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synthesis of strong oxidizers

Department of Chemistry
University of Florida
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Attached is a summary of
the results of the project research for
the period October 1, 1959 to September 30, 1960

I. The Reactions of Dinitrogen Tetroxide with Lithium Carbonate, with a Series of Magnesium Compounds, and With Aluminum Chloride

We have recently been interested in the problem of the synthesis of new compounds possessing strong oxidizing characteristics and having low oxidation equivalent weights. Among the substances considered as possible interesting new species are complexes of light metal nitrates having ligands of relatively low molecular weight and high oxidizing capacity. We, therefore, have begun an investigation of such complexes of lithium nitrate, magnesium nitrate, and aluminum nitrate. Since these nitrates are not commercially available in an anhydrous condition and since most of the hydrated nitrates are difficult to dehydrate, we have investigated the possible synthesis of these nitrates by means of the reactions of liquid dinitrogen tetroxide with various lithium and magnesium compounds. At the same time we have been interested in the formation of dinitrogen tetroxide adducts of these metal nitrates. Specifically, the reactions of dinitrogen tetroxide with lithium carbonate, magnesium carbonate, magnesium oxide, magnesium hydroxide, magnesium chloride hexahydrate, magnesium perchlorate and aluminum chloride, have been studied.

Experimental

Materials: Dinitrogen tetroxide supplied by the Matheson Company was purified by slow distillation through a 60 cm. tube packed with a mixture of phosphorus (V) oxide and sand. It was stored at Dry Ice temperature until ready for use. Chemically Pure or reagent Grade lithium, magnesium, and aluminum compounds were used throughout this study.

Procedure: The purification of the dinitrogen tetroxide and its reactions with the various lithium, magnesium and aluminum compounds were all carried out in an all glass apparatus which was fitted with Teflon plug stopcocks and Teflon sleeve joints. Fluorocarbon grease was used to lubricate ball joints. A diagram of the reaction apparatus is given in Fig. 1. A weighed sample of the metal compound was placed in Flask A, and an excess of dinitrogen tetroxide condensed over it from transfer cell B. The reflux condenser C was kept at 0°C to prevent the escape of dinitrogen tetroxide during the reaction period. Agitation in A was provided by a magnetic stirrer. At the end of the reaction period evaporation of excess dinitrogen tetroxide through trap D filled with Kel-F oil was permitted.

Analyses: Magnesium and aluminum were estimated by titration with ethylenediamine tetracetic acid solution using Eriochrome Black T as indicator. In the case of aluminum, an excess of ethylenediamine tetracetic acid solution was added and the excess titrated with standard Zn^{++} solution. Total nitrogen was determined by Devarda's method, and chloride by the Volhard procedure. Nitrite was determined by oxidation with potassium permanganate. Karl Fischer reagent was used to estimate water content where such estimates were possible. Samples for X-ray diffraction and mulls for infrared measurements were prepared in the dry box.

Reaction of Lithium Carbonate with Dinitrogen Tetroxide. Lithium carbonate was used as the starting material for the preparation of lithium nitrate. Liquid dinitrogen tetroxide reacts only very slowly with dry lithium carbonate, but the addition of a small amount of water speeds up the reaction. The reaction is practically complete after 96 hours of contact at temperatures between 0° and 20° yielding an essentially anhydrous product, even though up to 20% water has been added. The overall equation, suggested by Addison (1)

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(1) O. C. Addison and J. Lewis, Jr., Chem. Soc. 1319-20 (1953)

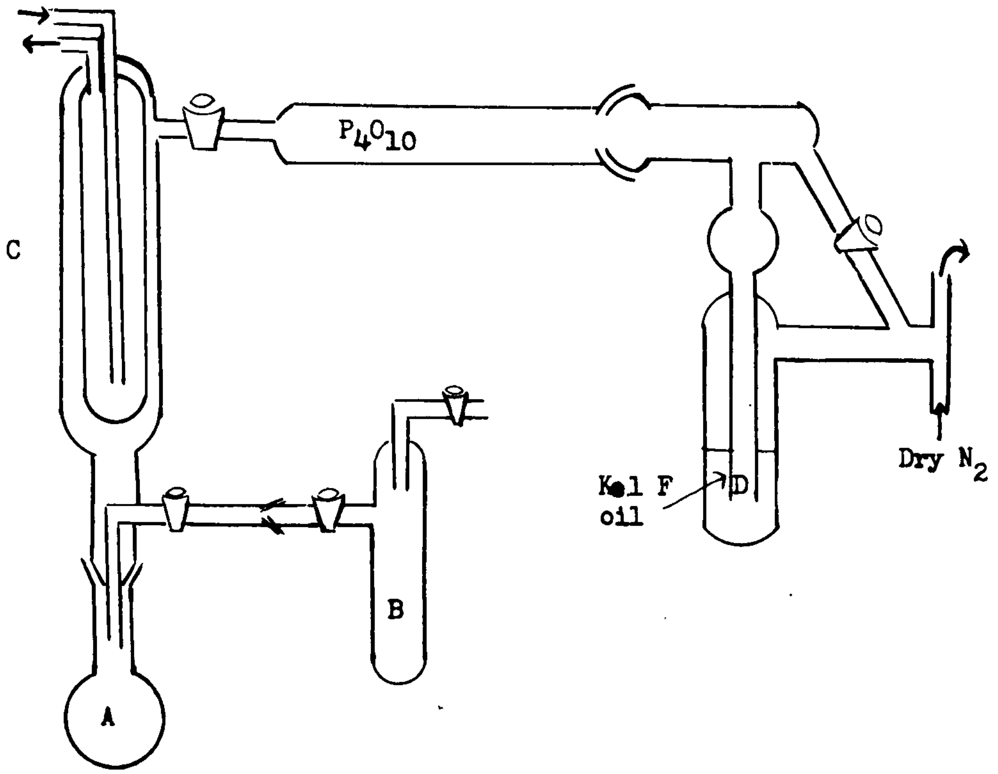

Fig. 1

for the sodium salt, seems to result from two successive reactions:

$$2\ N_2O_4 + H_2O \longrightarrow 2\ HNO_3 + N_2O_3$$

$$2\ HNO_3 + Li_2CO_3 \longrightarrow 2\ LiNO_3 + H_2O + CO_2$$

$$2\ N_2O_4 + Li_2CO_3 \longrightarrow 2\ LiNO_3 + N_2O_3 + CO_2$$

The formation of N_2O_3 is evidenced by the appearance of a blue-green liquid at low temperatures. The experimental conditions and the yield of lithium nitrate obtained in different runs are summarized in Table I. It should be noted even where 19% water is added, only trace amounts of nitrates are found in the product.

Table I

Water content in carbonate	Reaction temperature	Reaction time	% $LiNO_3$	% $LiNO_2$
Dry at 140°C	17-21°C	38 hours	26.35	----
Dry at 140°C	-5.0° C	33 "	30.13	----
Undried	0-10° C	36 "	43.30	----
1.5%* added	10-20°C	36 "	70.61	----
5.0%* added	10-20°C	48 "	81.3	0.1
15%* added	10-20°C	45 "	94.8	0.2
19%* added	0-20° C	96 "	98.2	0.2

*Based on dry weight of carbonate.

No evidence was found to indicate the formation of an adduct of lithium nitrate with dinitrogen tetroxide under the conditions of the experiment. We believe that the above experiments demonstrate a useful procedure for preparing anhydrous lithium nitrate.

Reactions of Basic Magnesium Carbonate, Magnesium Oxide, and Magnesium Hydroxide with Dinitrogen Tetroxide. Reactions of liquid dinitrogen tetroxide with basic magnesium carbonate, magnesium oxide, and magnesium hydroxide were carried out in accordance with procedures already described. The reactions take place much more slowly than in the case of the lithium compound and their rates appeared to decrease as the reaction proceeded. In no case was the reaction carried to completion. Typical experiments are summarized in Table II.

Table II

Reactant	% Water added**	Reactive Temp. °C	Reaction time (hrs)	% $Mg(NO_3)_2$ in Product
Basic Magnesium carbonate	0	5-20	20	56.3
	0	0-20	54	68.2
Magnesium Oxide	25	0-20	40	60.7*
	50	0-20	42	61.5*
Magnesium Hydroxide	0	0-20	90	74*

*Based on the assumption that all the nitrogen present in the sample is in the form of NO_3^-, i.e. that there is no NO_2^- or N_2O_4 present.

**Based on the dry weight of oxide, carbonate, or hydroxide.

It is believed that the slowing down of the reaction results from the formation of a layer of magnesium nitrate over the surface of the carbonate, oxide, or hydroxide particles.

Reaction of Hydrated Magnesium Chloride and Anhydrous Magnesium Chloride with Dinitrogen Tetroxide. It was readily shown that various hydrates of magnesium chloride are readily converted to the corresponding hydrated nitrates without appreciable change in the hydration of the magnesium ion.

$$[Mg(H_2O)n]Cl_2 + 2N_2O_4 \longrightarrow [Mg(H_2O)n](NO_3)_2 + 2NOCl$$

However, the reaction of anhydrous magnesium chloride with liquid dinitrogen tetroxide appears quite promising as a method for preparing anhydrous magnesium nitrate. Reaction of anhydrous magnesium chloride with liquid dinitrogen tetroxide at 20° for a period of nine days yielded a product having the composition expressed by the formula $Mg(NO_3)_2 \cdot 0.62N_2O_4$, plus about two percent of reacted magnesium chloride. This product was a white powder with a low vapor pressure of dinitrogen tetroxide but lost weight only very slowly at 25° under vacuum. When the product was kept in contact with liquid dinitrogen tetroxide an additional day the composition changed to correspond to the formula $Mg(NO_3)_2 \cdot 0.74N_2O_4$. It is probable that the product contains an adduct of N_2O_4 with $Mg(NO_3)_2$ and that it consists of a mixture of $Mg(NO_3)_2$ with that adduct (probably $Mg(NO_3)_2 \cdot N_2O_4$). The X-ray diffraction pattern contains lines characteristic of anhydrous magnesium nitrate plus additional unassigned lines. When this product is heated to constant weight at 110° under vacuum the resulting product gave the following analysis: 15.82% Mg; 17.80% N; 1.77% Cl. Calcd. for $Mg(NO_3)_2$: 16.40% Mg; 18.90% N. The product thus consists of 94.23% $Mg(NO_3)_2$ and 2.37% $MgCl_2$ with the balance no larger in amount than the insoluble impurity present in the original magnesium chloride. The x-ray diffraction pattern of the product agrees perfectly with that reported by Huebel (2) for anhydrous magnesium nitrate.

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2. J. Huebel, Bull. Soc. Chim. 162 (1952)

Reaction of Magnesium Perchlorate with Dinitrogen Tetroxide. The product of the reaction of magnesium perchlorate with dinitrogen tetroxide has an elemental composition corresponding roughly to the formula $Mg(ClO_4)_2 \cdot 2N_2O_4$, as shown in Table III. The product could also be formulated as the nitrosonium salt of a complex anion, $[NO]_2\ [Mg(ClO_4)_2(NO_3)_2]$, or as the mixture $Mg(NO_3)_2$ + 2 $NOClO_4$, all of which have the same elemental composition.

Table III

Reaction Temperature	Reaction time	% Mg	% N	N/Mg
0-15°C	26 hours	5.42	14.4	4.6/1
0-20°C	56 "	6.22	14.0	3.90/1
Calculated for $Mg(ClO_4)_2 \cdot 2N_2O_4$		5.97	13.75	4.0/1

The simple molecular addition compound can be ruled out as the major component, since the infrared spectrum (A-15) shows two bands of medium intensity at 2300 and 2270 cm^{-1}, characteristic of the NO^+ ion, (3) and also a strong band at 1383 cm^{-1} which belongs to the NO_3^- ion. On the other hand, the X-Ray diffraction pattern indicates that both magnesium nitrate and nitrosyl perchlorate are major constituents of this product. The overall reaction thus appears to be as follows:

$$Mg(ClO_4)_2 + 2\ N_2O_4 \longrightarrow Mg(NO_3)_2 + 2\ NOClO_4$$

The hydration of this mixture yields $Mg(ClO_4)_2 \cdot 6H_2O$, probably through the reaction of perchloric acid with the nitrate. The thermal decomposition of the solid mixture in vacuum failed to give pure magnesium nitrate, as expected, but seems to give a mixture of nitrate and perchlorate containing 9 to 11% nitrogen.

Reaction of Aluminum Chloride with Dinitrogen Tetroxide. A large excess of dinitrogen tetroxide was condensed over a sample of Merck reagent grade anhydrous aluminum chloride held at Dry-Ice temperature. As the temperature was allowed to rise, reaction began even before the dinitrogen tetroxide was

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3. C. C. Addison and B. J. Hathaway, J. Chem. Soc. 1468 (1960).

completely melted, yielding a red liquid (NOCl). The solid took on a spongy appearance and after one to two days stirring, a yellow, crystalline compound appeared. The reaction was continued at the boiling point of dinitrogen tetroxide (21°) for five days, the remaining liquid removed, after which the solid product contained no appreciable chloride. The product was then dried under vacuum at 25° and analyzed.

	%N	%Al	%Cl	Ratio N/Al
Found	21.20	10.90	0.01	3.76/1.0
Calcd. for $Al(NO_3)_3$	19.73	12.66	-	3.0/1.0
Calcd. for $Al(NO_3)_3 \cdot N_2O_4$	22.97	8.84	-	5.0/1.0

The analysis corresponds to the empirical formula $Al(NO_3)_3 \cdot 0.38N_2O_4$. The infrared spectrum of the product contained a band of medium intensity at 2260 cm^{-1}, characteristic of the NO^+ ion, the same band appearing in the spectrum of $NO[AlCl_4]$ at 2238 $cm.^{-1}$ (4). Strong bands also appear in the region 1460-1600 cm^{-1}, characteristic of the nitrate group ($-ONO_2$) in covalent nitrates. (5) Two other bands at 1730 and 1275 cm^{-1}, can be attributed to either $-ONO_2$ or to N_2O_4. (3) Thus, we believe the reaction leads to a mixture of $Al(NO_3)_3$ and $NO[Al(NO_3)_4]$ in accordance with the equations:

$$AlCl_3 + 3N_2O_4 \longrightarrow Al(NO_3)_3 + 3NOCl; \quad Al(NO_3)_3 + N_2O_4 \longrightarrow NO[Al(NO_3)_4]$$

When heated to 80° under vacuum for 4 hours, the yellow, crystalline solid loses 33% of its weight and becomes white. Analysis of the white product:

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4. O. J. Miller and D. Watson, J. Chem. Soc. 1369 (1957).

5. C. C. Addison and B. M. Gatehouse, J. Chem. Soc. 613 (1960).

	%Al	% N	Ratio N/Al
Found	15.5	17.18	2.13/1.0
Calcd. for $Al(NO_3)_3$	12.66	19.73	3.0/1.0
Calcd. for $Al_2O(NO_3)_4$	16.98	17.61	2.0/1.0

The infrared spectrum of this product shows a much weaker NO^+ band than the above and two very strong $-ONO_2$ bands at 1570 and 1610 cm^{-1}. It appears, therefore, that most of the $NO[Al(NO_3)_4]$ has decomposed to $Al(NO_3)_3$, and that some of the $Al(NO_3)_3$ has been converted to a basic aluminum nitrate such as $Al_2O(NO_3)_4$ in accordance with the equation:

$$2\ Al(NO_3)_3 \longrightarrow Al_2O(NO_3)_4 + 2NO_2 + NO_2$$

Discussion

Addison and his coworkers have pointed out that dinitrogen tetroxide can act as a potential source of both NO_2^- and NO_3^- ions through the two dissociation mechanisms

$$N_2O_4 \rightleftharpoons NO_2^+ + NO_2^-$$

$$N_2O_4 \rightleftharpoons NO^+ + NO_3^-$$

The results reported herein show that in its reactions at or near room temperature with lithium carbonate, with magnesium oxide, carbonate, chloride, and perchlorate, and with aluminum chloride, dinitrogen tetroxide reacts in accordance with the second of these possibilities. Previously reported work with sodium carbonate and sodium hydroxide, with calcium carbonate, (6) with zinc carbonate and zinc sulfide (7), and with sodium peroxide, calcium oxide, and zinc, (8) are in agreement with this result:

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6. E. Briner, P. Lugrin and R. Mounier, Helv. Chim. Acta 13, 64 (1930).
7. V. T. Oza, J. Indian Chem. Soc., 33, 911-6 (1956).
8. C. C. Addison and J. Lewis, J. Chem. Soc., 1874-9 (1953).

It has previously been shown (9, 10, 11, 12) that zinc nitrate, copper nitrate, and ferric nitrate form dinitrogen tetroxide adducts which have in some instances been formulated as nitrosyl salts containing nitrate metalate complexes, as e.g. $(NO)_2[Zn(NO_3)_4]$ for $Zn(NO_3)_2 \cdot 2N_2O_4$. This study, however, presents the first reported evidence for the formation of dinitrogen tetroxide adducts of magnesium and aluminum nitrates. Furthermore, the evidence obtained indicates, that since these magnesium nitrate and aluminum nitrates adducts have only a low vapor pressure of oxides of nitrogen at room temperature, the bonding of the dinitrogen tetroxide to the metal nitrate is moderately strong.

Finally we believe that the preparation of anhydrous magnesium nitrate by the thermal decomposition of the reaction product of anhydrous magnesium chloride and dinitrogen tetroxide is a distinctly more convenient method than the currently used procedure involving the reaction of magnesium hydroxide with dinitrogen pentoxide.

It is interesting to note that even in the presence of excess dinitrogen tetroxide, the hydration of the magnesium ion is unaffected and the reaction of hydrated magnesium chloride with dinitrogen tetroxide affects only the chloride ion.

The failure to obtain pure anhydrous aluminum nitrate from the thermal decomposition in vacuo of the product of the reaction of dinitrogen tetroxide with anhydrous aluminum chloride, and the formation instead of a basic aluminum nitrate is not entirely unexpected in view of the known reaction of boron

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9. C. C. Addison, B. J. Hathaway, N. Logan, J. Inorg. and Nucl. Chem. 8, 569-71 (1958).
10. C. C. Addison, B. J. Hathaway, N. Logan, Proc. Chem. Soc. 51-2 (1958).
11. C. C. Addison, N. Hodge, J. Chem. Soc. 1138-43 (1954).
12. C. C. Addison, J. Lewis, R. Thompson, J. Chem. Soc. 2829-33 (1951).

trichloride with dinitrogen tetroxide (13) to yield boric oxide and nitrosyl chloride. It is possible that the decomposition of the aluminum nitrate-dinitrogen tetroxide adduct under somewhat less stringent conditions than those used in this study might yield pure, anhydrous aluminum nitrate.

II. Solubilities of Light Metal Perchlorates in H_2O—H_2O Mixtures

The solubilities of $KClO_4$ and $NaClO_4$ at 30.00°C were determined in the mixed solvent H_2O—H_2O as a function of solvent composition, and ternary phase diagrams were constructed for these systems.

Potassium Perchlorate

The solubility of $KClO_4$ in H_2O—H_2O_2 mixtures increases markedly with increasing H_2O_2 concentration to more than twice the pure water solubility in 95% hydrogen peroxide. This may be due to preferential solvation of the potassium ion by hydrogen peroxide in the liquid phase. However, as evident from the appearance of the phase diagram, solid solvates of $KClO_4$ with H_2O_2 were not formed at 30°C. Table IV lists the experimental results and Fig. 2 to Fig. 4 the graphical presentation of solubility changes, density changes and the phase diagram, respectively.

Table IV

Solubility of $KClO_4$ in H_2O—H_2O_2 Mixtures at 30°C

Wt.% $KClO_4$	Wt.% H_2O_2	Wt.% H_2O	Density	Wt.% $KClO_4$	Wt.% H_2O_2	Wt.% H_2O	Density
2.42	0.00(14)	97.58	1.0105	3.97	67.96	28.07	1.3348
3.11	36.66	60.23	1.1521	4.20	72.16	23.64	1.3212
3.29	46.37	50.34	1.1970	4.25	73.94	21.81	1.3665
3.42	50.31	46.27	1.2108	4.47	78.43	17.10	1.3767
3.74	61.95	34.31	1.2770	4.70	83.35	12.45	1.4109
3.75	60.80	35.45	1.2786	4.76	84.30	10.94	1.4018
3.92	67.20	28.88	1.3114	5.38	90.92	3.70	1.4554
				5.48	91.08	3.44	1.4645

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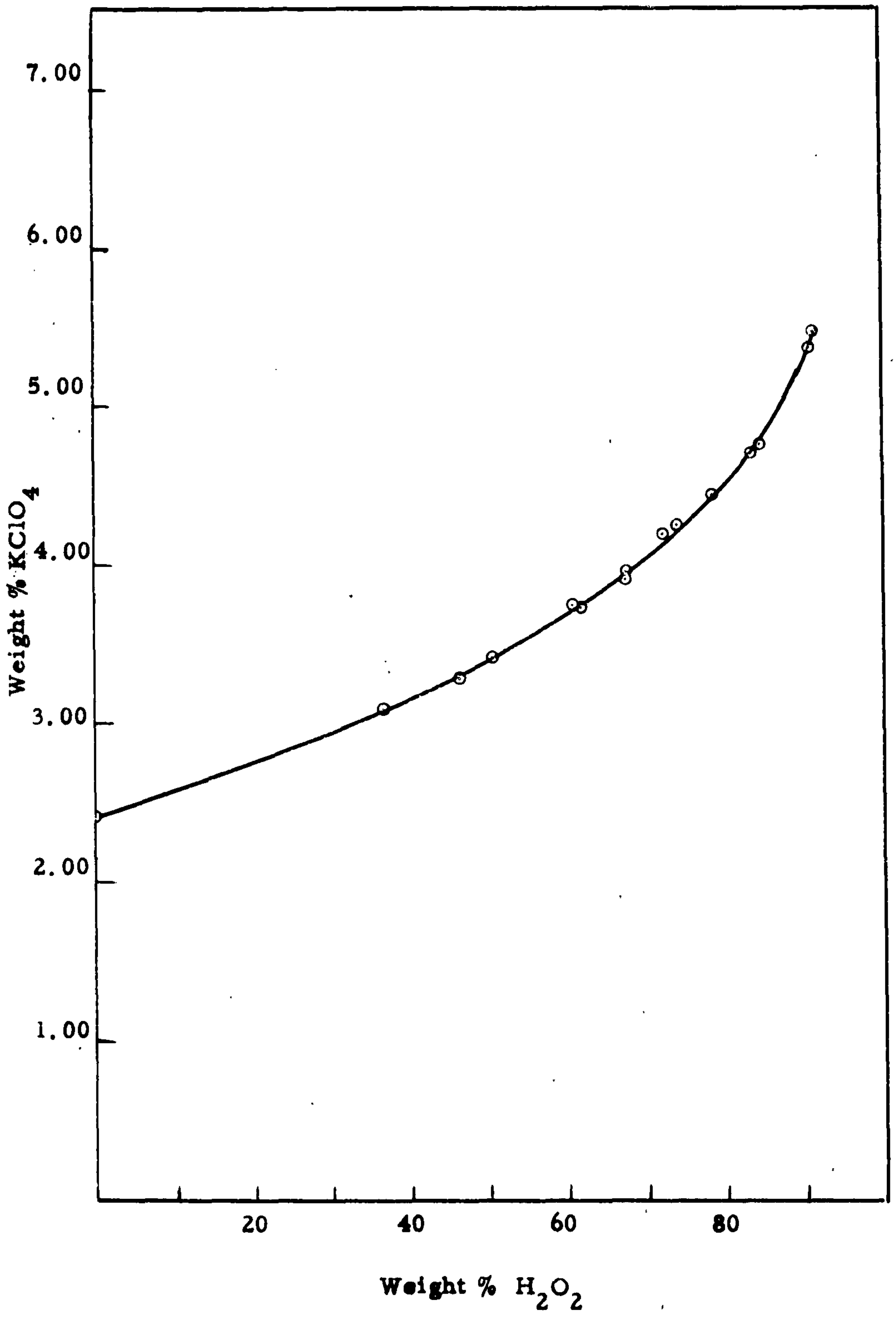
13. J. R. Partington and A. L. Whynes, J. Chem. Soc. 3130 (1954).

Fig. 2

SYSTEM

$KClO_4$-H_2O_2-H_2O AT 30°C



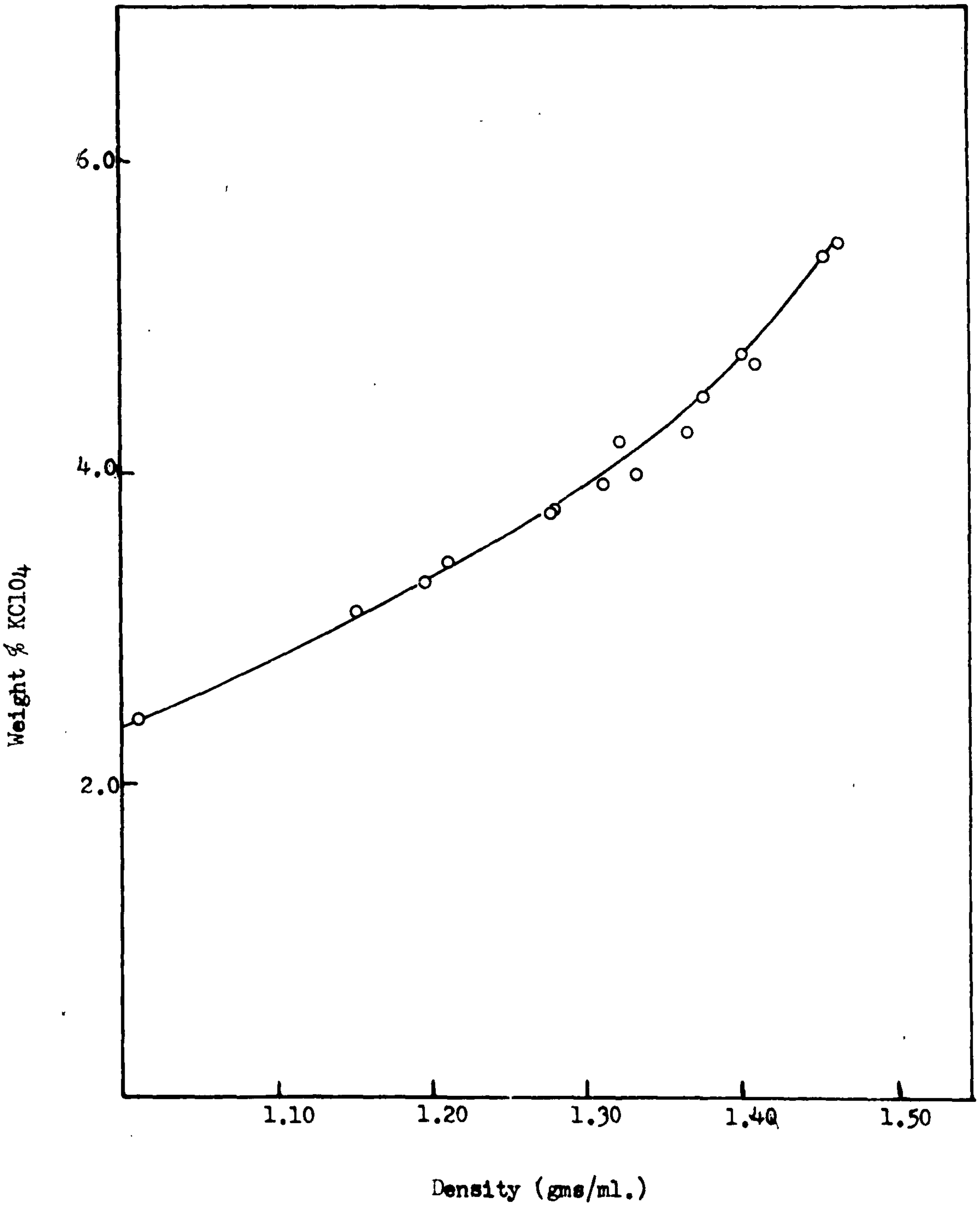


Fig. 3

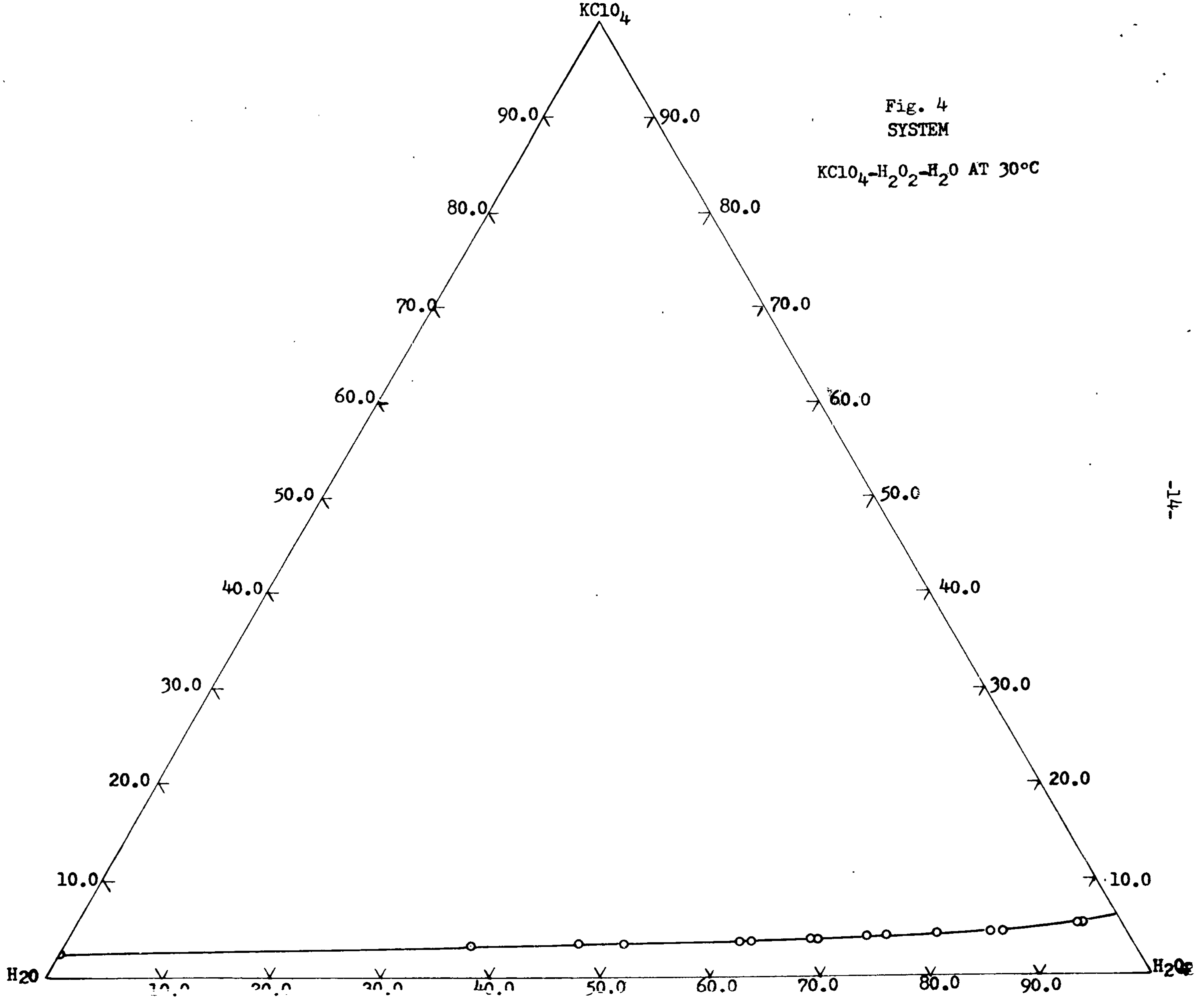


Fig. 4
SYSTEM

$KClO_4$-H_2O_2-H_2O AT 30°C

SYSTEM

$NaClO_4$-H_2O_2-H_2O AT 30°C

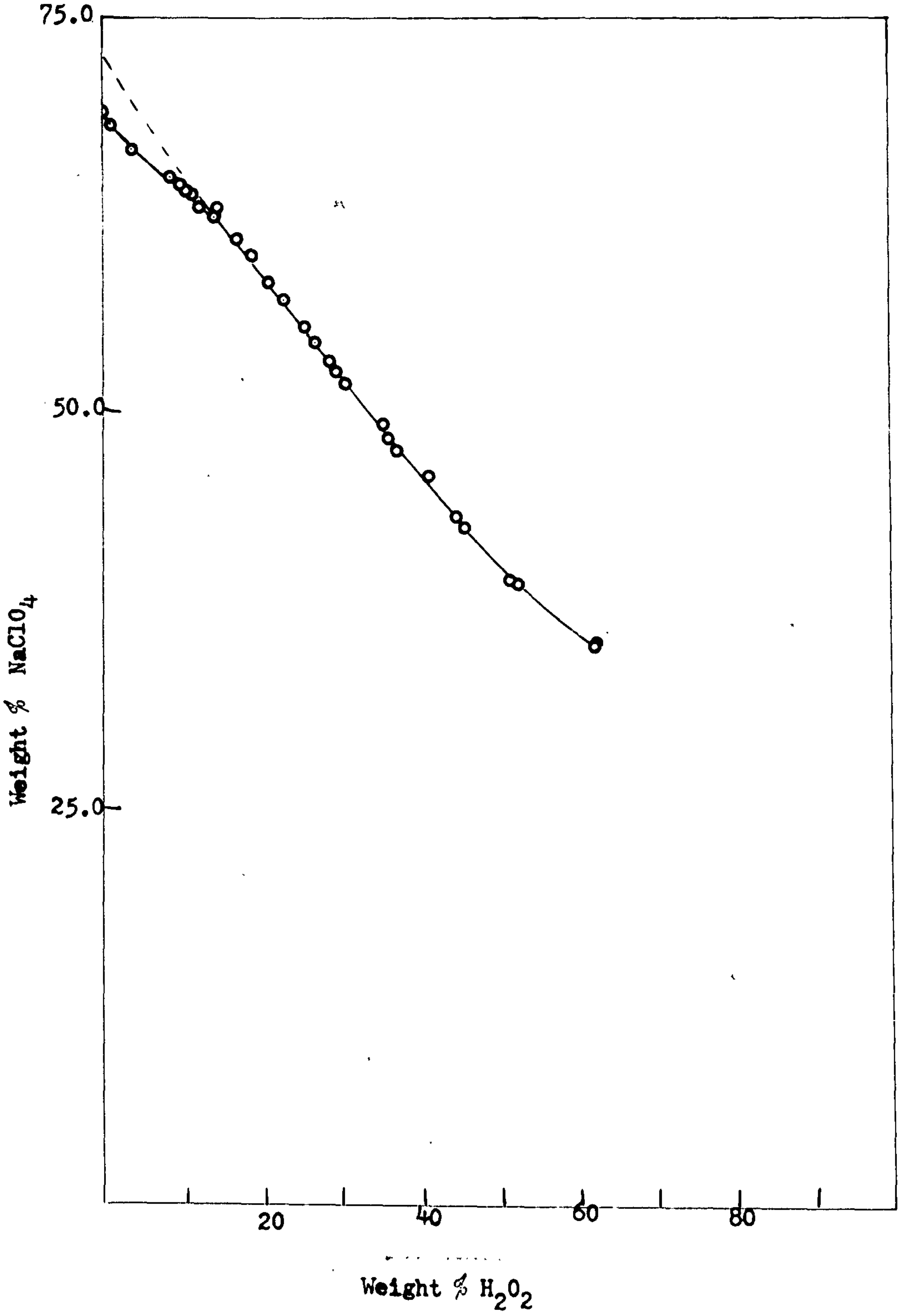


Fig. 5

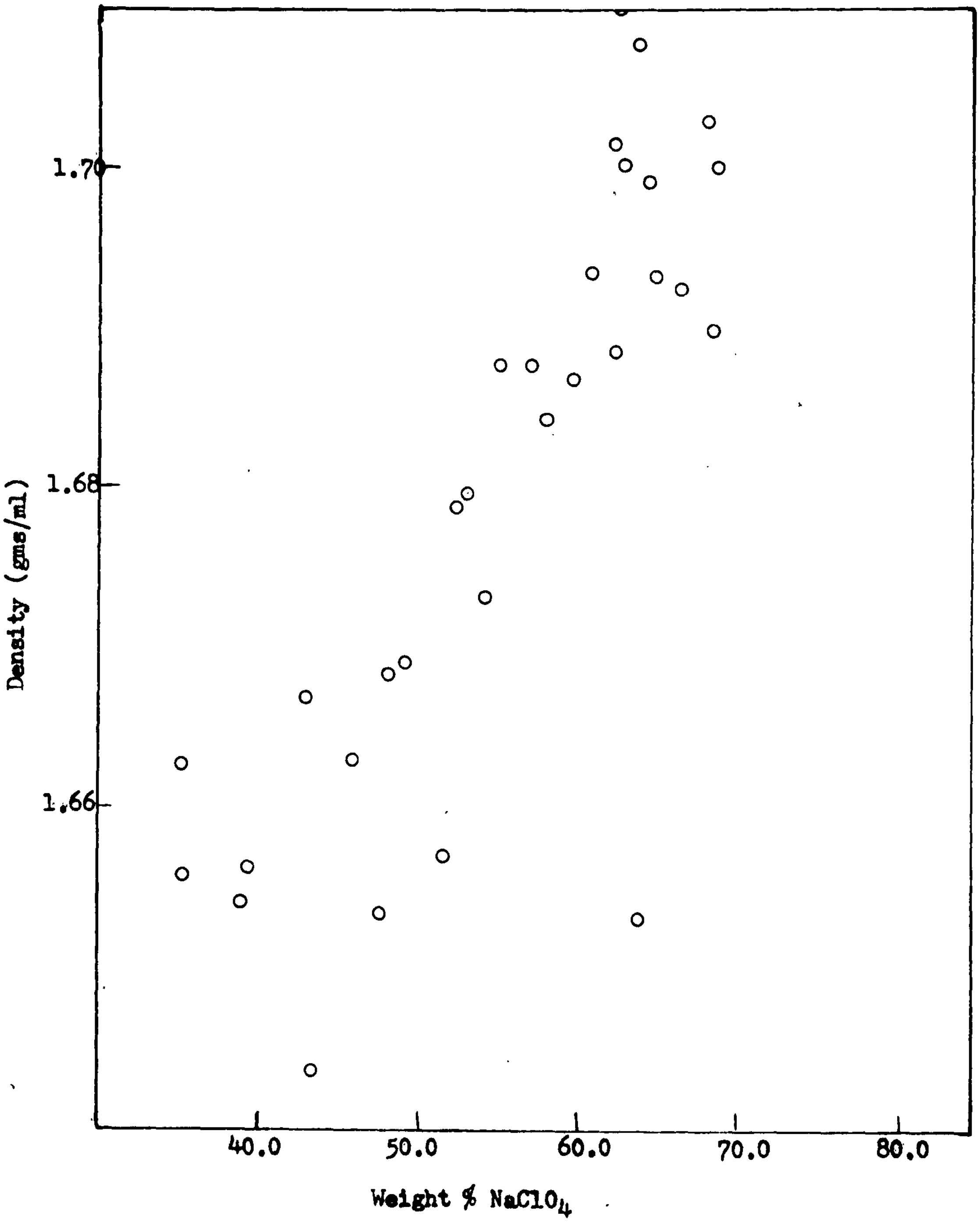


Fig. 6

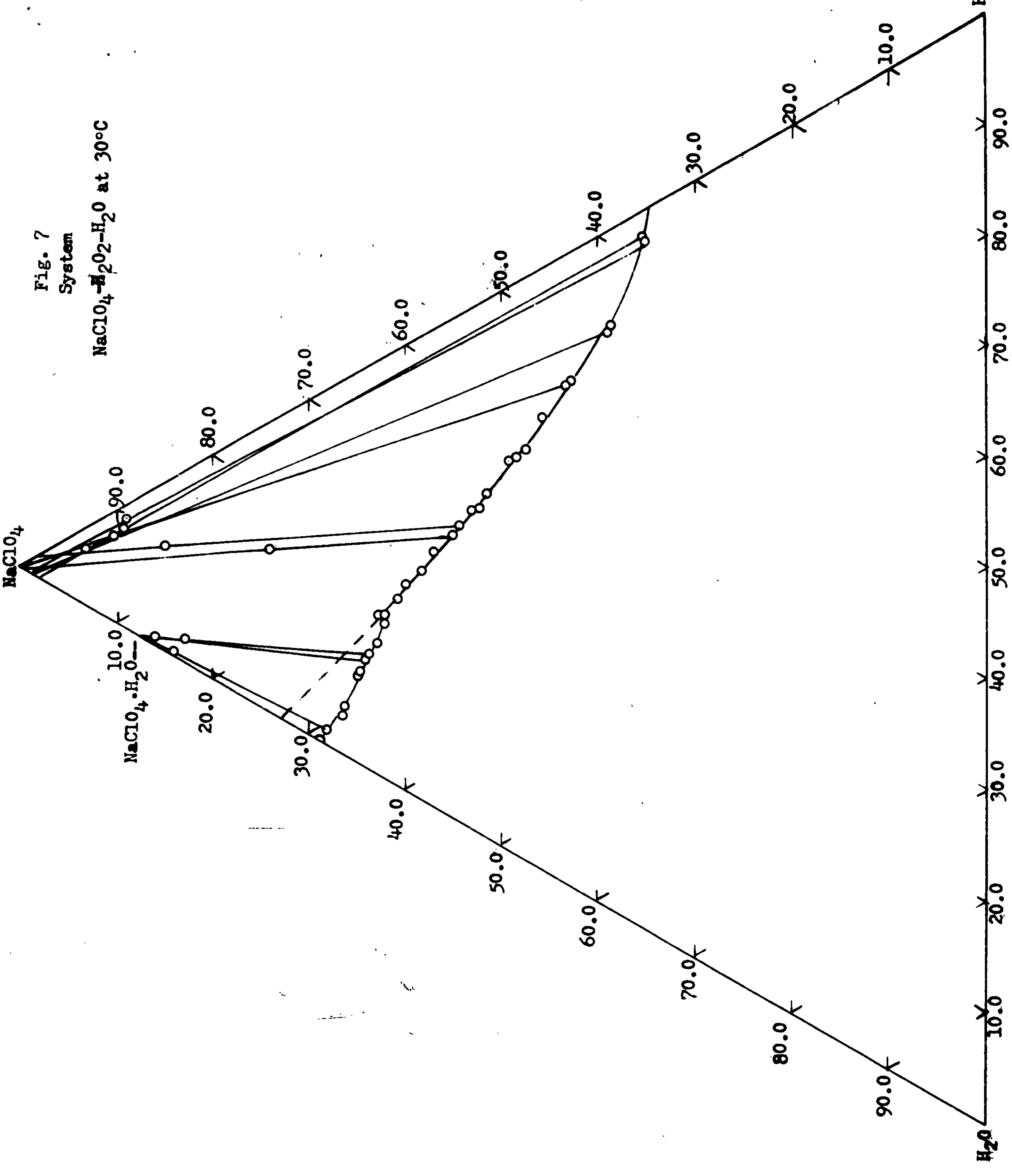


Fig. 7
System
$NaClO_4$-H_2O_2-H_2O at 30°C

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14. Lit. values d:1.0105; % $KClO_4$: 2.5; % H_2O: 97.5; Perchlorates ACS Monograph No. 146, Jos. Schumacher, ed., Reinhold Publishing Company, New York, New York, 1960, p. 224.

Sodium Perchlorate

The results of the solubility studies on $NaClO_4$ are presented in Table V and Figures 5 to 7.

Table V

Solubility of $NaClO_4$ in H_2O—H_2O_2 Mixtures at 30°C

			Wet Residue		
Wt. % $NaClO_4$	Wt. % H_2O_2	Wt. % H_2O	$NaClO_4$	H_2O_2	Density
35.16	61.97	2.87	89.0	9.7	1.6627
35.31	61.93	2.76	89.6	8.5	1.6556
38.97	52.16	8.87			1.6542
39.29	51.47	9.24	93.1	5.0	1.6564
42.79	45.38	11.83	90.5	7.3	1.6669
43.30	44.71	11.99			1.6437
45.96	40.51	13.53			1.6631
47.59	36.84	15.57			1.6584
48.30	35.86	15.84			1.6685
49.18	35.00	15.82			1.6692
51.69	30.84	17.47			1.6571
52.47	29.19	18.34			1.6788
53.18	28.44	18.38			1.6799
54.40	26.52	19.08	85.2	9.1	1.6732
55.27	25.09	19.64	74.1	14.3	1.6876
57.02	22.72	20.26			1.6877
58.26	20.45	21.29			1.6844
59.97	18.22	21.81			1.6869
60.93	16.77	22.30			1.6934
62.17	14.59	23.24			1.6882
62.33	13.57	24.10			1.7017
62.89	14.35	22.76			1.7104
62.91	11.75	25.34			1.7031
63.73	11.06	25.21			1.6582
64.42	9.75	25.83	83.0	2.0	1.6993
64.97	8.20	26.83			1.6932
66.55	3.42	30.03			1.6925
68.16	0.91	30.93			1.7030
68.62	1.21	30.17	83.3	0.3	1.6900
68.98	0.00	31.02	84.5	0.0	1.7003

It is seen that the solubility of $NaClO_4$ decreases with increasing hydrogen peroxide concentration. In addition there appear two solid phases, $NaClO_4$ and $NaClO_4 \cdot H_2O$. The composition of these phases was established by analysis of the moist solid in equilibrium with the solutions. No evidence was found for the formation of solid hydrogen peroxide solvates. Since the densities of the mixtures varied very little with concentration, the density plot was made on a much expanded scale. This scale change accounts for the apparent scatter in the data.

Experimental

Saturated solutions of the salts were prepared by equilibrating a large amount of solid anhydrous salt with the H_2O—H_2O_2 mixture. The samples were immersed in a thermostat held to 30.00 ± 0.01°C and shaken or stirred for several days. Duplicate samples were pipetted for H_2O_2 analysis, density determination and cation analysis from a preheated glass-pitted filter tube. Analysis was then repeated the next day as a test for equilibration.

In the region where there is a transition from $NaClO_4 \cdot H_2O$ to the anhydrous salt equilibration often was very slow. In these cases the mixture was heated to 45°C before immersion in the constant temperature bath and stirred mechanically for at least 48 hours before the first sample was taken.

H_2O_2 was determined by permanganate titration, salt concentration indirectly by passing the sample through a Dowex 50 cation exchange column and titrating the effluent with standard base. The H_2O content was then calculated by difference. The density was found from the weight of a sample delivered from a volumetric pipette. Weighed samples of moist solids were analyzed after rapid filtration of the equilibrium mixture through a glass frit, the filtration apparatus being immersed in the constant temperature bath.