The Decomposition of Hypochlorite–Hypobromite Mixtures in the pH Range 7–10

BY MENACHEM LEWIN AND MENASHE AVRAHAMI

The system hypochlorite–hypobromite was investigated in the pH range 7–10. It was found that the behavior of this system is characterized by the formation of chlorate and bromate and that the decomposition of hypochlorite is catalyzed by the presence of hypobromite. The rate is increased by roughly three orders of magnitude as a result. While both the decomposition of hypochlorite alone and of hypobromite alone are second-order reactions, an approximate special mechanism is proposed for the behavior of the hypochlorite–hypobromite system in the pH range 7–10, accounting for the behavior of the system at different pH's within the range, as well as for the effect of adding certain neutral salts.

In a previous communication it was shown that bromides in the pH range 10 to 13 are quantitatively oxidized by hypochlorite to hypobromite.[1] The oxidation takes place according to

$$HOCl + Br^- \longrightarrow HOBr + Cl^- \qquad (I)$$

In the pH range 7 to 10 the mixtures of hypochlorite and hypobromite are unstable, and chlorate and bromate are formed. It was also found, subsequent to the publication of the previous paper[1] that measurable quantities of chlorate and bromate are formed in the pH range even above 11, after several hours standing, i.e., after the reaction I has gone to completion. While the kinetics of the decomposition of pure hypohalite solutions have been extensively investigated,[2–15] only investigations of an analytical nature have thus far been published on the reaction which takes place in mixtures of hypochlorite and hypobromite. Various authors[16–19] described the conditions for the quantitative oxidation of bromide to bromate. The formation of chlorate is mentioned only by van der Meulen.[16]

In the present paper some kinetical data on the rate of formation of chlorate and bromate in solutions of hypochlorite–hypobromite mixtures at various pH values are given, and a mechanism is proposed.

Experimental

The preparation of the solutions has been described.[20] Into dark-colored, glass-stoppered flasks of 300-ml. capacity which were kept in a thermostat at $25 \pm 0.1°$, the reagents were added in the

(1) L. Farkas, M. Lewin and R. Bloch, THIS JOURNAL, **71**, 1988 (1949).
(2) F. Foerster and Jorre, J. prakt. Chem., **59**, 60 (1899).
(3) F. Foerster, ibid., **63**, 141 (1901).
(4) J. Clarens, Compt. rend., **157**, 216 (1913).
(5) F. Foerster and P. Dolch, Z. Elektrochem., **23**, 137 (1917).
(6) H. Kauffman, Z. angew. Chem., **37**, 364 (1924).
(7) J. J. Weiss, Z. Elektrochem., **37**, 20 (1931).
(8) H. A. Liebhafsky and B. Makower, J. Phys. Chem., **37**, 1037 (1933).
(9) R. M. Chapin, THIS JOURNAL, **56**, 2211 (1934).
(10) A. Skrabal and A. Berger, Monatsh., **70**, 163 (1937).
(11) A. Skrabal and R. Skrabal, ibid., **71**, 251 (1938).
(12) A. Skrabal, ibid., **72**, 200, 223 (1938); **73**, 269 (1941).
(13) A. Skrabal, Z. Elektrochem., **48**, 314 (1942).
(14) C. F. Prutton and S. H. Maron, THIS JOURNAL, **57**, 1652 (1935).
(15) P. Engel, A. Oplatka and B. Perlmutter-Hayman, ibid., **76**, 2010 (1954).
(16) J. H. van der Meulen, Chem. Weekblad, **28**, 82 (1931).
(17) T. F. Dixon, Biochem. J., **28**, 48 (1934).
(18) H. H. Willard and A. Heyn, ibid., **15**, 321 (1934).
(19) I. M. Kolthoff and H. Yutzy, Ind. Eng. Chem. Anal. Ed., **9**, 75 (1937).
(20) L. Farkas and M. Lewin, Anal. Chem., **19**, 662, 665 (1947).

following order: water, buffer, hypochlorite, bromide. The time of the reaction was measured from the moment the bromide was added. At certain intervals, samples were withdrawn and pipetted into 50-ml. measuring flasks containing an excess of alkali, which stops the reactions. After diluting the samples to 50 ml., the analyses were carried out on aliquot parts.

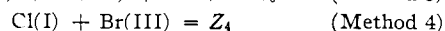The composition of the reacting mixtures was determined by the following four volumetric methods.
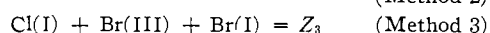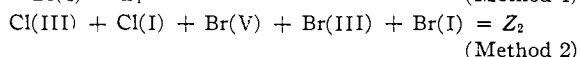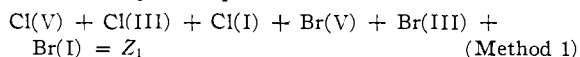
(1) The sum of normalities of chlorate Cl(V), chlorite Cl(III), hypochlorite Cl(I), bromate Br(V), bromite Br(III) and hypobromite Br(I), was determined by the ferrous sulfate–permanganate method. It was ascertained by a separate experiment that no gaseous oxygen is evolved in these conditions.

(2) The sum of chlorite, hypochlorite, bromate, bromite and hypobromite was determined by adding the samples to an acidified solution of potassium iodide and titrating with thiosulfate.

(3) The sum of hypochlorite, bromite and hypobromite was determined by means of the arsenite–iodine titration.

(4) The estimation of hypochlorite and bromite was carried out by the phenol–arsenite–iodine method.[9,20]

The analytical procedure can be schematically described by the equations

$$Cl(V) + Cl(III) + Cl(I) + Br(V) + Br(III) +$$
$$Br(I) = Z_1 \qquad \text{(Method 1)}$$
$$Cl(III) + Cl(I) + Br(V) + Br(III) + Br(I) = Z_2$$
$$\text{(Method 2)}$$
$$Cl(I) + Br(III) + Br(I) = Z_3 \qquad \text{(Method 3)}$$
$$Cl(I) + Br(III) = Z_4 \qquad \text{(Method 4)}$$

where all symbols are expressed in moles hypohalite per liter. By means of these titrations the concentrations of hypobromite $(Z_3 - Z_4)$ and chlorite $(Z_1 - Z_2)$ are accurately determined. Beside the concentrations of these two components only the sum of bromate and chlorite $(Z_2 - Z_3)$ and the sum of hypochlorite and bromite (Z_4) can be given. However, the sum of bromate, bromite and hypobromite present in the reaction mixture, and expressed in moles is equal at any time to the initial concentration of hypobromite, i.e.

$$^1/_3 Br(V) - ^1/_2 Br(III) - Br(I) = b$$
$$^1/_3 Br(V) - ^1/_2 Br(III) = b - Br(I) = \Delta Br(I)$$

where b is the initial concentration of hypobromite in the solution and $\Delta Br(I)$ is the concentration of hypobromite decomposed at a given time.

Since the bromite is determined only together with chlorite $(Z_2 - Z_3)$ the equation will change into

$$[^{1}/_{3}Br(V) + {}^{1}/_{2}Cl(III)] + {}^{1}/_{2}Br(III) \approx \Delta Br(I)$$

If the difference $\Delta Br(I) - [^{1}/_{3} Br(V) + {}^{1}/_{2} Cl(III)]$ is positive the lower limit of the bromite present in the solution is determined, since the chlorite possibly present will decrease the value of the difference. On the other hand, a negative difference will determine the lower limit of the chlorite present in the solution, since a part of the hypobromite may have yielded bromite and thus a larger part of the titrated quantity $Z_2 - Z_3$ might be attributed to chlorite.

As the quantities of bromite and chlorite could not be determined independently and as the lower limits calculated in the above way were very small, they were not recorded in the tables of this paper.

The pH of the solution was measured with a glass electrode with an accuracy of ± 0.02 pH unit and was, unless otherwise stated, adjusted by means of a borate buffer to which alkali or acid were added. In spite of the high buffer concentrations, the pH of the solution decreased somewhat and therefore occasionally had to be adjusted during the experiment. This is due to the decrease of hypochlorite

Fig. 1.—Decomposition of hypochlorite (A) and of a hypochlorite–hypobromite mixture (B-E) at pH 7. Change in concentration of bromate plus hypobromite plus hypochlorite (B), of hypochlorite plus hypobromite (C), of hypochlorite (D) and of hypobromite (E) with time.

Fig. 2.—Decomposition of hypochlorite (A) and of a hypochlorite–hypobromite mixture (B-E) at pH 9.04. Change in concentration of bromate plus hypobromite plus hypochlorite (B), of hypochlorite plus hypobromite (C), of hypochlorite (D) and of hypobromite (E) with time.

and hypobromite concentrations which exert an additional buffer action in the pH range 7 to 10. The pH values appearing in the tables are mean values computed from the values recorded during the experiments. The total electrolyte concentration in all experiments, unless otherwise stated, was 0.18 mole per liter and was brought to this value by the addition of appropriate amounts of neutral salts.

The hypobromite solutions used in this investigation were usually prepared immediately before the experiments by adding an equivalent amount of potassium bromide to a hypochlorite solution at pH 9–9.4.[20] The hypobromite solutions prepared in this way were practically free of bromide.[21]

Bromite solutions were prepared according to a method described by Chapin.[9] The solutions contained considerable amounts of bromate and bromide. Most of the bromate and all of the bromide were removed by precipitation with $Ba(OH)_2$, and freshly prepared Ag_2O. The bromite solutions were kept in a refrigerator and their composition did not appreciably change after six months storage.

Chlorite solutions were prepared from pure chlorite powder produced by N. V. Ned. Patent en Kristal Sodafabrick.

Experiments with bromite and chlorite were carried out at conditions similar to those described above for the experiments with hypochlorite and bromide.

Results and Discussion

The course of a typical experiment is shown in Table I and Figs. 1 and 2. The meaning of symbols κ, k_1 and k_3 is explained below. It will be seen from Fig. 1 that the rate of decomposition of hypochlorite in the presence of hypobromite is much higher than in the absence of hypobromite (dotted line).
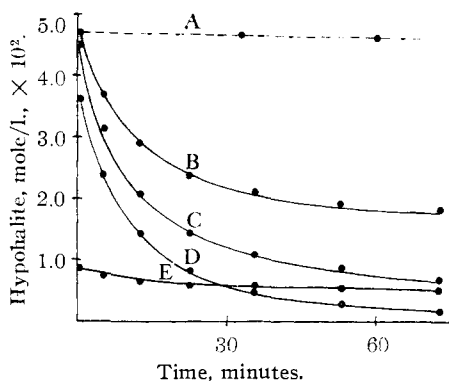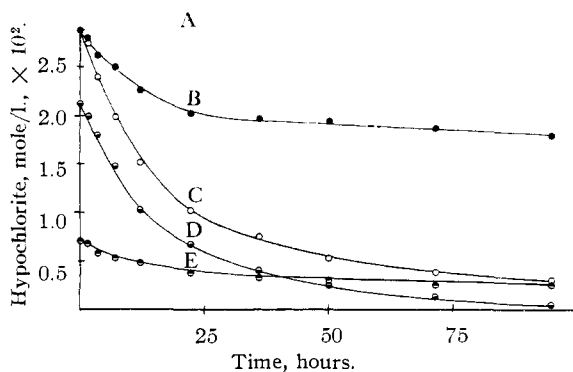
TABLE I

THE COURSE OF A TYPICAL EXPERIMENT[a]

$t = 25 \pm 0.1°$, pH $= 7$, 0.1 mole/l. borax.

Time, min.	Br-(V)+ Br-(I)+ Cl(I), mole/l., 10^2	Cl-(I)+ Br(I), mole/l., 10^2	Cl(I), mole/l., 10^2	Cl(V), mole/l., 10^2	Br(V), mole/l., 10^2	$\kappa + \dfrac{}{2}$	k_3, l./ mole. min.	k_1, l./ mole. min.
0	4.739	4.562	3.666	...	...	...	...	...
5.25	3.735	3.180	2.405	1.004	0.555	7.427	1.091	2.55
12.5	2.934	2.136	1.461	1.805	0.798	8.786	1.092	2.55
22.25	2.397	1.448	0.837	2.342	0.949	9.251	1.065	2.49
35.5	2.137	1.102	.526	2.602	1.035	9.542	0.925	2.16
53	1.947	0.845	.306	2.792	1.102	9.601	0.833	1.95
72.25	1.860	0.698	.170	2.879	1.162	9.433	0.787	1.84

[a] All concentrations in this and subsequent tables of this paper are expressed in moles of hypohalite per liter.

TABLE II

DECOMPOSITION OF HYPOCHLORITE IN THE ABSENCE AND IN THE PRESENCE OF HYPOBROMITE

$t = 25 \pm 0.1°$, 0.1 mole/l. borax.

pH	Cl(I), mole/l., 10^2	Br(I), mole/l., 10^2	(Cl-), mole/l.	μ	Half-time period
9.12	2.65	0	0.43	0.56	4000 hr.
9.11	2.12	0.71	.43	.57	15 hr.
7.94	3.83	0	.03	.08	394 hr.
7.85	2.89	0.81	.03	.10	30 min.
7.0	4.40	0	.04	.20	22 hr.
7.0	3.67	0.90	.04	.22	10 min.

(21) M. Lewin, Bull. Res. Counc. Israel, 2, 101 (1952).

The same effect may be seen for three pH values from Table II. The half-time period of the decomposition of hypochlorite in the presence of hypobromite is shorter by three orders of magnitude.

In Table III, half-time values of decomposition of hypobromite in the presence and absence of hypochlorite are summarized. It is seen that the rates are of a similar order of magnitude.

TABLE III

DECOMPOSITION OF HYPOBROMITE IN THE ABSENCE AND IN THE PRESENCE OF HYPOCHLORITE
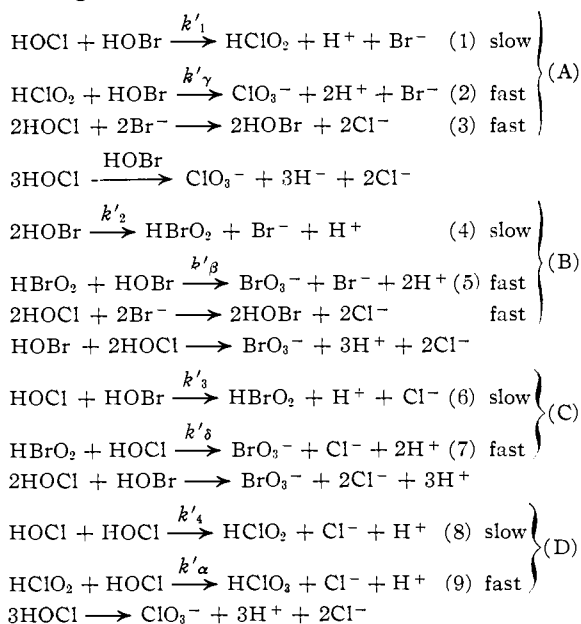
$t = 25 \pm 0.1°$, 0.1 mole/l. borax.

pH	[Br(I)], mole/l., 10^2	[Cl(I)], mole/l., 10^2	Half-time period, min.
7.9	2.46	0	174
7.85	0.81	2.89	190

TABLE IV

THE INFLUENCE OF pH ON THE RATE OF DECOMPOSITION OF HYPOCHLORITE-HYPOBROMITE MIXTURES

Temp. $= 25 \pm 0.1°$, 0.1 mole/l. borate buffer, 0.05 mole/l. $> (Cl') > 0.03$ mole/l.

pH	$a \times 10^2$, mole/l.	$b \times 10^2$, mole/l.	μ	κ	$k_3 \times 10^3$, l./mole.min.	$k_1 \times 10^3$, l./mole.min.	Remarks
7.0	3.666	0.896	0.22	7.0	968	2260	
7.4	3.122	.778	.18	6.9	983	2260	
7.85	2.890	.810	.16	6.1	420	850	
7.9	3.125	.775	.18	5.6	490	915	
8.25	3.092	.778	.18	3.6	237	286	
8.75	2.809	.929	.18	2.2	78.3	57.5	
9.0	2.163	.707	.17	2.6	37.5	32.5	
9.0	2.041	.730	.37	2.5	25.4	21.2	KNO_3 0.2 mole/l.
9.1	2.138	.680	.37	2.4	32	26.1	$KClO_3$ 0.2 mole/l.
9.15	2.473	.417	.18	1.1	39	14.3	
9.6	2.083	.720	.22	1.6	4.4	2.35	
9.9	2.370	.690	.47	1.5	4.0	1.97	Carbonate bicarbonate buffer

The reactions involved can best be understood in the light of the following approximate mechanism

$$HOCl + HOBr \xrightarrow{k'_1} HClO_2 + H^+ + Br^- \quad (1) \text{ slow}$$

$$HClO_2 + HOBr \xrightarrow{k'_\gamma} ClO_3^- + 2H^+ + Br^- \quad (2) \text{ fast}$$

$$2HOCl + 2Br^- \longrightarrow 2HOBr + 2Cl^- \quad (3) \text{ fast}$$

$\left.\right\}$ (A)

$$3HOCl \xrightarrow{HOBr} ClO_3^- + 3H^- + 2Cl^-$$

$$2HOBr \xrightarrow{k'_2} HBrO_2 + Br^- + H^+ \quad (4) \text{ slow}$$

$$HBrO_2 + HOBr \xrightarrow{b'_\beta} BrO_3^- + Br^- + 2H^+ \quad (5) \text{ fast}$$

$$2HOCl + 2Br^- \longrightarrow 2HOBr + 2Cl^- \quad \text{fast}$$

$\left.\right\}$ (B)

$$HOBr + 2HOCl \longrightarrow BrO_3^- + 3H^+ + 2Cl^-$$

$$HOCl + HOBr \xrightarrow{k'_3} HBrO_2 + H^+ + Cl^- \quad (6) \text{ slow}$$

$$HBrO_2 + HOCl \xrightarrow{k'_\delta} BrO_3^- + Cl^- + 2H^+ \quad (7) \text{ fast}$$

$\left.\right\}$ (C)

$$2HOCl + HOBr \longrightarrow BrO_3^- + 2Cl^- + 3H^+$$

$$HOCl + HOCl \xrightarrow{k'_4} HClO_2 + Cl^- + H^+ \quad (8) \text{ slow}$$

$$HClO_2 + HOCl \xrightarrow{k'_\alpha} HClO_3 + Cl^- + H^+ \quad (9) \text{ fast}$$

$\left.\right\}$ (D)

$$3HOCl \longrightarrow ClO_3^- + 3H^+ + 2Cl^-$$

The rate of the autodecomposition of hypochlorite (D) as seen in Table II is negligible and was therefore disregarded.

The hypobromite solutions decompose in the pH range 7–10 at a much higher rate than the hypochlorite solutions at equal temperatures and concentrations (cf. Tables II and III). Since it is generally assumed that both reactions pass through the stage of the halite and that the formation of the halite is the rate-determining step,[9,15] it is evident that HOBr is in this pH range much more reactive than HOCl. If the formation of chlorate in the hypochlorite–hypobromite system also proceeds through the stage of chlorite, it may be assumed that the chlorite is formed by HOCl and HOBr according to reaction (1). The rate of reaction (1) would have to be at least by two orders of magnitude higher than the rate of reaction (8) in order to account for the accelerating action of the hypobromite on the rate of the decomposition of hypochlorite.

Another possibility might have been the formation of chlorate via the stage of bromite according to the equations

$$HOCl + HOBr \longrightarrow HBrO_2 + H^+ + Cl^- \quad (6)$$
$$HBrO_2 + HOCl \longrightarrow ClO_3^- + Br^- + 2H^+ \quad (7')$$
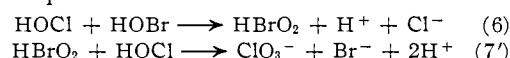
This possibility seems, however, highly improbable, as it involves two oxidizing stages in reaction (7').

It is of course possible that reaction (1) and the other reactions listed in the above mechanism may be composite and proceed through intermediate stages owing to the complicated nature of the reactions. It was outside the scope of this investigation to study the intimate mechanism of each of the separate steps.

In order to decide whether the chlorate is formed from the chlorite by reaction (2) or by reaction (9), separate experiments have been carried out at pH 9.2, and concentrations of 3×10^{-2} mole per liter and the second–order rate constants k_γ and k_α were found to be 3.5 ± 0.04 and 0.49 ± 0.02 min.$^{-1}$ mole^{-1} l., respectively.

From similar experiments carried out at pH 8.5 values of 23.8 ± 0.6 for k_γ and 13.7 ± 2.5 min.$^{-1}$ mole^{-1} l. for k_α were found. It seems, therefore, more justified to assume that the formation of chlorate proceeds through reaction (2) rather than through reaction (9).

Experiments were also carried out at pH 9.2 and 8.2 and concentrations in the range of 0.0045–0.0075 mole per liter in order to determine whether the bromate is formed from the bromite by reaction (5) or by reaction (7). The second-order rate constants k_β were found to be 0.59 ± 0.08 min.$^{-1}$ mole^{-1} l. at pH 9.2 and 13.5 ± 0.5 at pH 8.2 for reaction (5). For reaction (7) the constants k_δ were 1.3 ± 0.7 and 48 ± 10 min.$^{-1}$ mole^{-1} l. at pH 9.2 and 8.2, respectively. Whereas the values of the second-order rate constants for reaction (5) seem to be in reasonable agreement with the value of 1.10 ± 0.20 found by Perlmutter-Hayman, et al.,[15] at pH 8.84, no such values at similar conditions seem to be recorded in the literature[5,9,22] for reaction (9) and no data were found on reactions (2) and (7).

The rate constants of reaction (7) were calculated from the first 20% of the reaction in which

(22) J. F. White, M. C. Taylor and G. P. Vincent, Ind. Eng. Chem., 34, 782 (1942).

almost only bromate is formed. In the later stages of this reaction the effect of a reaction between bromate, initially present in the bromite solution at a concentration of 0.08 mole/l. and the hypochlorite producing hypobromite and chlorate (see later) is complicating the results.

The assumption that the formation of bromate from bromite proceeds through reaction (7) seems therefore to be more probable than through reaction (5), when considering that the conditions of the experiments reported in this paper involved appreciably higher concentrations of hypochlorite than of hypobromite (see Table IV). The close values, however, of the rate constants of all four reactions considered, especially in the lower pH range, indicate possible contributions of the reactions (5) and (9) to the reaction mechanism.[23]

We have thus assumed three simultaneous reactions, (A), (B) and (C). In the chlorate formation (A), the hypobromite appears as a catalyst, and its concentration remains constant. Reaction (3) being very fast in this pH range, the bromide concentration is practically zero and no elementary bromine is produced. Kinetically we have

$$\frac{dx}{dt} = 3k_1 (a - x) (b - y) + 2k_3 (a - x) (b - y) + 2k_2 (b - y)^2 \quad (10)$$

$$\frac{dy}{dt} = k_3(a - x)(b - y) + k_2(b - y)^2 \quad (11)$$

where $(a - x)$ and $(b - y)$ are the respective concentrations of (HOCl) + (ClO$^-$) and (HOBr) + (BrO$^-$) at the time t.

The quotient of (10) and (11) gives:

$$\frac{dx}{dy} = \frac{3k_1(a - x)}{k_3(a - x) + k_2(b - y)} + 2 \quad (12)$$

Neglecting expression $k_2(b - y)$ in (12) a procedure which will be justified later, and integrating

$$\frac{x}{y}\kappa = + 2, \text{ where (14) } \kappa = \frac{3k_1}{k_3} \quad (13)$$

κ will therefore be independent of time for a given pH.

In Fig. 3, x was plotted against y for two experiments carried out at pH 7 and 9.1, respectively. The experiments were carried up to a decomposition of 95.4% of the initial hypochlorite at pH 7 and 96.3% at pH 9.1. The straight lines in Fig. 3 show
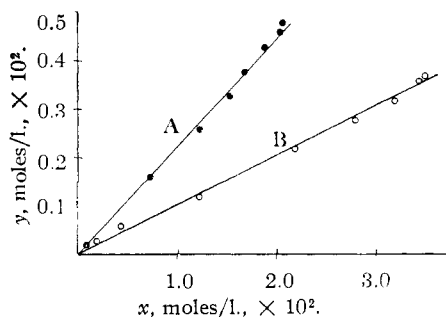

Fig. 3.—Plots of y (hypobromite) against x (hypochlorite) for experiments at pH 9.08 (A) and at pH 7 (B).

(23) The reactions (2), (5), (7) and (9) are not strictly of the second order, and intermediates, such as ClO₂ in case of reaction (9), are formed. The rate constants reported here are average values of the over-all reactions.

that reaction (B) plays an insignificant part in the mechanism and may be neglected. It will be seen that a small deviation from the straight line occurs only at the highest values of x and y, when almost all the hypochlorite has decomposed and the remaining hypobromite decomposed by itself according to reaction (B). It is only in the last 10% of the reaction that the expression $k_2(b - y)$ in equation 12 becomes significant, causing κ to decrease slightly.

Equations 10 and 11 may therefore be written as

$$\frac{dx}{dt} = 3k_1(a - x)(b - y) + 2k_3(a - x)(b - y) \quad (10a)$$

$$\frac{dy}{dt} = k_3(a - x)(b - y) \quad (11a)$$

Substituting (14) into (10a) and putting $d = b(\kappa + 2)$, we get

$$\frac{dx}{dt} = k_3(a - x)(d - x) \quad (15)$$

Upon integration

$$k_3 = \frac{2.303}{t(a - d)} \log \frac{d(a - x)}{a(d - x)} \quad (15a)$$

κ was calculated from (13), using titration data and graphs similar to those of Fig. 3. It should be realized that a small error is introduced in this calculation as the values of x determined according to titration (4) (see "Experimental") contain some bromite. κ was also calculated from the expression

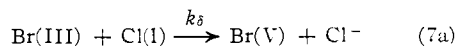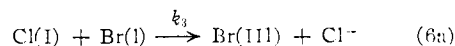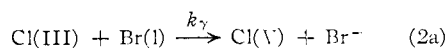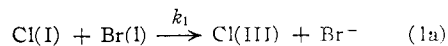$$\kappa + 2 = \frac{3(ClO_3^-) + 2(BrO_3^-)}{(BrO_3^-)} \quad (16)$$

as 3 molecules of hypochlorite decompose, giving one molecule of chlorate and 2 molecules of hypochlorite are reduced in the formation of one molecule of bromate.

On calculating values of κ from expression (16), a different error is introduced, as the amounts of bromate determined from the titrations (2) and (3) contain some chlorite. The values of κ calculated from (13) corresponded fairly well to those calculated from (16), thus indicating that the errors caused by the possible small amounts of chlorite and bromite are not too serious. k_3 and k_1 were calculated from (15a) and (14), respectively.

It will be seen from Table I that κ, k_1 and k_3 are reasonably constant, especially if the small changes in pH during the experiment are taken into account, pointing to second-order kinetics.

Some evidence on the maximum concentrations of chlorite and bromite in the reaction mixture may be obtained by the following kinetic considerations. Reactions (1), (2), (6) and (7) may be rewritten

$$Cl(I) + Br(I) \xrightarrow{k_1} Cl(III) + Br^- \quad (1a)$$

$$Cl(III) + Br(I) \xrightarrow{k_\gamma} Cl(V) + Br^- \quad (2a)$$

$$Cl(I) + Br(I) \xrightarrow{k_3} Br(III) + Cl^- \quad (6a)$$

$$Br(III) + Cl(I) \xrightarrow{k_\delta} Br(V) + Cl^- \quad (7a)$$

The change in the concentration of chlorite is given by the following rate equation, derived from (1a) and (2a)

$$\frac{d\,[Cl(III)]}{dt} =$$
$$k_1[Cl(I)][Br(I)] - k_\gamma\,[Cl(III)][Br(I)] \quad (17)$$

At the point where the chlorite reaches its maximum concentration this equation changes into

$$\frac{[Cl(III)]_{max}}{[Cl(I)]} = \frac{k_1}{k_\gamma} = R_{Cl} \qquad (18)$$

The analogous expression for the maximum concentration of bromite is obtained from (6a) and (7a)

$$\frac{[Br(III)]_{max}}{[Br(I)]} = \frac{k_3}{k_\delta} = R_{Br} \qquad (19)$$

From the known values of k_1 (see Table IV) and k_γ the values of R_{Cl} were calculated to be 0.004 and 0.007 for pH 9.2 and 8.5, respectively. In the same way the values of R_{Br} have been found from the values of k_3 and k_δ to be 0.023 and 0.005 for pH 9.2 and 8.2. Hence the maximum concentrations of chlorite are below 1% of the concentration of hypochlorite and the maximum concentrations of bromite are not higher than 2.3% of the concentration of hypobromite. These concentrations being in the limits of the analytical errors will not influence significantly the kinetical calculations, in agreement with the previous consideration on the possible errors introduced by the bromite and chlorite.

The behavior of the hypochlorite–hypobromite system with the change in pH may be explained by the following considerations: The rate-determining reactions in the formation of chlorate and bromate were assumed to be (1) and (6), so we may write

$$\frac{d(ClO_3^-)}{dt} = k_1(a - x)(b - y) = k_1{}'(HOCl)(HOBr) \quad (20)$$

$$\frac{d(BrO_3^-)}{dt} = k_3(a - x)(b - y) = k_3{}'(HOCl)(HOBr) \quad (21)$$

Since the titration values $(a - x) = (HOCl) + (ClO^-)$ and $(b - y) = (HOBr) + (BrO^-)$, the concentrations of HOCl, ClO$^-$, HOBr and BrO$^-$ are given by

$$(HOCl) = \frac{(a_{H^+})\,f_{xO^-}}{K_{HOCl} + (a_{H^+})\,f_{xO}}(a - x) =$$
$$F_{Cl}(a - x) \quad (22)$$

$$(ClO^-) = (1 - F_{Cl})(a - x) \qquad (22a)$$

$$(HOBr) = \frac{(a_{H^+})f_{xO^-}}{K_{HOBr} + (a_{H^+})\,f_{xO^-}}(b - y) =$$
$$F_{Br}(b - y) \quad (23)$$

$$(BrO^-) = (1 - F_{Br})(b - y) \qquad (23a)$$

where $K_{HOCl} = 3.7 \times 10^{-8}$,[11,24] $K_{HOBr} = 2.06 \times 10^{-9}$,[25] and $\log f = 0.505\ \sqrt{\mu}/(1 + aB\ \sqrt{\mu})$,[26] for $a = 2.5\ 10^{-8}$ and $B = 3.29 \times 10^7$.

Substitution of (22) and (23) into (20) and (21) gives

$$k_1{}' = \frac{k_1}{F_{Cl}F_{Br}} \qquad (24)$$

$$k_3{}' = \frac{k_3}{F_{Cl}F_{Br}} \qquad (25)$$

(24) G. F. Davidson, J. Text. Inst., **24**, T 185 (1933).

(25) L. Farkas and M. Lewin, THIS JOURNAL, **72**, 5766 (1950).

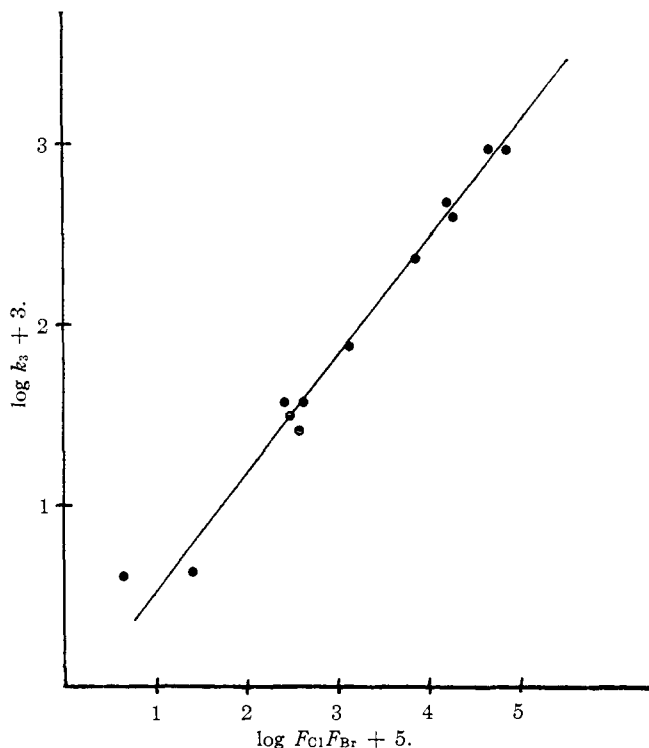(26) S. Glasstone, "Textbook of Physical Chemistry," D. Van Nostrand Co., Inc., New York, N. Y., 1952, p. 967.

Fig. 4.—Plot of log k_3 against log $F_{Cl}\,F_{Br}$; experiments with addition of 0.2 mole/l.: KClO$_3$ (◐); KNO$_3$ (◑).

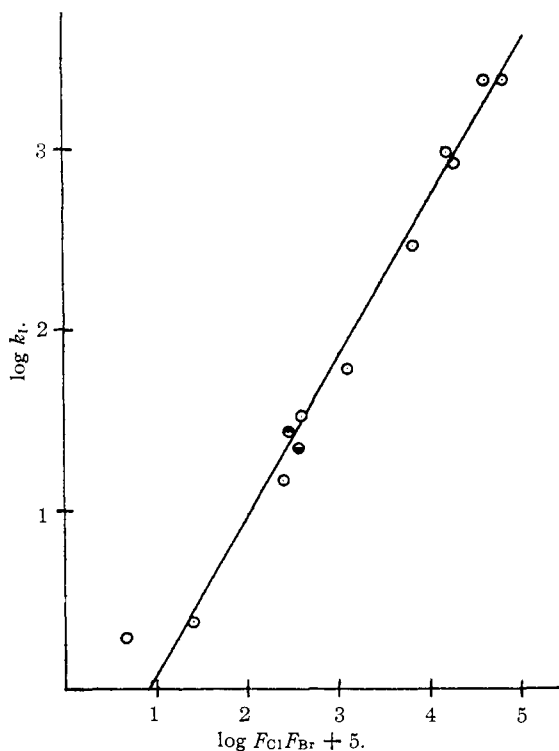Fig. 5.—Plot of log k_1 against log $F_{Cl}F_{Br}$; experiments with addition of 0.2 mole/l.: KClO$_3$(◐); KNO$_3$(◐).

where $k_1{}'$ and $k_3{}'$ no longer depend on pH and ionic strength.

It may be seen from Table IV that k_1 and k_3 both increase with decreasing pH, the increase in k_1 being more pronounced than the increase in k_3.

The dependence on pH proposed in equations 24 and 25 is checked graphically in Figs. 4 and 5. The plots of log k_3 and of log k_1 against log $F_{Cl}F_{Br}$ yield straight lines, confirming the assumption made previously in equations 1 and 6 that the hypohalous acids are the main participants in the rate-determining steps of the bromate and chlorate formation. The reaction mechanism covers now also the retarding effect of the neutral salts, nitrate and chlorate, on the reaction rate. Values of k_1' and k_3' of 3.87 and 1.54 mole^{-1} min.$^{-1}$ l., respectively, were computed from these graphs. Attempts were also made to check the other possibilities for the explanation of the influence of the pH on the reaction rates. One possibility would seem to be according to the equations

$$HOCl + BrO^- \longrightarrow HClO_2 + Br^- \quad (1b)$$

$$HOCl + BrO^- \longrightarrow HBrO_2 + Cl^- \quad (6b)$$
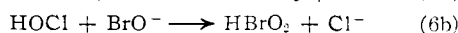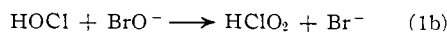
which lead to

$$\frac{d(ClO_3^-)}{dt} = k''_1(HOCl)(BrO^-) \quad (20a)$$

$$\frac{d(BrO^-_3)}{dt} = k''_3(HOCl)(BrO^-) \quad (21a)$$

Substitution of (22) and (23a) into (20a) and (21a) gives

$$k''_1 = \frac{k_1}{F_{Cl}(1 - F_{Br})} \quad (24a)$$

$$k''_3 = \frac{k_3}{F_{Cl}(1 - F_{Br})} \quad (25a)$$

The plots of log k_3 and log k_1 against log $F_{Cl}(1 - F_{Br})$ (see Fig. 6) do not yield straight lines and the scattering of the points is much higher than in Fig. 4 and 5, thus excluding the possibility that only re-
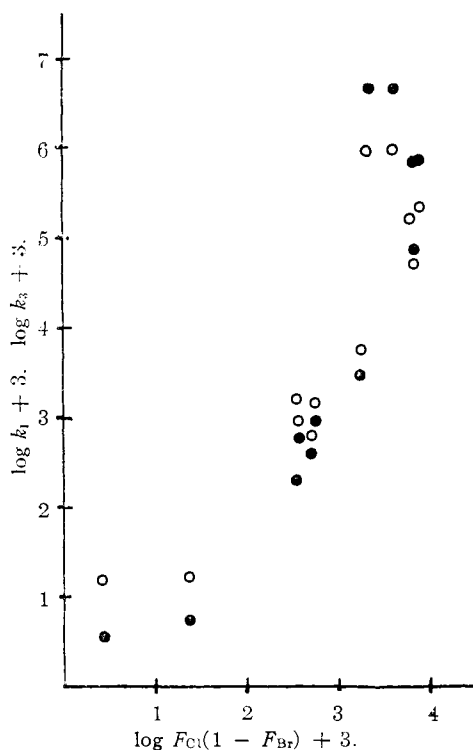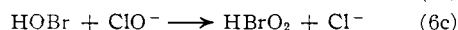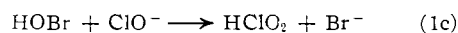

Fig. 6.—Plot of log k_1 (●) and log k_3 (○) against log $F_{Cl}(1 - F_{Br})$.

actions (1b) and (6b) are responsible for the formation of bromite and chlorite in the reaction mechanism.

A second possibility might have been the assumption that hypobromous acid and hypochlorite ions are reacting in the rate determining steps according to equations

$$HOBr + ClO^- \longrightarrow HClO_2 + Br^- \quad (1c)$$

$$HOBr + ClO^- \longrightarrow HBrO_2 + Cl^- \quad (6c)$$

The treatment of this assumption on the lines similar to the previous case also yielded negative results.

The third possibility treated was the assumption that reactions (1) and (1c) and reactions (6) and (6c) occur simultaneously and at similar rates in the reaction mechanism. The corresponding plots of log k_1 and log k_3 against log F_{Br} yielded curved lines, precluding this possibility. Another possibility involves the assumption that reactions (1) and (1b) and reactions (6) and (6b) occur simultaneously and at similar rates in the reaction mechanism. The evaluation of this possibility by plotting of log k_1 and log k_3 against log F_{Cl} yielded straight lines in which the scattering of the points was not significantly higher than in the case of Figs. 4 and 5. This result points to the possibility that hypobromite ions may participate to a certain extent in the rate-determining steps. The accuracy of the present data, however, seems to be insufficient for a decision, whether the reaction proceeds only through (1) and (6) or whether there is some contribution from (1b) and (6b).

Similar calculations have been carried out in order to gain some information on the dependence of the rates of reactions (2), (7), (5) and (9) on the pH. From the values of k_γ, k_δ, k_β and k_α at the various pH values, the values of the pH independent constants k'_γ, k'_δ, k'_β and k'_α were computed using the following general equations based on the assumption that the free hypohalous and halous acids are participating in the reactions

$$\frac{d[X(V)]}{dt} = k_\rho[X(III)][X(I)] = k'_\rho[HXO_2][HXO] \quad (26)$$

and

$$k'_\rho = \frac{k_\rho}{F_{X(III)}F_{X(I)}} \quad (27)$$

for

$$F_{X(III)} = \frac{a_{H^+}}{K_{HXO_2} + a_{H^+}}$$

and

$$F_{X(I)} = \frac{a_{H^+}}{K_{HOX} + a_{H^+}}$$

where α, β, γ and δ may be substituted for ρ and Cl and Br for X in the four reactions involved. In these computations the value of 1.1×10^{-2} for the dissociation constant of the chlorous acid has been used.[27] Since no value for the dissociation constant of bromous acid was found in the literature, the value of the chlorous acid was used, assuming both constants to be close, in analogy to the dissociation constants of the hypochlorous and hypobromous acids. As may be easily seen, this approximation will influence the absolute values of k'_β

(27) B. Barnett, Dissertation, Univ. of California, 1935.

and k'_δ by the same multiplication factor for all the pH values considered. For pH 9.2 and 8.5 the values of 5.1×10^8 and 6.0×10^8 obtained for k'_α by these computations are close enough and allow the conclusion that the free hypochlorous and chlorous acids participate in reaction (9). The comparatively close values of 4.4×10^7 and 3.5×10^7 obtained for k'_3 at pH 9.2 and 8.5 provide some evidence that in the formation of bromate according to reaction (5) the hypobromous and bromous acids are the reacting species. These values are in reasonable agreement with the value 2.2×10^7 calculated by us from $k_\beta = 1.1 \pm 0.20$ which Perlmutter-Hayman[15] found at pH 8.84, by an indirect method.

Computations of k'_γ for pH 9.2 and 8.2 yielded values of 2.6×10^8 and 1.3×10^8, respectively, while for k'_δ values of 1.3×10^9 and $5.7 + 10^8$ were obtained. Since the accuracy of the experimental determination of k_γ and k_δ is not high, it is difficult to draw conclusions from these figures. To a rough approximation, however, the pH dependence of reactions (2) and (7) may be explained by assuming that in this case two simultaneous reactions occur involving the interaction of the free hypochlorous and bromous acids as well as the interaction of a free acid and an anion.

Table V shows the effect of the variation of initial concentrations of hypochlorite and bromide at pH 8.

TABLE V

VARYING INITIAL CONCENTRATIONS OF HYPOCHLORITE AND HYPOBROMITE

Temp. $= 25 \pm 0.1°$, 0.1 mole/l. borax, $(\text{Cl}') = 0.04$ mole/l.

pH	$a \times 10^2$, mole/ l.	$b \times 10^2$, mole/ l.	κ	k_1, l./ mole. min.	k_3, l./ mole. min.	$k_4 \times 10^4$, l./ mole. min.	$k_2 \times 10^2$, l./ mole. min.	Remarks
7.85	2.890	0.810	6.1	0.85	0.42	..	..	$a > b$
7.94	3.827	0	...	...	....	4.0	..	$b = 0$
7.95	3.658	0.027	...	...	....	4.0	..	$a \gg b$
8.00	3.727	0.054	(5.1)	(2.6)	(0.51)	3.7	..	$a \gg b$
7.9	0	2.464	...	...	....	..	7.7	$a = 0$
7.86	0.918	2.712	...	...	....	..	8.7	$a < b$

If no hypobromite is present $(b = 0)$, we have the decomposition of hypochlorite alone. k_4 is the second-order constant of this reaction.

If the hypobromite is present in small quantities only $(a \gg b)$, the reaction is identical with the above after the small quantity of hypobromite originally present had been converted into bromate. k_4 was calculated from the moment the bromate concentration had reached a constant value and will be seen to be equal to k_4 calculated for $b = 0$.

It seems that the whole amount of bromide initially added has been quantitatively oxidized to bromate and has no further effect on the reaction rate.

In the case where a was greater than b, but still of the same order of magnitude, the value of κ, k_1 and k_3 will be seen to agree with those calculated for the case $a \gg b$, before all the hypobromite had been converted to bromate.

If $a = 0$, we have the case of decomposition of hypobromite alone. The second-order rate constant k_2 of this reaction was calculated from separate experiments according to

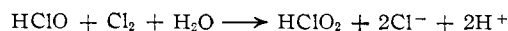$$\frac{d[\text{Br(I)}]}{dt} = 3k_2[\text{Br(I)}]^2 \qquad (28)$$

The values of this constant recorded in Table IV are apparently different from the values found by Perlmutter-Hayman, et al.[15] This difference is accounted for when taking into consideration the influence of the concentration of bromide on the reaction rate (see Fig. 4 in the above paper[15]). Since the hypobromite solutions used in the present investigation initially contained no bromide (see "Experimental"), their rates of decomposition were lower. The value of k_2 for $a = 0$ agrees well with that calculated for the case where hypobromite was in excess over the hypochlorite $(a < b)$ after all the hypochlorite had been converted to chlorate.

Comparing k_2 with k_3 in Table V shows that reaction (B) is considerably slower than reaction (C), thus supporting further the assumption made previously that reaction (B) plays an insignificant part in the reaction mechanism.
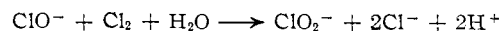
It will be seen from the above considerations that the suggested mechanism agrees fairly well with the experimental data of the decomposition of the hypochlorite–hypobromite mixtures while the decomposition of hypobromite alone and of hypochlorite alone are both second-order reactions with different second-order rate constants.

Experiments carried out in the presence of increasing amounts of chloride ions showed an acceleration of the reaction rates, followed by retardation as the chloride concentration increased to about 0.5 mole/liter. Addition of chloride to hypobromite solutions did not influence the rate of the decomposition. The decomposition of hypochlorite alone, however, was accelerated by the addition of chloride.

The increase in the k_1 and k_3 with increasing chloride concentration is not explained by the present reaction mechanism. It may possibly be explained by a reaction between halogen and hypohalous acid already previously assumed in Skrabal's[12] reaction scheme.

$$\text{HClO} + \text{Cl}_2 + \text{H}_2\text{O} \longrightarrow \text{HClO}_2 + 2\text{Cl}^- + 2\text{H}^+$$

or

$$\text{ClO}^- + \text{Cl}_2 + \text{H}_2\text{O} \longrightarrow \text{ClO}_2^- + 2\text{Cl}^- + 2\text{H}^+$$

As the concentration of chlorine is determined by the equilibrium

$$\text{Cl}^- + \text{H}^+ + \text{HClO} \rightleftharpoons \text{Cl}_2 + \text{H}_2\text{O}$$
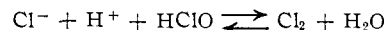
it is seen that the addition of chloride would accelerate the rate of the formation of chlorite and chlorate. A similar assumption has been made by Perlmutter-Hayman, et al., in order to account for the accelerating action of bromide on the decomposition of hypobromite.[15]

The ordinary retarding effect of the neutral salt would seem to be superimposed on the accelerating action of the chloride and seem to predominate at the higher chloride concentrations.

Experiments have also been carried out with the addition of potassium bromate in concentrations of 0.2–0.8 mole/l. to the hypochlorite–hypobromite mixtures. In this case again a strong acceleration of the reaction rates has been noted. This acceleration was attributed to a reaction between hypo-

chlorite and bromate described in a previous publication,[28] according to the following general equation

$$HBrO_3 + HOCl = HClO_3 + HOBr$$
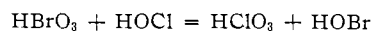
This is a slow reaction and proceeds at a measurable

(28) M. Lewin and M. Avrahami, Bull. Res. Counc. Israel, **3**, 445 (1954).

rate only in concentrations of at least one order of magnitude higher than the concentrations of bromate formed in the reactions described in this paper.

We are indebted to Dr. B. Perlmutter-Hayman from the Department of Physical Chemistry, Hebrew University, for helpful discussion.

JERUSALEM, ISRAEL

The System Sodium Chlorite–Sodium Chlorate–Water at Various Temperatures

BY GEORGE L. CUNNINGHAM AND TONG SAN OEY

The system sodium chlorite–sodium chlorate–water has been studied at 15, 25, 35 and 45°. The system is simple; the solid phases are sodium chlorate, sodium chlorite and sodium chlorite trihydrate. No hydrate of sodium chlorate was found.

In a previous article[1] a study of the system sodium chlorite–sodium chloride–water was reported. Similar measurements have been made on the corresponding system involving sodium chlorate in place of sodium chloride. The system is a simple one; no double salts are formed within the temper-

TABLE I

THE TERNARY SYSTEM SODIUM CHLORITE, SODIUM CHLORATE AND WATER

Solid Phase: A, $NaClO_2 \cdot 3H_2O$; B, $NaClO_2$; C, $NaClO_3$.

Compn. of soln. x	w	Sp. gr.	Compn. of wet residue x	w	Solid phase
Temp., 15					
0.0000	8.18	1.327	....	..	A
.1422	7.23	1.361	0.0479	4.00	A
.2142	6.55	1.383	.0852	4.19	A
.2537[a]	6.30	1.394	.1163	4.31	A
.4066	5.12	1.457	.1950	3.94	A
.4448	4.78	1.482	.5316	2.33	A, C
.5063	4.78	1.483	.8774	0.90	C
.5273	5.09	1.460	.8800	1.17	C
.7051	5.55	1.439	.9273	1.18	C
.8574	5.86	1.424	.9716	1.03	C
1.0000	6.49	1.409	....	..	C
Temp., 25°					
0.0000	6.50	1.375	....	..	A
.0426	6.22	1.394	0.0120	3.76	A
.0598	5.98	1.391	.0275	4.39	A
.0788	5.97	1.402	.0428	4.43	A
.1374	5.58	1.421	.0710	4.30	A
.1692	5.41	1.463	.0984	4.30	A
.2351	4.88	1.461	.1337	4.02	A
.2594	4.72	1.474	.1566	4.00	A
.3241	4.22	1.508	.1795	3.60	A
.3652	3.86	1.535	.3550	2.71	A, C
.3941	4.22	1.520	.8381	1.02	C
.5004	4.56	1.498	.8851	0.98	C
.6278	4.87	1.472	.9125	1.12	C
.7269	5.07	1.461	.9456	0.94	C
.8053	5.24	1.456	.9599	1.02	C
.8486	5.30	1.450	.9691	0.96	C
.9046	5.50	1.446	.9824	0.89	C
1.000	5.88	1.444	....	..	C

(1) G. L. Cunningham and T. S. Oey, THIS JOURNAL, **77**, 799 (1955).

Compn. of soln. x	w	Sp. gr.	Compn. of wet residue x	w	Solid phase
Temp., 35°					
0.0000	4.95	1.406	....	..	A
.0464	4.54	1.478	0.0296	3.50	A
.1202[a]	4.06	1.515	.0701	3.50	A
.2276	3.56	1.563	.1036	3.18	A
.2918	3.42	1.571	.1101	2.97	A
.3177	3.15	1.595	.7394	0.86	A, C
.3171	3.13	1.595	.4250	2.11	A, C
.4475	3.82	1.540	.8425	0.99	C
.5411	4.17	1.516	.8788	0.97	C
.7103	4.55	1.490	.9326	0.97	C
.8657	4.89	1.473	0.9706	0.97	C
1.0000	5.06	1.467	....	..	C
Temp., 45°					
0.0000	4.28	1.501	....	..	B
.1482	3.64	1.543	0.0937	2.41	B
.2550	3.25	1.586	.1556	2.03	B
.3524	2.85	1.621	.5668	1.20	B, C
.4112	3.16	1.590	.8220	0.85	C
.5141	3.54	1.558	.8766	.77	C
.6397	3.97	1.529	.9277	.67	C
.7745	4.18	1.510	.9479	.84	C
1.0000	4.41	...	....	..	C

[a] Tube put in bath for 5 and 10 days.

ature interval 15–45°, the solid phases being sodium chlorate, sodium chlorite and sodium chlorite trihydrate. No evidence was found for the existence of hydrated sodium chlorate in the equilibrium mixture.

Experimental

As in the previous work, the Schreinemaker's wet residue method was used. The apparatus and procedures were the same. The sodium chlorate was C.P. grade. The water was distilled. The sodium chlorite was prepared from the commercial, technical grade of sodium chlorite as described in the previous article. The technical sodium chlorite used in this investigation was donated by the Mathieson Chemical Corporation.

The figures given in the table are in moles of salts and moles of water. The x function is the moles of sodium chlorate divided by the sum of the moles of sodium chlorate and the moles of sodium chlorite. The w function is the moles of water divided by the sum of the moles of sodium chlorate and the moles of sodium chlorite.

Analytical.—Procedures for the analysis of chlorite, chlo-