

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NEW YORK UNIVERSITY]

Some Isotherms of the System Sodium Chromate–Sodium Chlorate–Water

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Solubility measurements in the ternary system sodium chromate–sodium chlorate–water have been made with the purpose of testing any possible similarity with the behavior of the related system sodium sulfate–sodium chlorate–water, which forms a double salt of the formula $\text{NaClO}_3 \cdot 3\text{Na}_2\text{SO}_4$.¹ The present measurements, however, reveal neither compound formation nor solid solution between the salts Na_2CrO_4 and NaClO_3 over the temperature range studied, 19–50°.

Materials.—A c. p. grade of sodium chlorate was used, found to be 100.0% pure by reduction and precipitation of silver chloride. Recrystallized c. p. potassium dichromate was used for the standardization of the 0.2 *N* sodium thiosulfate titrating solution. Other chemicals used, such as sulfur dioxide and silver nitrate, were similarly of c. p. grade. The sodium chromate was used in the form of the tetrahydrate, supplied by the Mackay Company; the percentage of Na_2CrO_4 in this material, found by titration, was 69.15, and by dehydration, 69.25, as compared with the theoretical value of 69.21. The purity of this salt is further confirmed by the agreement of the solubility at 25° as determined by evaporation, with the value obtained by titration (see Table I): 45.63 and 45.59%, respectively.

Solubility Determinations.—Complexes were made up by weight from sodium chlorate, tetrahydrate and water, and rotated in a thermostat at the specified temperature ($\pm 0.02^\circ$), about three days being allowed for the attainment of equilibrium. Samples for analysis were taken in the usual way by means of pipets fitted with filter paper.

Analysis.—1. Sodium chromate in the presence of sodium chlorate. Gravimetric determination as barium chromate or as lead chromate (using excess of barium chloride or of lead nitrate) gave consistently high results in the determination of about 0.5 g. of potassium chromate in the presence of 0.5 to 2 g. of sodium chlorate, the errors being about +15 and +6 parts per 1000, respectively. These errors may indicate co-precipitation of the respective chlorates. A volumetric analysis was therefore employed, involving precipitation as barium chromate, filtration, re-solution in nitric acid and iodometric titration of the chromate with standard thiosulfate. The use of hydrochloric acid in re-dissolving the precipitate of barium chromate gave irregular, low results, by as much as thirty parts per thousand, apparently because of some reduction of chromate by the hydrochloric acid, during the process of solution of the precipitate. Nitric acid, however, gave satisfactory results (± 0.5 part per thousand); the procedure was tested on samples of ~ 0.35 g. of potassium chromate in the presence of 1–4 g. of sodium chlorate, the final titration being carried out with 3 g. of potassium iodide and 8 cc. of 6 *N* nitric acid in a total volume of 200 cc. Whatever small amounts of chlorate may have accom-

panied the precipitated barium chromate apparently caused no measurable interference under these conditions.

2. Sodium chlorate can be determined by difference from the percentage of total solid obtained by evaporation of the saturated solution at 110°. But because of some difficulty and uncertainty in the complete drying of sodium chromate residues, it was decided to supplement this indirect determination of sodium chlorate by the following direct analysis.

3. Direct gravimetric determination of the chlorate, by reduction with sulfur dioxide gas followed by the usual gravimetric determination of the resulting chloride as silver chloride. This procedure gave exact results both on pure sodium chlorate and in the presence of sodium chromate, as can be seen of course in the close agreement of the algebraic extrapolation of tie-lines for the identification of solid phases in the ternary system, described below.

Results.—The results for the solubility determinations for three isotherms, 19, 25 and 50°, are given in Table I. All compositions are in weight per cent. The first two columns under the caption "saturated solution" are the directly determined percentages of the two individual salts, and the percentage of water for the actual phase diagram was calculated by difference, using the sum of these percentages for the total solid. The percentage of total solid obtained by direct evaporation was considered probably slightly less dependable than the sum of the separate determinations. The third column under "saturated solution" gives the percentage of water determined by evaporation, and it may be seen that the total solid so determined is nevertheless in good agreement in general with the sum of the first two columns. The average discrepancy is +0.8 to 1.0 part per thousand for the evaporation figure, the maximum difference being six parts per thousand. All but eight of the analytical values given in Table I are averages of at least two duplicates; the average disagreement of duplicates was 1.3 parts per thousand. The sodium chlorate solubilities given in parentheses were determined by evaporation. Table II compares the solubilities of the single salts here reported with values from the literature.

The results, shown graphically for two temperatures in Fig. 1, indicate that in the range of temperature studied, the system is simple, the only solid phases being anhydrous sodium chlorate and one of the hydrates of sodium chromate. This is

(1) Ricci and Yanick, *This Journal*, **59**, 491 (1937).

TABLE I
 SYSTEM $\text{Na}_2\text{CrO}_4\text{-NaClO}_3\text{-H}_2\text{O}$

Original complex		Saturated solution			Solid phases
Wt., % Na_2CrO_4	Wt., % NaClO_3	Wt., % Na_2CrO_4	Wt., % NaClO_3	Wt., % H_2O by evapn.	
At 50°					
0.00	...	0.00	55.49	44.51	NaClO_3
5.00	60.00	6.36	48.49	45.11	NaClO_3
13.94	51.78	18.37	36.71	44.94	NaClO_3
23.00	44.00	31.45	23.55	44.69	NaClO_3
30.00	38.00	40.80	15.81	43.32	NaClO_3
39.00	25.00	43.13	13.87	42.90	$\text{NaClO}_3 + \text{Na}_2\text{CrO}_4 \cdot 4\text{H}_2\text{O}$
53.00	10.00	43.15	13.85	42.89	$\text{NaClO}_3 + \text{Na}_2\text{CrO}_4 \cdot 4\text{H}_2\text{O}$
Av.		43.14	13.86	42.90	$\text{NaClO}_3 + \text{Na}_2\text{CrO}_4 \cdot 4\text{H}_2\text{O}$
54.00	7.00	44.21	11.54	44.21	$\text{Na}_2\text{CrO}_4 \cdot 4\text{H}_2\text{O}$
55.00	4.00	47.32	6.20	46.47	$\text{Na}_2\text{CrO}_4 \cdot 4\text{H}_2\text{O}$
...	0.00	50.66	0.00	49.34	$\text{Na}_2\text{CrO}_4 \cdot 4\text{H}_2\text{O}$
At 25°					
0.00	...	0.00	(50.06)	49.94	NaClO_3
5.00	53.00	5.95	43.88	50.17	NaClO_3
9.98	49.87	12.45	37.06	50.36	NaClO_3
15.00	48.00	20.42	29.30	50.27	NaClO_3
20.00	44.99	28.51	21.50	50.03	NaClO_3
25.00	40.00	35.18	15.65	49.16	NaClO_3
34.00	33.00	36.43	14.43	49.04	$\text{NaClO}_3 + \text{Na}_2\text{CrO}_4 \cdot 4\text{H}_2\text{O}$
36.00	20.00	36.44	14.44	49.00	$\text{NaClO}_3 + \text{Na}_2\text{CrO}_4 \cdot 4\text{H}_2\text{O}$
46.88	10.00	36.43	14.43	49.04	$\text{NaClO}_3 + \text{Na}_2\text{CrO}_4 \cdot 4\text{H}_2\text{O}$
Av.		36.43	14.43	49.03	$\text{NaClO}_3 + \text{Na}_2\text{CrO}_4 \cdot 4\text{H}_2\text{O}$
48.00	7.00	39.47	9.82	50.71	$\text{Na}_2\text{CrO}_4 \cdot 4\text{H}_2\text{O}$
49.96	4.99	41.04	7.34	51.59	$\text{Na}_2\text{CrO}_4 \cdot 4\text{H}_2\text{O}$
...	0.00	45.59	0.00	54.37	$\text{Na}_2\text{CrO}_4 \cdot 6\text{H}_2\text{O}$
At 19°					
0.00	...	0.00	48.28	51.62	NaClO_3
4.93	55.01	6.43	41.91	51.64	NaClO_3
11.00	50.01	14.56	33.59	51.71	NaClO_3
20.00	42.00	27.00	21.57	51.39	NaClO_3
27.00	36.00	35.05	15.01	49.96	$\text{NaClO}_3 + \text{Na}_2\text{CrO}_4 \cdot 6\text{H}_2\text{O}$
35.00	21.00	35.03	15.03	49.96	$\text{NaClO}_3 + \text{Na}_2\text{CrO}_4 \cdot 6\text{H}_2\text{O}$
Av.		35.04	15.02	49.96	$\text{NaClO}_3 + \text{Na}_2\text{CrO}_4 \cdot 6\text{H}_2\text{O}$
43.00	8.00	37.26	10.70	51.99	$\text{Na}_2\text{CrO}_4 \cdot 6\text{H}_2\text{O}$
44.95	4.01	40.60	5.14	54.27	$\text{Na}_2\text{CrO}_4 \cdot 6\text{H}_2\text{O}$
45.00	2.00	42.26	2.31	55.35	$\text{Na}_2\text{CrO}_4 \cdot 6\text{H}_2\text{O}$
...	0.00	43.63	0.00	56.33	$\text{Na}_2\text{CrO}_4 \cdot 10\text{H}_2\text{O}$

TABLE II

INDIVIDUAL SOLUBILITIES

Salt	Temp., °C.	Observed	Literature	Solid phase
NaClO_3	19	48.3	48.75 ²	NaClO_3
	25	50.1	50.1 ^{2,3}	NaClO_3
	50	55.5	55.2 ³	NaClO_3
Na_2CrO_4	19	43.6	43.3 ⁴	$\text{Na}_2\text{CrO}_4 \cdot 10\text{H}_2\text{O}$
	25	45.6	45.8 ^{4,5}	$\text{Na}_2\text{CrO}_4 \cdot 6\text{H}_2\text{O}$
	50	50.7	51.0 ⁶	$\text{Na}_2\text{CrO}_4 \cdot 4\text{H}_2\text{O}$

(2) Interpolated from: Bell, *J. Chem. Soc.*, **123**, 2713 (1923); and Ricci and Yanick, ref. 1.

(3) Ricci, *THIS JOURNAL*, **60**, 2040 (1938).

(4) Interpolated from Salkowski, *Ber.*, **34**, 1947 (1901).

(5) Takeuchi, *Mem. Kyoto Imp. Univ.*, **1**, 249 (1916); cited in "Int. Crit. Tables," Vol. IV, p. 347 (1926).

(6) Interpolated from Mylius and Funk, *Wiss. Abh. Reichsanstalt*, **3**, 451 (1900); cited in Seidell "Solubilities, etc.," 1940, Vol. I, p. 1255.

the tetrahydrate for the whole sodium chromate solubility curve at 50°. The binary transition temperature to the hexahydrate is 25.9°, and that between the hexahydrate and the decahydrate lies at 19.5°. The stable solid phases for the solubility of the pure salt at the lower temperatures, 25 and 19°, are therefore the hexahydrate and the decahydrate, respectively, and they are so reported in the table. Apparently, however, these phases are in each case dehydrated to the next lower hydrate in the presence of even small concentrations of sodium chlorate, since the tie-lines for the ternary system in this region show only the tetrahydrate as the solid phase at 25° and

(7) Richards and Kelley, *THIS JOURNAL*, **33**, 847 (1911).

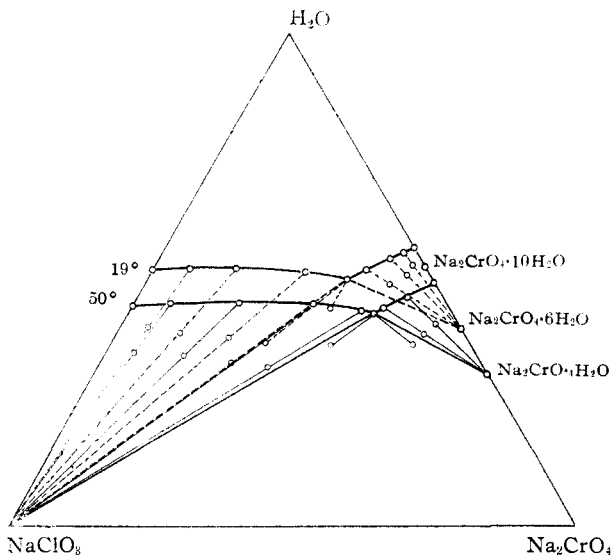


Fig. 1.—The system Na_2CrO_4 – NaClO_3 – H_2O at 19 and 50°.

only the hexahydrate at 19°. The isothermally invariant points for equilibrium, at each of these two temperatures, between the two adjacent hydrates in the ternary system were not determined.

The identity of the solid phases as reported is based on graphical and algebraic extrapolation of tie-lines. For the case of sodium chlorate as solid phase these tie-lines extrapolate to 100% sodium chlorate with an average absolute error, for all three isotherms, of 0.16%, calculated as % water. For the sodium chromate phases, the average error of extrapolation to the theoretical percentage of sodium chromate in the respective hydrates, is 0.11%, calculated as % sodium chlorate. There is consequently no indication, within the experimental error, of any solid solution formation between the equilibrium phases of the system.

Summary

Solubility determinations are reported for the ternary system sodium chromate–sodium chlorate–water at 19, 25 and 50°. No evidence is found for any compound formation or solid solution between the two salts in this temperature range.

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Absorption Spectra of Some Double Salts Containing Cobaltous Chloride*

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The blue color of solutions containing cobaltous chloride and hydrochloric acid or certain other chlorides in large excess has been shown by ion migration experiments¹ to be due to an anion of which cobalt is a constituent. It has been suggested frequently,² on the basis of indirect physico-chemical evidence, that this ion may be represented as CoCl_4^{--} .

The absorption spectra of solutions containing the ion in question have been observed, the most accurate measurements being those of Brode,³ Brode and Morton,⁴ and Kiss and Gerendas.⁵

* Presented before the Division of Physical and Inorganic Chemistry at the Buffalo meeting of the American Chemical Society, September, 1942.

(1) F. G. Donnan and H. Bassett, *J. Chem. Soc.*, **81**, 939 (1902).

(2) See "Gmelins Handbuch der anorganischen Chemie, System-Nummer 58, Kobalt, Teil A," Verlag Chemie G. m. b. H., Berlin, 8 aufl., 1932, p. 490 for a summary of the work done before 1932. W. Feitknecht, *Helv. Chim. Acta*, **20**, 659 (1937), has summarized the more recent results and has presented a critical discussion of the relationship between color and constitution for a number of cobaltous compounds.

(3) W. R. Brode, *Proc. Roy. Soc. (London)*, **118A**, 286 (1928).

(4) W. R. Brode and R. A. Morton, *ibid.*, **120A**, 21 (1928).

(5) A. v. Kiss and M. Gerendas, *Z. physik. Chem.*, **180A**, 117 (1937).

The spectrum consists of many relatively narrow bands extending from the near infra-red through the visible into the ultraviolet. In the present paper, the results of the comparison of the portion of this spectrum lying within the visible region with spectra of several blue double salts containing cobaltous chloride are reported.

The structure of one of these double salts, Cs_3CoCl_6 , has been determined by X-ray diffraction measurements.⁶ These experiments have shown that in the crystal there exists an approximately regular tetrahedral arrangement of four chloride ions about each cobalt ion, the cobalt–chlorine distance being 2.34 Å. The fifth chloride ion is separated from the cobalt ion by a much greater distance, about 6.0 Å. The absorption spectrum responsible for the blue color of this crystal may be ascribed to the presence of the tetrahedral CoCl_4^{--} group.

If this same complex is present in other crystals or in solution the absorption spectra ought to re-

(6) H. M. Powell and A. F. Wells, *J. Chem. Soc.*, 359 (1935).