^+ > \mathrm{Li}^+ > \mathrm{H}^+$$

It has been found that the "salting-in" of hydrogen peroxide is controlled by the same order in cations.[15]

The large variation in the effect of different univalent positive ions on the rate could be explained if complex ions were formed. Since no data have been found in the literature on complex ions with persulfate or $\mathrm{Cu(S_2O_3)_2^{-3}}$, this is merely speculation.

Acknowledgment.—This work was supported in part by funds supplied by the Graduate School of the University of Wisconsin and by the Wisconsin Alumni Research Foundation. The criticisms and suggestions of our colleagues are also gratefully acknowledged.

[12] (a) O. Foss, *Det Kgl. Norske Vidensk. Sels. Skrifter*, No. 2, 83 (1945); (b) J. O. Edwards, *Chem. Revs.*, in press.

[13] W. F. McDevit and F. A. Long, 118th National Meeting of the American Chemical Society on Sept. 7-8, 1950 at Chicago, Illinois.

[14] (a) M. N. Das and S. R. Palit, *J. Indian Chem. Soc.*, **26**, 322 (1949); **27**, 179 (1950); (b) R. O. Griffith, A. McKeown and A. G. Winn, *Trans. Faraday Soc.*, **28**, 107 (1932); (c) B. Holmberg, *Z. physik. Chem.*, **97**, 134 (1921); (d) W. J. Howells, *J. Chem. Soc.*, 463 (1939); (e) V. K. La Mer and R. W. Fessenden, THIS JOURNAL, **54**, 2351 (1932); (f) K. Nozaki and R. A. Ogg, Jr., *ibid.*, **64**, 697 (1942); (g) K. J. Pederson, *Trans. Faraday Soc.*, **23**, 316 (1927).

[15] M. H. Gorin, THIS JOURNAL, **57**, 1975 (1935).

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[CONTRIBUTION FROM THE MOORE LABORATORY OF CHEMISTRY, AMHERST COLLEGE]

The Potential of the Electrocapillary Maximum of Mercury. II

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The potential of the electrocapillary maximum of mercury has been measured for a number of electrolytes in water solution. Seven methods have been used in all, six of them new. Five of the methods have been described in Part I; the other two are described here, together with improvements in one of those described earlier. The results are believed to be accurate to within a few tenths of a millivolt in favorable cases. The thermodynamic and kinetic significance of the results is discussed. The behavior of cesium ion in electrocapillary studies is found to be self-consistent in terms of a simple hypothesis. The "rational" potential of the normal calomel electrode is found to be 0.472 volt.

In a previous paper[1] there were described five methods for the determination of the potential of the electrocapillary maximum of mercury and results obtained by these methods were presented for tenth-normal solutions of potassium and sodium chloride. In the present paper two additional methods are described and results are given for a considerable number of electrolytes.

The importance of the measurements to us arises from the fact that they are necessary for the utilization of differential capacity data. In particular, it is known that at the potential of the electrocapillary maximum (e.c. max.) the surface charge density of electricity on the metallic surface is zero and this fact serves to evaluate the constant of integration needed in the integration of the differential capacity.

In addition the potential of the e.c. max. has another kind of direct thermodynamic significance. It is a measure (through the relation $\Delta F = -n\mathfrak{F}E$)

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[1] D. C. Grahame, R. P. Larsen and M. A. Poth, THIS JOURNAL, **71**, 2978 (1949).