The excellent agreement of the entropies calculated from calorimetric and from molecular data supports the third law of thermodynamics and also adds to the substantial evidence that only protons or deuterons may cause molecular rotation in the solid state at the temperatures of liquid hydrogen.

We thank Dr. R. A. Ruehrwein for assisting with the measurements.

Summary

The heat capacity of solid and liquid chlorine has been measured from 14°K. to the boiling point.

The melting and boiling points were found to be 172.12 and 239.05°K., respectively (0°C. = 273.10°K.).

The heat of fusion is 1531 cal. mole^{-1} and the heat of vaporization at the boiling point is 4878 cal. mole^{-1}.

The vapor pressure of liquid chlorine has been measured and the results represented by the equation: triple point 172.12 — 240°K., $\log_{10} P$ (int. cm. Hg) = $-(1414.8/T) - 0.01206\,T + 1.34 \times 10^{-5}\,T^2 + 9.91635$.

The observed triple point pressure was found to be 1.044 cm.

The entropy of chlorine was found to be 51.56 and 53.32 cal. deg.$^{-1}$ mole^{-1} at 239.05 and 298.10° K., respectively, for the ideal gas by means of the third law of thermodynamics.

The data are in excellent agreement with a calculation based on band spectrum data giving 51.55 and 53.31 cal. deg.$^{-1}$ mole^{-1} at the two temperatures.

The Ternary Systems KBrO₃–KClO₃–H₂O at 25° and NaBrO₃–NaClO₃–H₂O at 25 and 50°[1]

BY THEODORE SWENSON AND JOHN E. RICCI

These systems have been investigated for the purpose of finding and studying other examples of the type of solid solution previously suggested[2] as a possible addition to the types in the usual Roozeboom classification, namely, the formation of a single incomplete or limited series of solid solutions between two salts without any experimentally measurable degree of mutual solubility for one of the components. Such solid solutions were noted between potassium chlorate and potassium nitrate[3] and between sodium bromate and sodium sulfate.[2] The combinations of potassium bromate and chlorate, and of sodium bromate and chlorate, were therefore studied, as ternary systems with water, using the usual phase rule methods for the investigation of the solubility relationships.

Experimental

High grade (99.9%) potassium bromate was used without recrystallization, while sodium bromate was purified by recrystallization. The chlorates both contained small amounts of the corresponding bromates; this bromate content was in each case determined, by the method described below, and the necessary corrections were then made when the dry chlorates were weighed out for the preparation of the ternary complexes.

The solubility determinations were made according to the usual procedure described in similar investigations, insofar as method of stirring, sampling, filtering, density determination and temperature control are concerned. Starting with complexes of known composition, and analyzing the saturated solutions at equilibrium, the solid phases were then determined by the usual methods of graphical or algebraic extrapolation, besides occasional analyses of wet and centrifuged residues.

The analytical method for the saturated solutions depended on the determination of the combined percentage of the two salts concerned, by evaporation, and iodometric titration of the bromate with thiosulfate, thus allowing the calculation of the percentage of the second salt by difference. This simple scheme involves the difficulty of titrating small quantities of bromate in the presence of large and varying amounts of chlorate. A preliminary investigation of this analytical problem was therefore necessary.

Iodometric Titration of Bromate in Presence of Chlorate.—The determination of bromate by iodometry, in the presence of chlorate, depends on the proper regulation of the acidity, the concentration of iodide, and the time allowed for reaction and titration. Conditions for the differential titration were first given by Junck,[4] chiefly

(1) The material of this paper is taken from the thesis of Mr. T. Swenson presented to the Graduate School of New York University in partial fulfilment of the requirements for the degree of Master of Science.

(2) Ricci, THIS JOURNAL, **57**, 805 (1935).

(3) Toda, J. Chem. Soc. (Japan), **43**, 320 (1922).

(4) Junck, Z. Ges. Schiess Sprengstoffwesen, **8**, 412 (1913).

from the point of view of the detection and estimation of bromate present as impurity in a chlorate. The literature was reviewed by Taradoire,[5] studying the problem for the same purpose, and employing many refinements in tech-nique for the exact determination of traces of bromate in chlorates. Barneby,[6] studying the general problem of the differential titration of the halogenates in mixtures, de-scribed the determination of 0.1 g. of potassium bromate in the presence of 0.1 g. of potassium chlorate. The prob-lem of much larger relative amounts of chlorate, however, such as are found in the present solubility measurements, was not touched upon, and the actual conditions required had therefore to be determined by experiment.

The conditions finally adopted, allowing the titration of up to 0.1 or 0.2 g. of potassium bromate in the presence of as much as 20 g. of sodium chlorate, in a volume of about 100 ml., were the following: sodium iodide, 5 g. (20 ml. of 25% solution), giving a concentration of 0.33 N after dilution to 100 ml.; 1.5 ml. of concd. hydrochloric acid (0.18 to 0.2 N after dilution); titration with 0.2 N sodium thiosulfate to be started one and one-half minutes after addition of the acid, and to be finished in five minutes, inclusive. The above acidity was found to be approximately the minimum for the complete and reasonably fast reaction of the bromate; the large quantity of iodide is required to keep the iodine well in solution. Tests showed these condi-tions to give complete reaction of the bromate, in the absence of chlorate, with an accuracy of one part in two thousand. When chlorate was added, two corrections had to be made. The first is a constant one depending on the quality and quantity of the chlorate, being caused by the bromate content of the latter. This was therefore determined by previous titration of the chlorate alone according to the method just described and taking account of the second correction too, which is an effect of the slow oxidation of iodide by chlorate under the conditions of the titration. This second effect, which was found to be approximately di-rectly proportional to the chlorate concentration and to the time, was evaluated by measuring the continued liberation of iodine from various initial weights of chlorate, by suc-cessive titration with a very dilute thiosulfate solution, and plotting the total volume of thiosulfate used against the time.

Tested on known mixtures, the procedure described, in-volving two corrections, gave an average error of only one part in two thousand, in six determinations of about 0.2 g. of sodium bromate in the presence of 10 g. of sodium chlo-rate of known bromate content. The same conditions, moreover, using a 0.02 N sodium thiosulfate solution for titration, and applying the time correction indicated, can be used for the detection of quantities as small as 0.001 (±0.0005)% of bromate in chlorate.

Results.—The results of the solubility deter-minations are shown in Tables I and II, which list the composition of original complexes, the com-position (and density, for some) of saturated solu-tions, and, in the last column, the composition of the solid phase calculated by the extrapolation of tie-lines, on the assumption of an anhydrous solid.

(5) Taradoire, *Bull. soc. chim.*, [5] **4**, 1759 (1937).
(6) Barneby, THIS JOURNAL, **38**, 330 (1916)

TABLE I
SYSTEM KBrO₃–KClO₃–H₂O AT 25°

Original complex wt. %		Satd. soln., wt. %			Solid phase Wt. %	
KBrO₃	KClO₃	KBrO₃	KClO₃	Density	KClO₃	Formula
	0	7.533	0	1.054	0	KBrO₃
19.98	2.00	6.46	2.26		0.46	S.S. I
7.04	4.04	5.75	4.08	1.067	1.10	S.S. I
18.03	3.99	5.63	4.29		2.0	S.S. I
13.11	6.92	4.936	6.546	1.078		S.S. I + S.S. II
8.10	13.95	4.945	6.531	1.078		S.S. I + S.S. II
4.02	15.98	4.02	6.75	1.072	96.0	S.S. II
2.79	9.05	2.79	7.08	1.064	97.2	S.S. II
2.02	20.14	2.07	7.26		98.3	S.S. II
1.01	10.04	1.02	7.60	1.053	99.1	S.S. II
0	...	0	7.895	1.048	100	KClO₃

TABLE II
SYSTEM NaBrO₃–NaClO₃–H₂O

| Original complex, wt. %		Satd. soln., wt. %		Solid phase Wt. %	
NaBrO₃	NaClO₃	NaBrO₃	NaClO₃	NaClO₃	Formula
		25°			
...	0	28.29	0	0	NaBrO₃
42.45	12.98	16.46	18.91	−0.15	NaBrO₃
25.08	20.99	13.96	24.21	− .70	NaBrO₃
27.94	23.06	12.20	28.03	+ .31	NaBrO₃
17.98	32.97	8.68	36.75	− .37	NaBrO₃
10.84	39.37	7.14	40.98	+ .57	NaBrO₃
10.50	39.96	7.00	41.47	2.02	S.S. I
10.01	41.07	6.54	42.62	1.70	S.S. I
10.00	41.97	5.99	43.66	6.84	S.S. I
12.99	41.63	6.05	43.55	24.3	S.S. I + S.S. II (?)
7.10	44.50	5.33	44.64	40.4	S.S. II
5.98	45.64	5.07	44.98	64.2	S.S. II
5.01	46.54	4.49	45.66	71	S.S. II
6.11	52.98	3.79	46.46	83.2	S.S. II
5.03	51.08	3.69	46.56	85.0	S.S. II
3.04	48.50	2.84	47.42	89.4	S.S. II
2.00	49.49	1.89	48.36	91	S.S. II
1.01	50.46	0.96	49.16	98	S.S. II
0.95	56.89	0.79	49.36	98.5	S.S. II
0	...	0	50.07	100	NaClO₃
		50°			
...	0	35.50	0	0	NaBrO₃
...	...	27.3	10.8	....	NaBrO₂
20.0	35.1	11.2	38.9	0.79	NaBrO₃ or S.S.
11.1	46.1	7.00	47.7	22	S.S.
8.93	48.1	6.75	48.2	45	S.S.
6.92	50.1	5.80	49.1	68	S.S.
4.99	52.0	4.53	51.1	77	S.S.
3.02	54.0	2.83	53.0	84	S.S.
5.64	74.1	2.62	53.3	91	S.S.
1.39	55.8	1.35	54.4	96	S.S.
0	...	0	55.54	100	NaClO₃

Discussion

Both systems reveal solid solution formation. In the potassium salt system there are two series of limited solid solutions, one of potassium chlo-rate in potassium bromate (S.S. I) with a limit at 3% potassium chlorate, the other with a limit of 5% potassium bromate in potassium chlorate (S.S. II), (both limits estimated from the dia-gram). The isothermally invariant liquid solu-tion in equilibrium with these two mutually satu-rated solid solutions has the composition 4.94%

Fig. 1.—System KBrO₃–KClO₃–H₂O at 25°.
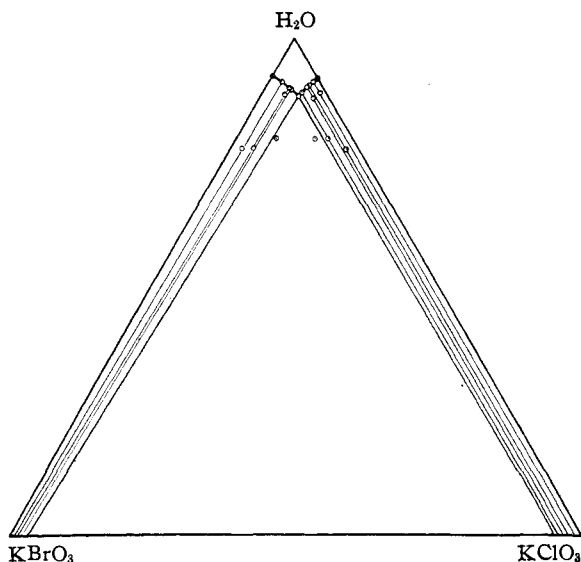
Fig. 2.—System NaBrO₃–NaClO₃–H₂O at 25°.

potassium bromate and 6.54% potassium chlorate. In one or two experiments the composition of the solid was determined by direct analysis of the dried residue, checking the values obtained by algebraic extrapolation of tie-lines. The time allowed for equilibrium was fourteen days, repeated analysis of saturated solutions having shown this time to be sufficient, when small amounts of solid were used.

The interpretation of the sodium salt system from the data collected is more difficult; perhaps more complete isotherms at both temperatures would be required for a complete interpretation. The chief difficulty in the experiments was the very long time required for the attainment of equilibrium in the formation of the solid solutions here involved; some of the complexes were stirred for periods of one or two months before analysis, some of them still showing small changes going on.

Considering the results at 25°, there is no indication of a break in the solubility curve starting with a solution (point A, Fig. 1) of sodium chlorate alone, until the liquid solution reaches the composition (point B) 6% sodium bromate and 44% sodium chlorate (approximately, as estimated from the diagram). The corresponding solid phase in equilibrium with these liquid solutions changes continuously from pure sodium chlorate, through a wide range of continuous solid solution composition up to 60–65% sodium bromate. A break in the liquid curve at point B (and therefore a corresponding discontinuity in
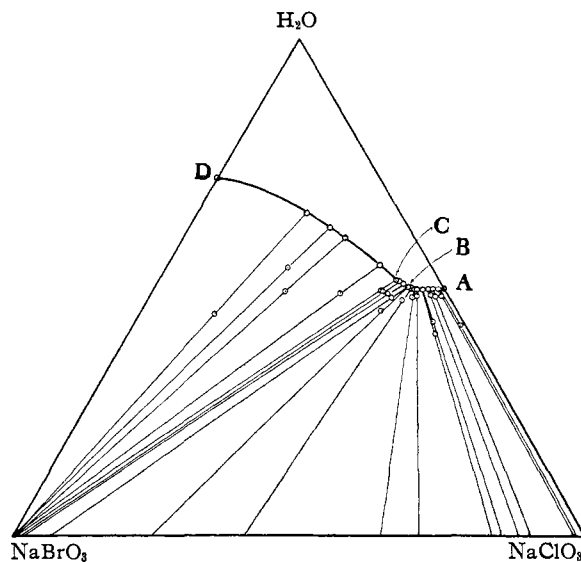
the solid phase) is strongly suggested by the shape of the curve. The solid phase saturating the remaining liquid solutions from B to D seems, however, to be not simply a corresponding solid solution of low sodium chlorate content, but apparently pure sodium bromate over a large part of the curve. For the portion of the curve from D to C (C being an estimated point) the saturating solid is apparently sodium bromate or at most a solid solution of negligible concentration of sodium chlorate in sodium bromate. The appearance of the solid in this region was always quite identical with that of the pure salt, equilibrium was very rapidly attained, and the extrapolation of the tie-lines gave an average algebraic deviation of −0.05% sodium chlorate and an average absolute deviation of 0.41% sodium chlorate, from the point representing pure sodium bromate. Within the experimental variation of the extrapolations, therefore, the phase here is not a solid solution. Beyond C, however, or between C and B, it is possible that a third solid phase is formed, a very finely divided milky solid, slow to settle and slow to come to equilibrium, with compositions, estimated from the disposition of the tie-lines, ranging from very low sodium chlorate content (if not actually pure sodium bromate) to about 5–10% sodium chlorate. This interpretation of three different solid phases would of course involve the existence of two isothermally invariant points for liquid solutions saturated with two adjacent solid phases. These, suggested as points B and C, were not determined; the limits of solid solution com-

position, in view of the slowness in the attainment of equilibrium, would be very difficult to fix.

An alternative possibility is that the two salts form a single solid solution, theoretically continuous from one pure salt to the other, but that the distribution of the salts between the solid and liquid phases is very uneven. The wide divergence of the tie-lines for complexes giving solutions containing approximately 6% sodium bromate (point B) would then simply indicate a marked tendency toward the formation of an isothermally invariant point, because of a tendency toward discontinuity in the solid phase. The observed curvature at the point B, however, suggests actual discontinuity, so that the latter interpretation, while not impossible, seems rather unlikely.

The solid phases are therefore suggested as being pure sodium bromate from D to C, solid solution of some sodium chlorate in sodium bromate (S.S. I) from C to B, and a solid solution (S.S. II) of wide range of proportions of the salts, up to pure sodium chlorate, from B to A. If this interpretation is correct, this system might then be taken as another example of the type of solid solution formation suggested as possible in connection with a study of the system $NaBrO_3$–Na_2SO_4–H_2O[2]; that is, a system in which the miscibility of the salts is such that while solid solutions are formed, a pure salt may still constitute one of the solid phases by itself.

The same general characteristics were noted for the system in the results of a partial isotherm at 50°, also shown in Table II.

Summary

1. In the system $KBrO_3$–$KClO_3$–H_2O, studied at 25°, the two salts dissolve to a limited extent in each other, forming two solid solutions containing up to 3% potassium chlorate in potassium bromate and up to 5% potassium bromate in potassium chlorate.

2. The salts in the system $NaBrO_3$–$NaClO_3$–H_2O studied at 25° (and incompletely at 50°) form a series of solid solutions which, though the evidence is not altogether conclusive, is apparently discontinuous. The solubility curve at 25° appears to be divided into three portions corresponding to the following solid phases: (1) pure sodium bromate, (2) a sodium bromate solid solution containing up to about 5–10% sodium chlorate, (3) a sodium chlorate solid solution containing from 0 to 60–65% sodium bromate.

3. Conditions for the differential iodometric titration of bromate in the presence of very large amounts of chlorate are examined; with proper correction for the slow reaction of chlorate with iodide in acid solution, small amounts of bromate (0.1–0.2 g.) can be determined accurately in the presence of up to 20 g. of chlorate.

The Electrostatic Effect of Substituents on the Dissociation Constants of Organic Acids. IV. Aromatic Acids[1]

By F. H. Westheimer

I

In 1923 Bjerrum[2] advanced the hypothesis that, except for a statistical factor, the effect of a substituent on the ionization constant of an organic acid is electrostatic in origin. Recently, a more satisfactory mathematical formulation of Bjerrum's hypothesis has been advanced by Kirkwood and the author.[3] This treatment differs from the old essentially in that the solute molecules are regarded as cavities of low dielectric constant within the sol-

vent. Shookhoff and the author[4] have applied the new equations with considerable success to a large number of saturated aliphatic acids, and have shown that it will account not only for the ratio of the first to the second dissociation constants of straight-chain dibasic acids, but also, in contrast to the equations of Bjerrum and of Eucken,[5] for the ratio of the dissociation constants of alkylated dibasic acids and for the effect of dipolar substituents on the ionization constants of monobasic acids.

The purpose of the present paper is to apply the new treatment to aromatic acids.

(1) Presented on April 5, 1939, at the Baltimore meeting of the American Chemical Society.

(2) Bjerrum, Z. physik. Chem., 106, 219 (1923).

(3) Kirkwood and Westheimer, J. Chem. Phys., 6, 506 (1938); Westheimer and Kirkwood, ibid., 6, 513 (1938).

(4) Westheimer and Shookhoff, This Journal, 61, 555 (1939).

(5) Eucken, Z. angew. Chem., 45, 203 (1932).