THE CHEMICAL KINETICS OF HIGH VALENCE TYPE ELECTROLYTES IN DILUTE AQUEOUS SOLUTIONS

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Introduction

In developing the theory of chemical reaction velocity in solution and particularly to account for the anomaly known as neutral salt effect, Brönsted[2] postulates that the reaction mechanism involves a series of intermediate unstable complexes. The rate of transformation of the most unstable complex, designated as X, determines the tempo of the reaction. For the velocity of a bimolecular reaction like

$$A + B \rightleftharpoons X \longrightarrow R_1 + R_2 + \ldots \tag{1}$$
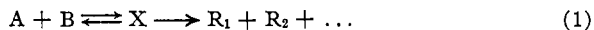
he gives the expression

$$\frac{dx}{dt} = k_0 \, C_A C_B \, f_A f_B / f_x \tag{2}$$

Here the factor, $F = f_A f_B / f_x$, representing the ratio of the activity coefficients is introduced as a correction to the classical expression valid for ideal solutes to account for the changes in velocity resulting from a change in the nature of the medium. Such environmental changes are produced by variation in the concentrations of the reactants or by the addition of chemically inert substances. It is important to subject the theory to a critical analysis to ascertain whether the introduction of activity coefficients, thermodynamic quantities which are independent of time, furnishes a sufficient correction. In a recent paper from this Laboratory[3] it was shown that the further assumption of a change in the degree of orientation of complex molecules on collision was necessary to account for the results for specially selected examples.

For an unequivocal test of the theory, it is necessary to measure these activity coefficients in precisely the same medium in which the reaction proceeds. The instability of A and B in the presence of each other frustrates such measurements. However, the theory can be tested by comparing the observed behavior of the factor, F, on changing concentration with predictions based upon measurements of stable ions of the same electric charge type. For this purpose, it has been customary to employ the

[2] Brönsted, Z. physik. Chem., 102, 169 (1922); 115, 337 (1925). A critical review and summary are given by La Mer, Chem. Rev., 10, 179 (1932).

[3] La Mer and Kamner, THIS JOURNAL, 53, 2832 (1931).

Debye–Hückel limiting law to predict the kinetic behavior.[4] Solubility studies,[5,6,7] however, have demonstrated that this simple law does not hold when the product of the charges of the ions of opposite sign is greater than four. Instead the solubility measurements have revealed a characteristic behavior which has proved to be at variance with the predictions of the theory as developed by Debye and Hückel but not inconsistent with the fundamental postulates of the theory provided a more complete mathematical solution of the Poisson–Boltzmann equation is employed.[8]

For example, the reaction

$$BrCH_2COO^- + S_2O_3^- \rightleftharpoons [X^-] \longrightarrow S_2O_3CH_2COO^- + Br^- \qquad (3)$$
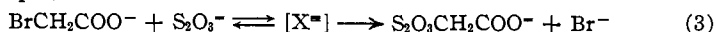
involves a critical complex with three negative charges. If the reactants are introduced in the form of their sodium salts, the valence product of ions of opposite sign does not exceed three for any pair in the mixture. Under such conditions the observed rate agrees[9] with the predictions of the equation

$$\log k = \log k_0 + Z_A Z_B \sqrt{\mu} \qquad (4)$$

obtained by introducing the Debye–Hückel limiting law

$$-\log f_i = -0.50 \, Z_i^2 \, \sqrt{\mu} \qquad (5)$$

into equation (2) and integrating on the assumption that the ionic strength, μ, remains unchanged during the course of the reaction. On the other hand, if the reactants are introduced in the form of their calcium, barium or magnesium salts, there will be ionic pairs involving the critical complex with a valence product equal to six. When bivalent cations are present, equations (5) and (4) will not be obeyed. However, if equation (2) is correct, we should expect the curves obtained on plotting the logarithm of the velocity constant against the square root of the ionic strength to have a form practically identical with those obtained by La Mer and Mason for the solubility of salts of the same valence type. The essential characteristic is an experimental limiting slope two to three times that predicted by the Debye–Hückel limiting law for the region 0.001μ to 0.01μ; and a point of inflection so that the limiting law is obeyed at extreme dilution.

The reaction between bromoacetate ion and the thiosulfate ion has been studied previously by Slator,[10] Krapivin,[11] La Mer[9] and Kappanna.[12] It is free from interfering side reactions since the constant for the hy-

[4] Brönsted and Livingston, This Journal, **49**, 435 (1927).

[5] La Mer and Mason, *ibid.*, **49**, 410 (1927).

[6] La Mer and Cook, *ibid.*, **51**, 2622 (1929).

[7] La Mer and Goldman, *ibid.*, **51**, 2632 (1929).

[8] La Mer, Gronwall and Greiff, *J. Phys. Chem.*, **35**, 2245 (1931). Gronwall, La Mer and Sandved, *Physik. Z.*, **29**, 358 (1928).
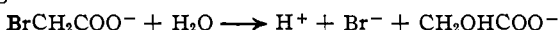
[9] La Mer, This Journal, **51**, 3341 (1929).

[10] Slator, *J. Chem. Soc.*, **87**, 481 (1905).

[11] Krapivin, *Z. physik. Chem.*, **82**, 439 (1913).

[12] Kappanna, *J. Indian Chem. Soc.*, **6**, 45 (1929).

drolysis of the bromoacetate ion to the glycolate ion with the formation of the hydrogen ion and the bromide ion

$$BrCH_2COO^- + H_2O \longrightarrow H^+ + Br^- + CH_2OHCOO^-$$

is of the negligible order[3] of 1×10^{-6}. There is no change in ionic strength as the reaction proceeds. It can be followed precisely by iodine titration even at great dilution.

In studying the effect of changing ionic environment upon this reaction two methods may be used. (a) The total ionic concentration may be changed by varying only the concentration of the reacting salts. (b) Neutral salts may be added to a fixed concentration of reactants. Method (a) is the simpler because only one cation and no foreign anions need be present in addition to the anions of the kinetic reaction. Method (b) has the objection that at least one foreign cation or anion must be introduced into the mixture. It is also not well adapted for work at very small concentrations since it is not possible to have a reasonable concentration of reactants and at the same time keep the ratio of added salts to reactants large. Method (a) was therefore adopted except for the studies with the lanthanum salts.

II. Preparation of Materials

Bromoacetic Acid.—Kahlbaum's bromoacetic acid was redistilled under reduced pressure (10 mm.). The bromine content of the purified acid was 99.5% of the theoretical value. Its acid titration value agreed with the theoretical within 1 part per thousand. When 0.0333 M bromoacetate was treated with 0.0666 M thiosulfate, 99.7% of the theoretical amount of the thiosulfate reacted in forty-eight hours. At these concentrations the reaction should have been completed to within 1 part per thousand in twelve hours. We may therefore safely assume a purity between 99.5–99.7%. The bromoacetic acid was kept in a desiccator over sulfuric acid in a dark bottle and closet.

Sodium and Potassium Thiosulfate.—The c. p. salts were recrystallized from distilled water.

Barium Thiosulfate.—C. p. barium thiosulfate was recrystallized from distilled water. Since this salt is only slightly soluble in water a saturated solution was prepared at 100°. After cooling to 15°, the crystals were filtered off and dried at room temperature.

Magnesium thiosulfate was prepared by a modification of the method of Rammelsberg.[13] Sulfur dioxide was passed into a suspension of 100 g. of magnesium oxide in 300 cc. of water until the mixture was slightly acid to litmus. An excess of sulfur was added together with sufficient water to make the total volume one liter. The mixture was boiled for four hours, replacing the water evaporated from time to time. The clear solution was decanted through a filter and allowed to cool. The magnesium thiosulfate was then precipitated by adding alcohol. The product was twice recrystallized from distilled water. In recrystallizing the magnesium thiosulfate it was found that a slight decomposition occurred if the solution was heated. Accordingly the crystals were dissolved in water without heating and the solution was allowed to evaporate at room temperature.

Calcium Thiosulfate.—The method was the same as that used for the magnesium salt.

Sodium Hydroxide.—Sticks of electrolytic sodium hydroxide were rinsed with distilled water and dissolved in freshly boiled water. The solutions were kept in paraffin-

[13] Rammelsberg, *Pogg. Ann.*, Second Series, **56**, 295 (1842).

coated bottles and protected from carbon dioxide by guard tubes of soda lime. The solutions were standardized against Bureau of Standards potassium acid phthalate using phenolphthalein as an indicator.

Potassium Hydroxide.—Electrolytic potassium hydroxide was used in making up solutions. The same procedure was followed as in the preparation of sodium hydroxide solutions.

Barium Hydroxide.—Solutions were prepared from c. p. barium hydroxide by the method given by Findlay.[14]

Calcium Hydroxide.—A suspension of calcium hydroxide was prepared from c. p. calcium chloride by treating a solution of the chloride with an equivalent amount of sodium hydroxide solution. The precipitate was washed by decantation until the clear supernatant solution gave no test for the chloride ion after acidification with nitric acid and the addition of silver nitrate.

Magnesium Hydroxide.—A suspension of the hydroxide was prepared from c. p. magnesium chloride by the method used for the preparation of calcium hydroxide.

Iodine.—Commercial resublimed iodine was used without further purification. All iodine solutions were made up with 4% potassium iodide and standardized against arsenious acid.

Potassium Iodide.—Merck's potassium iodide was used. Samples gave no color with starch in neutral solution after twenty-four hours in the dark and no color with starch after acidification.

Arsenious Acid.—Kahlbaum's "zur Analyse" arsenious oxide was used as a primary standard. Solutions were prepared after the method of Kolthoff,[15] and Washburn's[16] procedure was followed in titration using a sodium bicarbonate buffer.

Nitrogen.—Commercial nitrogen was passed through a solution of potassium pyrogallate to remove traces of oxygen, and next over heated copper gauze to remove any carbon monoxide formed. The gas was then washed with water and passed through a sample of the solution to be used before passing it into the reaction mixture.

Lanthanum Chloride.—A sample of cerium-free lanthanum chloride prepared by the Welsbach Company was used.[7]

All volumetric glassware was calibrated, and the distilled water boiled previous to use to remove oxygen and destroy microörganisms, which interfere with the stability of thiosulfate solutions.

III. Experimental Procedure

All velocity experiments were conducted at $25.00 \pm 0.02°$. The setting of the Beckmann thermometer was checked against a thermometer calibrated by the Bureau of Standards.

The thiosulfate solutions were titrated with a standard iodine solution and adjusted to the exact concentration desired. The bromoacetate solutions were prepared by weighing out the required amounts of bromoacetic acid and neutralizing with the hydroxides of the various metals using phenolphthalein as an indicator. Standard solutions of the soluble hydroxides were used as a check on the weighing. If the hydroxide was insoluble a suspension was used. After neutralization the solutions were diluted to the desired volume. In making up the reaction mixtures solutions of thiosulfate and bromoacetate were freshly prepared and standardized just before use.

[14] Findlay, "Practical Physical Chemistry," Longmans, Green and Company, 1925, p. 145.

[15] Kolthoff and Furman, "Volumetric Analysis," Vol. II, John Wiley and Sons. 1929, p. 354.

[16] Washburn, THIS JOURNAL, **30**, 31 (1908).

Experiments were carried out as follows. The two solutions containing the reactants were placed in the thermostat. When they had reached the temperature of the bath, the reactants were pipetted into the reaction vessel, taking the time of half delivery of the pipet when adding the second component as the initial time of the reaction. The very dilute reaction mixtures were prepared by diluting measured amounts of 0.01 M solutions of the reactants to the required volume in volumetric flasks and then transferred to the reaction vessel. At suitable intervals aliquots of the mixture were withdrawn and titrated with iodine. In experiments at the higher concentrations (0.01 M or greater), where the time error in stopping the reaction becomes important, the aliquot of the reaction mixture was pipetted into an amount of the iodine solution just insufficient to react with all the thiosulfate present in the sample. The conversion of the greater part of the reacting thiosulfate by the iodine effectively stopped the reaction. The titration was then completed by adding the standard iodine solution from a buret as quickly as possible. The dilute solutions in which the time error was small were titrated by introducing all the standard iodine directly into the aliquot of the reaction mixture.

The velocity constants were calculated by the formula $k = \dfrac{1}{a}\dfrac{1}{t}\dfrac{x}{(a-x)}$ where k is the velocity constant; t is the time in minutes; a is the initial concentration of the reactants in moles per liter; and x is the amount changed in time t. The value of a was determined by the dilution of the standard solutions used in making up the reaction mixtures and is expressed in moles per liter. The values of x and $(a-x)$ in the ratio were determined in terms of the volume of iodine solution used in titrating the reaction mixtures since these values do not need to be in absolute units as is necessary for the quantity $1/a$.

IV. Analytical Precision

In titrating the most dilute thiosulfate solutions there is a perceptible error in detecting the starch–iodine end-point which was corrected by appropriate blanks. Kolthoff[15] states that 1×10^{-5} M of iodine per liter is required to give the blue color with starch in the presence of 4×10^{-5} M of I$^-$ per liter. The sensitivity increases on increasing the iodide concentration. In this work the concentration of I$^-$ ion at the end-point of the titration was always greater than 0.01 M. With this concentration of I$^-$ ion the test was found in a north light to be sensitive to 1.5×10^{-6} M of iodine per liter in a volume of 250 cc.

In titrating iodine with thiosulfate in very dilute neutral solutions, Kolthoff[15] states that iodine is hydrolyzed to hypoiodite which oxidizes the thiosulfate to sulfate instead of to tetrathionate. This mechanism requires less thiosulfate than the normal reaction. He states that the reverse titration, that of thiosulfate with iodine, proceeds normally since the iodine is removed at once and has no opportunity to enter into the hydrolytic side reaction. Before we were acquainted with this explanation, experiments had been carried out to test the reliability of the procedure by adding iodine to the reaction mixture and then back-titrating with thiosulfate. In experiments at a concentration of 0.001 M it was found that the velocity constants varied with the volume of solution in which the titration was performed. In titrating directly with iodine no difference was detected on varying the volume. The results for the di-

rect titration were somewhat higher than for the back titration. At concentrations of 0.002 M and greater no difference in the velocity constants was produced by changing the order of adding the reagents in the titration.

V.   Stability of Thiosulfate Solutions

In very dilute solutions the stability of the thiosulfates may exercise a perceptible influence upon the results unless special precautions are taken.   By preparing the solutions in freshly boiled water as recommended by Kilpatrick and Kilpatrick[17] we found that 0.01 M thiosulfate solutions retain their titer to within 0.1% for a period of one week.   However, experiments in which the initial concentration of thiosulfate was of 0.001 M or less exhibited a slight increase in the velocity constants after a period of two days.   This drift in the values of the constants may be due to decomposition of the thiosulfate, for the increase was accelerated by the addition of traces of cupric ion (1×10^{-6} M per liter) in agreement with the studies of Abel.[18]

On the other hand, velocity experiments at an initial concentration of 0.00025 M thiosulfate performed under an atmosphere of nitrogen instead of air gave excellent constants!   A solution of 0.00025 M thiosulfate preserved under nitrogen also showed no change in the iodine titration after one week and a change of only 0.5% after two weeks.   All velocity experiments with 0.001 M thiosulfate or less which continued for more than two days were accordingly carried out under nitrogen.   Since no experiment was continued for more than ten days any decomposition of the thiosulfate was negligible.   It is not certain whether the decomposition observed in the dilute thiosulfate solutions was due to a reaction between oxygen and thiosulfate induced by minute traces of ions such as cupric or ferric ion present as impurities in our distilled water or whether it was due to bacteria whose growth or action is inhibited by the removal of the oxygen.   The important point is that the results in the presence of nitrogen were reproducible in highly dilute solution and the constants under these conditions showed no drift with time!

When it was necessary to use nitrogen in an experiment, the purified gas was bubbled through the reaction mixture for forty-five minutes or more at the start of the experiment to remove the oxygen.   Nitrogen was bubbled through the mixture daily to remove any trace of oxygen present due to possible leakages.   Samples of the solution were removed by a pressure of nitrogen.   The reaction mixtures in experiments performed under nitrogen were kept in glass-stoppered flasks of the type designed by MacInnes and Dole[19] for work in an atmosphere of inert gas.

[17] M. J. Kilpatrick and M. L. Kilpatrick, THIS JOURNAL, **45**, 2131 (1923).

[18] Abel, *Ber.*, **56**, 1076 (1923).

[19] MacInnes and Dole, THIS JOURNAL. **51**, 1119 (1929).

VI.   Experimental Results

To illustrate the character of the results three representative runs are included, one at each of the two lowest (0.00025 M) concentrations and one at the highest (0.05 M) concentration used.

EXPT. No. K 32. $a = b = 0.00025\ M$

100 ml. of 0.005 M $K_2S_2O_3$ No. 20 and 50 ml. of potassium bromoacetate 0.01 M No. 20.   Made up to 2 liters in a volumetric flask.   200-ml. aliquots titrated with iodine No. 20.   Nitrogen used.   Blank on iodine in this volume, 0.28 ml.

t, min.	Titer. ml.	x	$a - x$	k
0	24.52			
2778	20.52	4.00	20.24	0.285
4500	18.53	5.99	18.23	.292
5886	17.24	7.28	16.96	.292
8456	15.40	9.12	15.12	.285
9867	14.40	10.12	14.12	.290
12727	12.86	11.66	12.58	.291
14445	12.07	12.45	11.79	.292

Average 0.289 ± 0.003

The identical Expt. No. K31 gave 0.288 ± 0.001

EXPT. No. Ba 6. $a = b = 0.0005\ M$

200 ml. of barium thiosulfate 0.005 M No. 2 and 100 ml. of barium bromoacetate 0.005 M No. 2.   Made up to two liters in a volumetric flask.   200-ml. aliquots titrated with iodine No. 18.   Nitrogen used.   Blank on iodine in this volume, 0.20 ml.

t, min.	Titer. ml.	x	$a - x$	k
0	43.75			
1115	36.05	7.70	35.85	0.385
1355	34.79	8.96	34.59	.382
2418	30.11	13.64	29.91	.377
2545	29.58	14.17	29.38	.379
2704	28.92	14.83	28.72	.382
3885	25.33	18.42	25.13	.377
4128	24.70	19.05	24.50	.379

Average 0.380 ± 0.002

The identical Expt. No. Ba 5 gave 0.386 ± 0.001

EXPT. No. Na 6. $a = b = 0.0500\ M$

50 ml. of sodium thiosulfate 0.1 M and 50 ml. of sodium bromoacetate 0.1 M. 10-ml. aliquots titrated with iodine No. 8.

t, min.	x. ml.	$a - x$	k
0		27.90	
10	7.40	· 20.50	0.722
15	9.93	17.97	.736
20	11.74	16.16	.727
25	13.30	14.60	.728
30	14.58	13.32	.730
35	15.63	12.27	.728
40	16.53	11.37	.726
45	17.33	10.57	.729
51	18.19	9.71	.734

Average 0.729 ± 0.003

The deviations recorded are the average deviations from the arithmetical mean. This deviation was less than 1% except for three runs (Ba P8, Na P1 and K 32) and was considerably less at the higher concentrations.

The results of one hundred experiments are reported in Tables I and II. Some preliminary experiments performed in developing the method

TABLE I

THE EFFECT OF IONIC STRENGTH UPON THE VELOCITY OF THE THIOSULFATE–BROMO-ACETATE REACTION IN THE PRESENCE OF VARIOUS CATIONS

No.	C $a = b$	$\sqrt{\mu}$	k	$\log k$ (characteristic negative)	$\log k/k_0$	$\dfrac{\log k/k_0}{2\sqrt{\mu}}$
			Potassium as Cation			
K 38	0.0333	0.365	0.697 $\pm$ 0.0020	1.843	0.457	0.63
K 39	.0333	.365	.697 $\pm$ .002	1.843	.457	.63
K 23	.0250	.316	.657 $\pm$ .002	1.816	.433	.69
K 25	.0250	.316	.640 $\pm$ .002	1.806	.420	.66
K 26	.0250	.316	.630 $\pm$ .002	1.799	.413	.65
K 27	.0250	.316	.629 $\pm$ .002	1.799	.413	.65
K 4	.0200	.282	.598 $\pm$ .006	1.777	.391	.69
K 6	.0200	.282	.595 $\pm$ .003	1.775	.389	.69
K 5	.0100	.200	.491 $\pm$ .001	1.691	.305	.76
K 8	.0100	.200	.485 $\pm$ .002	1.686	.300	.75
K 9	.0050	.141	.427 $\pm$ .003	1.630	.244	.87
K 11	.0050	.141	.429 $\pm$ .003	1.632	.246	.87
K 17	.0050	.141	.431 $\pm$ .003	1.635	.249	.88
K 24	.0025	.100	.378 $\pm$ .001	1.578	.192	.96
K 28	.0025	.100	.371 $\pm$ .001	1.569	.183	.92
K 21	.0016	.080	.349 $\pm$ .001	1.543	.157	.98
K 18	.0016	.080	.350 $\pm$ .002	1.544	.158	.98
K 20	.0010	.0632	.334 $\pm$ .002	1.524	.138	1.04
K 29	.0010	.0632	.326 $\pm$ .001	1.513	.127	1.00
K 37	.00075	.0548	.313 $\pm$ .001	1.496	.110	1.00
K 22	.00050	.0447	.301 $\pm$ .003	1.479	.093	1.04
K 33	.00050	.0447	.295 $\pm$ .002	1.470	.084	0.94
K 34	.00050	.0447	.205 $\pm$ .002	1.470	.084	0.94
K 35	.00050	.0447	.300 $\pm$ .001	1.477	.091	1.02
K 36	.00050	.0447	.3003 $\pm$ .0007	1.4776	.092	1.03
K 31	.00025	.0316	.288 $\pm$ .001	1.459	.073	1.15
K 32	.00025	.0316	.289 $\pm$ .003	1.461	.075	1.18
K 1P	.0025	.100	.368 $\pm$ .003	1.566	.180	0.90
K 15	.0025	.100	.366 $\pm$ .004	1.563	.177	0.88
			Sodium as Cation			
Na 1	0.0250	0.316	0.590 $\pm$ 0.003	1.771	0.385	0.61
Na 5	.0250	.316	.610 $\pm$ .001	1.785	.399	.63
Na 6	.0500	.447	.729 $\pm$ .003	1.863	.477	.53
Na 7	.0333	.365	.650 $\pm$ .0005	1.813	.427	.58
Na 3	.0100	.200	.477 $\pm$ .002	1.679	.293	.73
Na 4	.0050	.141	.415 $\pm$ .001	1.618	.232	.82
Na 2	.0025	.100	.377 $\pm$ .003	1.576	.190	.95
Na P1	.0025	.100	.377 $\pm$ .006	1.576	.190	.95

TABLE I   (*Continued*)

No.	C $a = b$	$\sqrt{\bar{\mu}}$	k	log k (characteristic negative)	log k/k_0	$\dfrac{\log k/k_0}{2\sqrt{\bar{\mu}}}$
			Barium as Cation			
μ = ionic strength = 5.5 a. $a = b$ = mole/liter of reacting ions -						
Ba 2	0.0075	0.203	0.696 ± 0.001	1.843	0.457	1.13
Ba 1	.0050	.166	.632 ± .001	1.801	.415	1.25
Ba P4	.0050	.166	.629 ± .005	1.799	.413	1.24
Ba 10	.0020	.105	.522 ± .002	1.718	.332	1.58
Ba P8	.0020	.105	.522 ± .007	1.718	.332	1.58
Ba 4	.0010	.0742	.456 ± .002	1.659	.273	1.84
Ba 7	.0010	.0742	.416 ± .012	1.649	.263	1.77
Ba 5	.0005	.0520	.386 ± .001	1.587	.201	1.93
Ba 6	.0005	.0520	.380 ± .002	1.580	.194	1.87
Ba 8	.00025	.0370	.339 ± .003	1.530	.144	1.95
Ba 9	.00025	.0370	.337 ± .003	1.528	.142	1.92
Ba P10	.001	.0742	.452 ± .003			
			Calcium as Cation			
Ca 23	0.0333	0.428	0.938 ± 0.003	1.972	0.586	0.68
Ca 20	.0250	.371	.888 ± .002	1.948	.562	.76
Ca 21	.0200	.332	.850 ± .002	1.929	.543	.82
Ca 22	.0125	.262	.762 ± .002	1.882	.496	.95
Ca 24	.0125	.262	.759 ± .001	1.880	.494	.94
Ca 1	.0100	.235	.723 ± .003	1.859	.473	1.01
Ca 7	.00500	.166	.618 ± .001	1.791	.405	1.22
Ca 11	.00500	.166	.618 ± .001	1.791	.405	1.22
Ca 6	.00333	.135	.558 ± .002	1.747	.361	1.33
Ca 9	.00333	.135	.561 ± .004	1.749	.363	1.34
Ca 12	.00200	.105	.502 ± .001	1.701	.315	1.50
Ca 4	.00200	.105	.501 ± .001	1.700	.314	1.50
Ca 18	.00150	.0908	.466 ± .002	1.668	.282	1.55
Ca 8	.00100	.0742	.425 ± .003	1.628	.242	1.63
Ca 17	.00100	.0742	.423 ± .001	1.626	.240	1.62
Ca 16	.00050	.0520	.361 ± .001	1.558	.172	1.65
Ca 19	.00050	.0520	.362 ± .001	1.559	.173	1.66
Ca 14	.00025	.0370	.323 ± .002	1.509	.123	1.66
Ca 15	.00025	.0370	.320 ± .002	1.505	.119	1.61
Ca 13	thio = .00667 bromo- acetate .0033	.178	.636 ± .005 $a = b$	1.803	.417	1.17
			Magnesium as Cation			
Mg 18	0.0333	0.428	0.883 ± 0.002	1.946	0.560	0.65
Mg 3	.0250	.371	.827 ± .003	1.918	.532	.72
Mg 19	.0200	.332	.801 ± .004	1.904	.518	.78
Mg 20	.0125	.262	.720 ± .001	1.857	.471	.90
Mg 7	.0100	.235	.690 ± .003	1.839	.453	.96
Mg 1	.0050	.166	.576 ± .002	1.760	.374	1.12
Mg 11	.0050	.166	.589 ± .003	1.770	.384	1.16

TABLE I (*Concluded*)

No.	$\frac{C}{a = b}$	$\sqrt{\mu}$	k	log k (characteristic negative)	log k/k_0	$\frac{\log k/k_0}{2\sqrt{\mu}}$
Mg 2	0.00333	0.135	0.531 ± 0.002	1.725	0.339	1.25
Mg 12	.00333	.135	.537 ± .002	1.723	.337	1.25
Mg 10	.00200	.105	.485 ± .001	1.686	.300	1.43
Mg 14	.00200	.105	.484 ± .001	1 685	.299	1.42
Mg 6	.00150	.0908	.450 ± .002	1.653	.267	1.47
Mg 5	.00100	.0742	.408 ± .001	1.611	.225	1.52
Mg 13	.00050	.0520	.355 ± .002	1.550	.164	1.58
Mg 15	.00050	.0520	.348 ± .002	1.542	.156	1.50
Mg 16	.00025	.0370	.309 ± .001	1.490	.104	1.41
Mg 17	.00025	.0370	.312 ± .001	1.494	.108	1.46

TABLE II

EFFECT OF ADDED SALTS UPON THE VELOCITY OF THE SODIUM THIOSULFATE–SODIUM BROMOACETATE REACTION

No.	Concn., mole/ liter of re- acting ions $a = b$	Mole of added salt per liter	$\sqrt{\mu}$	k	log k	log k/k_0	$\frac{\log k/k_0}{2\sqrt{\mu}}$
				Added salt LaCl$_3$			
La 1	0.001	0.00343	0.157	2.85 ± 0.01	0.455	1.069	3.4
La 2	.001	.00572	.196	3.05 ± .03	.484	1.098	2.8
La 3	.0005	.00172	.111	2.71 ± .02	.433	1.047	4.7
La 4	.0005	.001372	.101	2.55 ± .02	.406	1.020	5.1
La 5	.0005	.001022	.0902	2.26 ± .05	.354	0.968	5.4
La 6	.0005	.000695	.0785	1.91 ± .02	.281	0.895	5.7
				MgSO$_4$			
Mg 21	.005	.002125	.242	.823 ± .002	$\overline{1}$.915	...	..
				MgCl$_2$			
Mg 22	.005	.0425	.394	.899 ± .004	$\overline{1}$.954	...	..
				NaCl			
Na C	.004	3.0 NaCl	1.735	1.55 ± .02	0.190	.80	0.23
Na D	.004	{ 3.0 NaCl / 0.05 MgCl$_2$	1.779	1.50 ± .03	0.176	.79	0.22
			Saturated Carbon Dioxide				
Na E	.01	P_H = 4.8	0.200	0.645	...	...	..

Compare Na E with Na 3 of Table I.

and five others which showed large deviations from the smooth curve when plotted were rejected.

The results in Table II were obtained by adding salts with trivalent cations to a dilute reaction mixture of the sodium salts. While this method does not permit measurements at very low ionic strengths it shows the profound catalytic effect of trivalent cations upon this reaction.

The theoretical meaning of the results given in the last two columns of Tables I and II will be discussed in detail in another section. Otherwise the headings of the columns are self-explanatory.

VII. Discussion of Results

By plotting the logarithm of the observed velocity constant k against the square root of the ionic strength, equation (4) demands that a straight line be approached having a slope equal to the product of the valences of the reacting ions, namely, $Z_A \cdot Z_B$. The intercept on the ordinate when the ionic strength equals zero corresponds to the value of k_0, the specific reaction velocity constant, which is free from the disturbing concentration influences of interionic attraction provided the experimental data in finite concentrations obey equation (4) with sufficient precision to render the extrapolation trustworthy. A number of investigators have demonstrated the general validity of equation (4) but examples in which it fails are not lacking.[20.3]
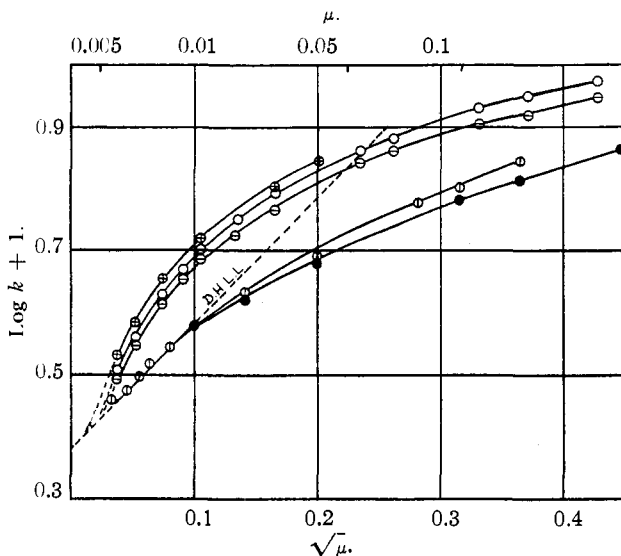
Fig. 1.—$\oplus$, Barium; $\bigcirc$, calcium; $\ominus$, magnesium; $\oplus$, potassium; $\bullet$, sodium salts.

Our experimental results are shown graphically in Figs. 1 and 2 to test the validity of equation (4). The curve for the univalent potassium ion coincides with the limiting slope ($Z_A Z_B = 2.0$) for values of the square root of the ionic strength less than 0.03. In other words, the limiting law holds for the reaction in the presence of the univalent potassium ion in agreement with the conclusion reached by La Mer[9] for the reaction in the presence of the sodium ion. The new results for the sodium and potassium ion are also identical within the experimental error for values of $\sqrt{\mu}$ less than 0.1 as shown by Fig. 1. This agreement of the experimen-

[20] Conant and Peterson, THIS JOURNAL, 52, 1220 (1930). See page 1227. See Ref. 3 for reaction of β-bromopropionate ion and thiosulfate ion in highly dilute solutions.

tal results with the Debye–Hückel limiting law in the presence of these univalent cations is in accord with the results of the solubility studies, no appreciable discrepancy having been found for trivalent ions in the presence of univalent ions of opposite sign.
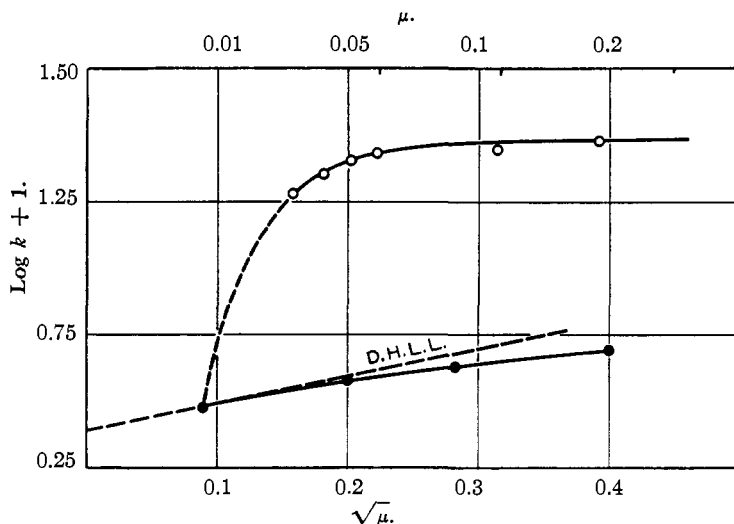

Fig. 2.—Dots, sodium salts; circles, lanthanum chloride added to lowest concentration of sodium salts of reactants.

The kinetic data obtained for this reaction involving a trivalent critical complex are of quite a different character in the presence of divalent cations. The curves for those cations cross the limiting slope at relatively high concentrations and with increasing dilution show a decided downward curvature with a slope steeper than the theoretical. The data are consistently specific for each cation. This specificity persists down to the lowest concentration studied, namely, $\sqrt{\mu} = 0.037$ or 0.00025 M for each reacting ion.

The form of these curves can be interpreted by the solubility studies of La Mer and Mason[5] and the theoretical contributions of Gronwall, La Mer and Sandved.[21] These authors[5,6,7] have shown that the activity coefficients of high valence ions in the presence of high valence ions of opposite sign are considerably smaller than the values calculated by the Debye–Hückel limiting law. The kinetic factor in the reaction under discussion is of the type $f_1 f_2 / f_3$ where f_1 refers to the activity coefficient of the bromoacetate ion; f_2 to the thiosulfate ion and f_3 to the triply charged critical complex X. The effect of a high valence cation in the environment will be to give f_3 a value very much smaller than that calculated by the Debye–Hückel limiting law. The values of f_1 and f_2 will also de-

[21] Gronwall, La Mer and Sandved, *Physik. Z.*, **29**, 358 (1928).

crease somewhat in the presence of a high valence cation but the decrease will not be sufficient to effect the decrease in f_3. The total effect on changing the environment from a univalent to a divalent or trivalent cation will be to increase the value of $f_1 f_2/f_3$. The experimental results agree with this prediction. The velocity constants for the reaction in the presence of divalent cations are always greater than those for the univalent potassium or sodium ion. Since this work was completed a paper by King and Jacobs[22] upon the kinetics of the persulfate–iodide reaction has been published. Their results furnish another excellent example of the validity of equation (4) in the presence of the univalent potassium ion. In the presence of added *magnesium sulfate* there is also evidence of a "hump" type curve in their reaction. Unfortunately, as they point out, their reaction is complicated by the presence of the thiosulfate added to measure the progress of the reaction and consequently does not constitute an unambiguous example of this anomaly. The large "hump" noted with the persulfate additions is very likely due to reaction between thiosulfate and persulfate and should not be confused with the present anomaly since it appears at high concentrations.

Since the value of k_0, the velocity constant for the reaction at infinite dilution, must be the same for all cations, all the curves must extrapolate to the same point. Any extrapolation to a limiting value is always burdened with some degree of uncertainty. A linear extrapolation with the aid of a theory based on reasonable postulates and in agreement with the data at finite concentrations involves the least possible uncertainty. We have accordingly evaluated k_0 by a linear extrapolation of the data for the reaction in the presence of the potassium ion in accordance with the limiting slope. The selection of the potassium data is justified by the disappearance of the specific effects of the sodium and potassium ions as demanded by the Debye–Hückel limiting law and by the agreement of the linear portion of the curve with the theoretical value of the limiting slope. This extrapolation gives log $k_0 = \bar{1}.386$ or $k_0 = 0.243$. Extrapolation of the previous[9] results for this reaction in the presence of the sodium ion gives log $k_0 = \bar{1}.385$, or $k_0 = 0.243$.

Since the curves for calcium, barium and magnesium must extrapolate to the same value of log k_0 as those of the univalent cations, a point of inflection must occur in the curves for the divalent cations if the limiting slope is reached at extreme dilution. The existence of such a point of inflection is in harmony with the requirements of the Gronwall, La Mer and Sandved[21] extension of the Debye–Hückel theory and with recent experimental data on the behavior of the activity coefficients of cadmium sulfate and of zinc sulfate in high dilution.[23,24]

[22] King and Jacobs, THIS JOURNAL, **53**, 2704 (1931).
[23] La Mer and Parks, *ibid.*, **53**, 2040 (1931).
[24] Cowperthwaite and La Mer, *ibid.*, **53**, 4333 (1931).

A plot of the results with lanthanum chloride added to the reaction mixture (method b) is given in Fig. 2. These results demonstrate the profound catalytic effect produced by changing from a divalent to a trivalent cation. Since lanthanum chloride was added to the sodium salts of the reactants, the curve for lanthanum must join the sodium curve at a point corresponding to the concentration of the sodium salts alone. There will be, therefore, an abrupt change of slope at this point just as in the solubility studies where a foreign neutral salt is added to a solute to increase the solubility. This abrupt change in slope will always occur in the kinetic case when method (b) is used. With method (a) (only one cation and no foreign anions present) the curve will be smooth and pass through a point of inflection.
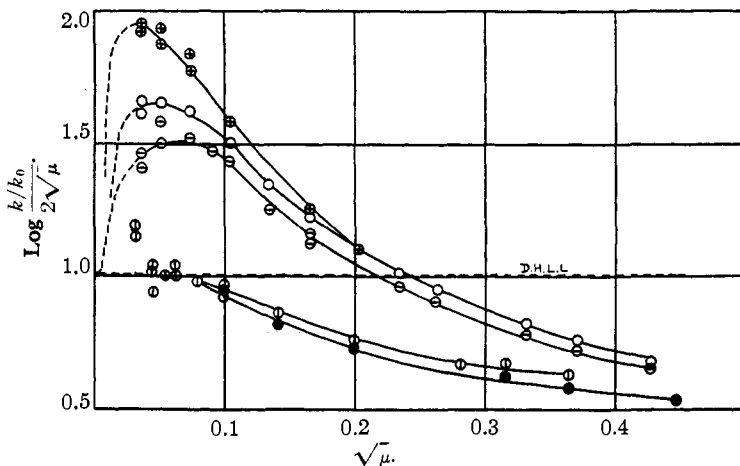

Fig. 3.—$\oplus$, Ba^{++}; O, Ca^{++}; $\ominus$, Mg^{++}; $\oplus$, K^{+}; $\bullet$, Na^{+}.

The kinetics of the reaction $2[\text{Co(NH}_3)_5\text{Br}]^{++} + \text{Hg}^{++} \rightleftharpoons [\text{X}]^{++++} \longrightarrow$ $2 [\text{Co(NH}_3)_5\text{H}_2\text{O}]^{+++} + \text{HgBr}_2$ involving a tetravalent positive ion as the critical complex were studied by Brönsted and Livingston[4] for the purpose of testing the obedience of the kinetic factor to the limiting law. Although precise activity coefficients have never been obtained for tetravalent ions, nevertheless there is reason to surmise from the freezing point data on $\text{K}_4\text{Fe(CN)}_6$ and from the e. m. f. data on the ferro–ferricyanide electrode[25] that deviations from the limiting law should persist down to the lowest concentrations studied by Brönsted and Livingston. An examination of their most consistent series (Fig. 5, no added salt) actually yields a limiting *experimental slope of 7 to 8 instead of the theoretical value of 4.* This series also exhibits the same curvature we have shown in Fig. 1 for the divalent cations.

[25] La Mer and Sandved, THIS JOURNAL, 50, 2656 (1928).

Brönsted and Livingston avoid this conclusion by ignoring their data at the lowest concentrations. Instead they[26] pass a straight line of theoretical slope through the data at intermediate concentrations. The present investigation shows this to be an unwarranted procedure, particularly for reactions between ions of the same sign. Our interpretation would involve a considerable displacement in the extrapolated value of k_0 employed by these authors.
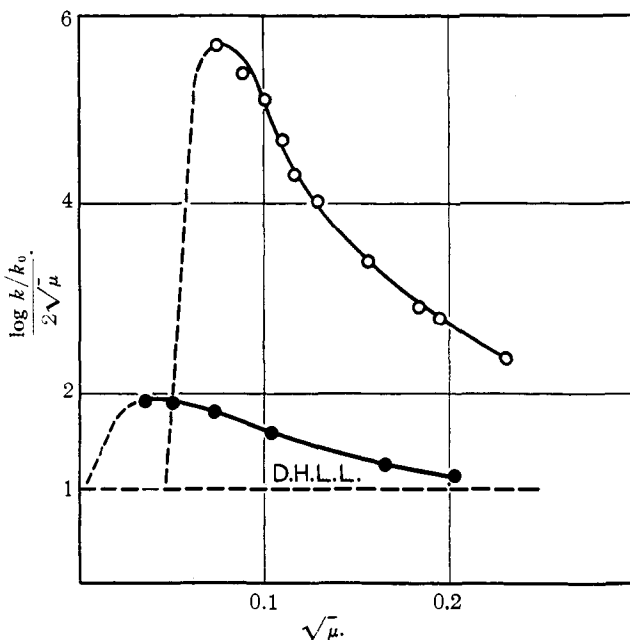

Fig. 4.—O, La^{+++}; ●, Ba^{++}.

From equation (4) it is evident that $\log(k/k_0)/Z_A Z_B \sqrt{\mu}$ is the ratio between the experimental value of the kinetic activity coefficient factor and the ideal limiting value. The values of $\log(k/k_0)/2 \sqrt{\mu}$ are given in Tables I and II and plotted in Fig. 3. This plot furnishes a more severe test of the experimental precision in the dilute region and shows the changes in slope as a function of the $\sqrt{\mu}$. The curves for sodium and potassium give a horizontal line (value equal to unity) agreeing within experimental error with the limiting law up to $\sqrt{\mu} = 0.030$. At higher concentrations the ratio decreases. With barium, calcium and magnesium the curve does not approach the limiting value at the lowest concentrations studied. At the higher concentrations the value of $\log(k/k_0)/2 \sqrt{\mu}$ is less than unity as in the univalent case. The ratio increases with dilution until it be-

[26] Livingston, *J. Chem. Education*, 7, 2887 (1930), where a part of the data is replotted.

comes from 40 to 90% greater than the limiting value. The effect is still more pronounced with the lanthanum ion, Fig. 4. At $\sqrt{\mu} = 0.196$ the ratio is over 100% greater than the limiting value and at $\sqrt{\mu} = 0.90$ it has increased to 5.4.

No attempt has been made to treat the kinetic results quantitatively by use of the mathematical expressions for the higher terms of the Poisson–Boltzmann equation as developed for the unsymmetrical case by La Mer, Gronwall, and Greiff.[8] To avoid the introduction of more than one arbitrary parameter the assumption of an average ion size for the three salt types involved is necessary. Such an assumption does not seem justifiable. Furthermore, the structure of the critical complex is so uncertain that any arbitrary assignment of an ion size in the present state of knowledge would be pure speculation. However, the forms of the curves are in such close agreement with the predictions of the solubility studies that there can be little doubt of the common origin of the anomaly. The observed deviations from the limiting law may, therefore, be safely ascribed more to failure of the individual ion activity coefficients in high valence mixtures to conform to the Debye–Hückel limiting law than to an incorrect form of the kinetic activity coefficient correction given by the Brönsted rate equation.[2] However some modifications will very likely be needed to account for orientation,[3] viscosity and non-thermodynamic factors of kinetic influence.

VIII. Summary

The kinetics of the thiosulfate–bromoacetate reaction have been studied at 25° in the presence of sodium, potassium, magnesium, calcium, barium and lanthanum ions in the region of highly dilute solution.

The velocity constants for the thiosulfate–bromoacetate reaction are reproducible in an atmosphere of nitrogen at a concentration of 0.00025 M and show no drift with time.

The experimental results for the reaction in the presence of the univalent sodium and potassium ions agree with the theoretical equation developed on the basis of the Debye–Hückel limiting law.

In the presence of the divalent cations deviations of 40 to 80% from the limiting equation were observed while in the presence of the trivalent lanthanum ion a deviation of 440% is found at $\sqrt{\mu} = 0.09$.

A plot of log k against $\sqrt{\mu}$ for the results in the presence of high valence cations exhibits the characteristic types of curves predicted from solubility data for similar valence types and by the La Mer, Gronwall and Greiff extension of the Debye–Hückel theory to unsymmetric valence types, a result which verifies Brönsted's theory of ionic catalysis, but necessarily limits the applicability of the Debye–Hückel limiting law as an extrapolation equation for reactions between ions of the same sign.

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