2. Alanine has been synthesized by a new method using 2-amino-1-propanol as the starting material.

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[CONTRIBUTION FROM THE RESEARCH DEPARTMENT OF THE PENNSYLVANIA SALT MANUFACTURING CO.]

The Reciprocal Salt Pair $NaClO_3 + KCl \rightleftarrows NaCl + KClO_3$ in Water at 0 and 40°

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Introduction

In the course of an investigation of the production of potassium chlorate from sodium chlorate cell liquors and potassium chloride, it was necessary to secure solubility data on the quaternary system of the reciprocal salt pair $NaClO_3 + KCl \rightleftarrows NaCl + KClO_3$ in water.

The only significant experimental work previously reported for this quaternary system was that given by C. Di Capua and U. Scaletti,[1c] who investigated this reciprocal salt pair and the various component ternary systems involved at 20°.

In view of the fact that in the interpretation of their data for the ternary systems $KClO_3$–KCl–H_2O and $KClO_3$–$NaClO_3$–H_2O at 20°, Di Capua and Scaletti arrived at isothermally invariant point compositions which were at considerable variance with other reported data, new determinations of these invariant points for the two ternary systems were also undertaken. Rather than repeat their work at the same temperature (20°), the quaternary system and the ternary systems were studied at 0 and 40°.

Materials.—All the salts employed in this study were of C. P. grade and were used without further purification. The chlorate salts employed were found to average 99.9+% pure based on the determination of chlorate content.

Apparatus.—Two types of apparatus were used in this investigation. For the 0° experiments, the mixtures of the solid salts and water sealed in Pyrex bottles were fastened to a rotor suspended in a constant temperature bath. An aqueous glycol solution was used as the bath liquid. The temperature was maintained at 0±0.1° by intermittent circulation of a brine solution (−15 to −5°) through a cooling coil immersed in the well lagged bath. The circulation of the brine was controlled by a mercury thermoregulator.

In the 40° experiments, the mixtures of the solid salts and water were placed in a 250 ml. 3-necked flask and immersed in a constant temperature water-bath. The contents of the flasks were agitated by glass stirrers provided with mercury seals. A thermometer was inserted in each flask. The temperature was maintained at 40±0.05° by a heater controlled by a mercury thermoregulator.

The actual bath temperature in each instance was set and checked by means of a U. S. Bureau of Standards calibrated thermometer.

Procedure.—For each system studied, a preliminary experiment was carried out in which an original mixture of the solid salts and water was gradually augmented by small additions of the solid salts until the density and composition of the resultant solution became constant. From these data, mixtures of the solid salts and water known to result in a solution saturated with respect to the salts were prepared for the final tests. Saturation with respect to the salts was checked in the 40° tests by X-ray analysis of the dried and ground solid residues.

Sampling and Analysis.—The equilibrium solutions were sampled by withdrawing the clear supernatant solutions through cotton filtering plugs directly into the density pipet. After determining the density, the samples were diluted to a convenient volume and aliquots taken for analysis. The chloride ion was determined by the Volhard method as modified by Caldwell and Moyer.[2] The chlorate ion was determined by the method of Ditz as described by Kolthoff and Furman.[3] The sodium ion was determined by direct precipitation with zinc uranyl acetate as described by Barber and Kolthoff.[4] The potassium ion was determined by calculation based on the ionic balance. The water content was found by difference. The volumetric ware employed was recalibrated.

Results

The compositions of the solutions at the quaternary isothermally invariant points determined at 0° and 40° are presented in Table I along with the data of Di Capua and Scaletti. The compositions of the solutions at the ternary isothermally invariant points determined are presented in Tables II and III along with the previously reported data of other workers, *i. e.*, J. Fleck,[5] M. Donald,[6] and Iljinski.[7]

TABLE I

Temp., °C.	Solid phases present	Wt. % composition of solution at isothermally invariant point: Cl	ClO_3	Na	K	H_2O	Density	Observer
0	$KClO_3 + NaCl + KCl$	16.54	0.91	8.63	3.99	69.93	1.235	
0	$KClO_3 + NaCl + NaClO_3$	9.52	19.64	11.39	0.34	59.11	1.349	Munter and Brown
20	$KClO_3 + NaCl + KCl$	16.95	1.41	7.98	5.82	67.84	...	
20	$KClO_3 + NaCl + NaClO_3$	8.50	22.80	11.20	1.00	56.50	...	Di Capua and Scaletti
40	$KClO_3 + NaCl + KCl$	17.17	2.84	7.60	7.34	65.05	1.257	
40	$KClO_3 + NaCl + NaClO_3$	5.60	33.41	12.02	1.39	47.58	1.450	Munter and Brown

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TABLE II

ISOTHERMALLY INVARIANT POINT IN THE SYSTEM $KClO_3$–KCl–H_2O

Temp., °C.	Wt. % composition at the isothermally invariant point KCl	$KClO_3$	H_2O	Observer
0	21.36	0.71	77.93	Munter and Brown
0	21.16	0.71	78.13	Fleck[5]
20	4	3	93	Di Capua and Scaletti[1]
20	24.60	1.55	73.85	Fleck[5]
20	25.0	1.56	73.4	Donald[6]
40	26.47	3.15	70.38	Fleck[5]

TABLE III

ISOTHERMALLY INVARIANT POINT IN THE SYSTEM $NaClO_3$–$KClO_3$–H_2O

Temp., °C.	Wt. % composition at the isothermally invariant point $NaClO_3$	$KClO_3$	H_2O	Observer
0	44.21	0.44	55.35	Munter and Brown
20	4	3.3	92.7	Di Capua and Scaletti[1]
24.2	49.18	1.53	49.29	Iljinski[7]
40	51.75	3.41	44.85	Munter and Brown
40	51.97	3.24	44.79	Iljinski[7]

Discussion

The 0, 20 and 40° isotherms for the quaternary system of the reciprocal salt pair

$$NaClO_3 + KCl \rightleftarrows KClO_3 + NaCl$$

in water are shown in Fig. 1, plotted after the method of Jänecke. This diagram was constructed from the results presented in Tables I, II and III, and from the data of Blasdale,[8] for the system NaCl–KCl–H_2O, and the data of A. L. Pitman, J. McLaren, F. Davis and P. Groggins[9] for the system $NaClO_3$–NaCl–H_2O.

In regard to the ternary systems, $NaClO_3$–$KClO_3$–H_2O and $KClO_3$–KCl–H_2O, it appears that Di Capua and Scaletti have mistaken the sharp curvature of the $KClO_3$ solubility isotherm in the range of low KCl and $NaClO_3$ concentrations as an indication of the location of the invariant point. In view of the agreement of the results secured in this investigation with those previously reported by Fleck, Donald and Iljinski for these systems, the results of Di Capua and Scaletti for these systems have not been used in the preparation of the quaternary phase diagram.

In regard to the quaternary isotherms, the location of the $KClO_3 + NaClO_3 + NaCl$ isothermally invariant point for 20° as given by Di Capua and Scaletti is irregular with respect to the 0 and 40° isothermally invariant points. In view of the regularity of the other points, it appears that further experiments on the 20° isothermally invariant point are desirable.

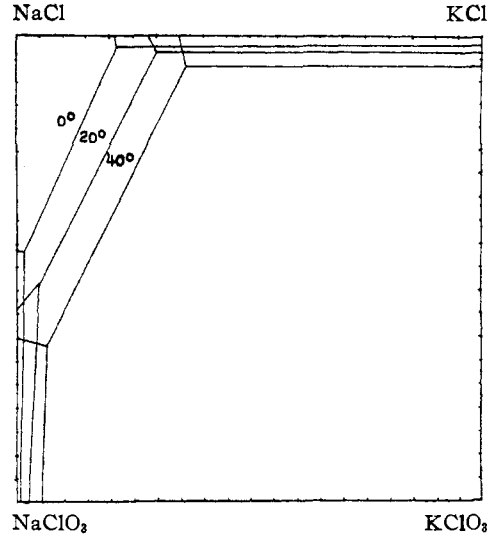

Fig. 1.—0, 20 and 40° isotherms for the reciprocal salt pair $NaClO_3 + KCl \leftrightarrows KClO_3 + NaCl$.

In general, it is apparent from the phase diagram that the salt pair $KClO_3$–NaCl is the stable salt pair in the temperature range from 0 to at least 100°. This is confirmed qualitatively by van't Hoff's solubility product rule. Further there is little indication that, in this temperature range, either of the two quaternary isothermally invariant points become incongruently saturated.

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Summary

1. The isothermally invariant points for the system of the reciprocal salt pair $NaClO_3 + KCl \rightleftarrows NaCl + KClO_3$ in water have been determined at 0 and 40°.

2. The stable salt pair in this system from 0 to 40° is $KClO_3$–NaCl. Indications are that this salt pair remains stable up to at least 100°.

3. The isothermally invariant point of the system $NaClO_3$–$KClO_3$–H_2O at 0° has been determined. The isothermally invariant point for the system $NaClO_3$–$KClO_3$–H_2O at 40° and that for the system $KClO_3$–KCl–H_2O at 0° were redetermined.

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