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 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

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

[CONTRIBUTION FROM THE APPLIED SCIENCE LABORATORY, UNIVERSITY OF CINCINNATI]

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

BY GEORGE L. CUNNINGHAM AND TONG SAN OEY

RECEIVED APRIL 5, 1955

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 temperature 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.

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.			Compn. of wet residue		Solid
x	w	Sp. gr.	x	w	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
		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.

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-

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

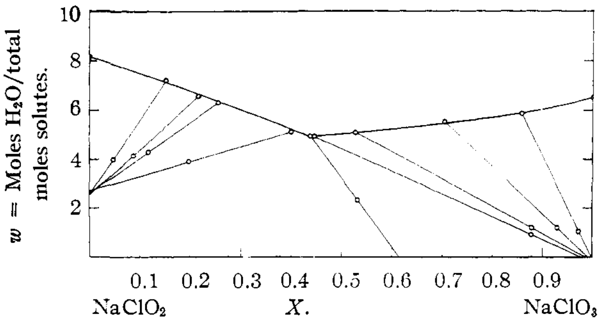

Fig. 1.—The system sodium chlorite–sodium chlorate–water at 15°.

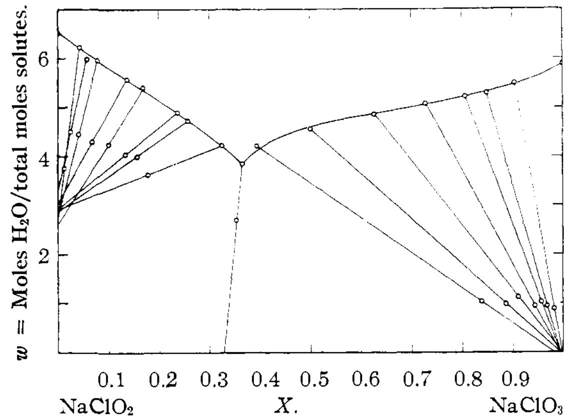

Fig. 2.—The system sodium chlorite–sodium chlorate–water at 25°.

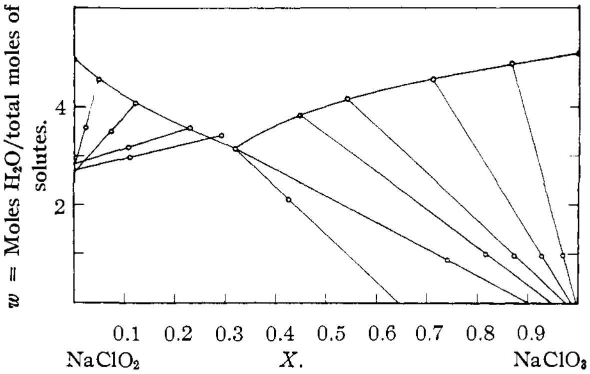

Fig. 3.—The system sodium chlorite–sodium chlorate–water at 35°.

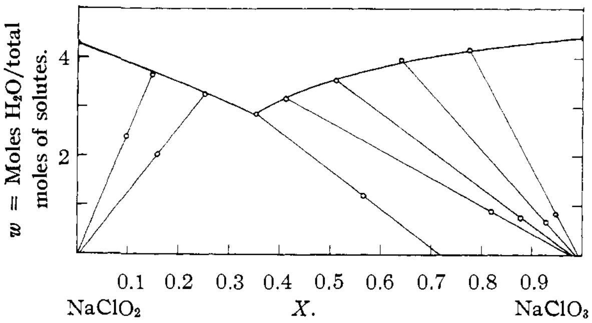

Fig. 4.—The system sodium chlorite–sodium chlorate–water at 45°.

ride, hypochlorite, chlorate and alkali have been described by White.[2]

The solutions and wet residues were analyzed for chlorite ion and chlorate ion. The water in the liquid phase and the wet residue solid were determined by difference.

The Ternary System Sodium Chlorite–Sodium Chlorate–Water.—In this system four isotherms have been worked out: 15, 25, 35 and 45°. The data are summarized in Table I and shown in Figs. 1, 2, 3 and 4. They show only the trihydrate of sodium chlorite already known, sodium chlorite and pure sodium chlorate.

CLEVELAND, OHIO

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[2] J. F. White, *Am. Dyestuff Reporter*, **31**, 484 (1942).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, WASHINGTON UNIVERSITY]

The Self-diffusion Coefficients of Potassium, Cesium, Iodide and Chloride Ions in Aqueous Solutions[1]

BY ARNOLD M. FRIEDMAN AND JOSEPH W. KENNEDY

RECEIVED MARCH 9, 1955

The self-diffusion coefficients of potassium, cesium, iodide and chloride ions have been measured in a series of aqueous metal halides of moderate to high concentration at 25°. The open-ended capillary method has been used for all experiments. Investigation of the sources of error of the capillary method has been extended. The self-diffusion coefficients of large unhydrated ions are found to exhibit the same type of linear relationship as was reported by Mills and Kennedy.[2] A possible explanation of the maxima obtained for hydrated ions is suggested.

During the past ten years considerable interest has arisen in the measurement of self-diffusion coefficients of ionic solutions by the use of radioactive tracers. Measurements have been made with diaphragm cells, of the diffusion coefficients of sodium ion in aqueous sodium chloride,[3] of sodium ion in aqueous sodium iodide,[4] and of sodium ion and chloride ion in aqueous sodium chloride,[5] all at 25°. Diffusion tubes have been used to measure the self-diffusion coefficients of sodium ion and chloride ion in aqueous sodium chloride,[6] and modified diffusion tubes have been used to measure the coefficients of sodium ion and iodide ion in aqueous sodium iodide.[7] More recently measurements have

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[1] Submitted by A. M. Friedman as part fulfilment of the requirements for the Ph.D. degree at Washington University, St. Louis.

[2] R. Mills and J. W. Kennedy, THIS JOURNAL, **75**, 5696 (1953).

[3] A. P. Brady and D. J. Salley, *ibid.*, **70**, 914 (1948).

[4] A. W. Adamson, *J. Chem. Phys.*, **15**, 762 (1947).

[5] A. W. Adamson, THIS JOURNAL, **74**, 446 (1952).

[6] L. P. Jehle, Ph.D. Thesis, University of California, Berkeley, 1938.

[7] J. H. Wang and J. W. Kennedy, THIS JOURNAL, **72**, 2080 (1950).