and for the corresponding composition N as P_N. There are now two possible methods of procedure.

Method 1.—(a) Plot P_M *vs.* P_N in weight per cent. on rectangular coördinates. This line represents all possible pairs of points having the correct refractive index relationship. (b) From the weight relationships in step (B), another curve can be derived. If the unknown had no component P (*i.e.*, $P_M = 0$), then the amount of P in the new mixture after the known weight W_2 of composition J had been added, can be readily computed as

$$\frac{\text{wt. of P in } W_2 \text{ g. of J}}{W_1 + W_2} \times 100 = P_N$$

This equation provides one point on the second curve. We may also imagine that M had the same composition as J. In this case, the percentage of P in J, P_J, would not have changed. Hence another point on the second curve is provided, the point being $P_M = P_J$ and $P_N = P_J$. Other points on this curve may be computed by assuming percentages of P in M. This step is not necessary since the curve is a straight line, and the first two points described are the simplest to compute. On this curve are contained all possible compositions that can be derived by adding W_2 grams of J to W_1 grams of M. (c) The intersection of these two curves gives us now directly P_N and P_M. The remaining components of the original unknown may be read off on the triangular graph.

Method 2.[2]—Plot P_M *vs.* the ratio of the distances $MN/NP = r$. Since $r = W_2/W_1$, read on the graph, the value of P_M from the value of r calculated from step (B).

These distances, which can be obtained with the aid of dividers, are equivalent to plotting $(P_N - P_M)/(P_J - P_M)$ *vs.* P_M.

Discussion.—Occasionally the triangular graph will have more complicated contours than those shown in Fig. 2. In such a case, two intersections may occur if method 1 is used, or equivalently, there may be two values of P_M for which $MN/NP = W_2/W_1$. In this case, the method may be repeated using a further amount of the known mixture J.

TABLE I

Component J was pure nitrobenzene; n_1 1.4724; n_2 1.4985; W_1 11.0898 g.; W_2 5.4079 g.

	Grams per cent. Nitrobenzene	Grams per cent. *n*-Butyl bromide	Grams per cent. Benzene
As prepared	23.42	65.41	11.17
As analyzed (1)	23.8	65.8	10.4
graphically (2)	23.8	65.6	10.6
by method 1 (3)	23.5	65.5	11.0
As analyzed (1)	21.1	63.0	15.9
graphically (2)	21.5	63.5	15.0
by method 2 (3)	22.3	64.1	13.6

Table I shows several determinations of the analysis of a known mixture by both methods 1 and 2. The values obtained from method 2 appear to be not quite as precise as those from method 1, at least in the analyses made thus far. This is due apparently to the extra manipulation or computations necessary in order to eliminate the second curve in method 1.

BROOKLYN 10, N. Y. RECEIVED MARCH 8, 1950

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[2] This method was suggested by the reviewer, Dr. J. E. Ricci.

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

The Ternary Systems $AgBrO_3$–$KBrO_3$–H_2O and $AgClO_3$–$NaClO_3$–H_2O at 25°

BY JOHN E. RICCI AND JACK A. OFFENBACH

For information significant in the preparation of silver salts by aqueous double decomposition, the 25° isotherms of the systems $AgBrO_3$–$KBrO_3$–H_2O and $AgClO_3$–$NaClO_3$–H_2O were studied. While the first is simple the second has two series of solid solutions as in the Roozeboom type V. The distribution between the solid and aqueous phases is such, however, that the preparation of $AgClO_3$ from $AgNO_3$ and $NaClO_3$ easily leads to a pure product.

Since the salts silver bromate and silver chlorate are usually prepared by double decomposition involving an alkali salt, the question of the formation of solid solution between the corresponding bromates or between the corresponding chlorates has to be considered in connection with the purification of the final silver salt. An earlier investigation of the ternary system $AgBrO_3$–$NaBrO_3$–H_2O in the range 5–50°[1] showed the formation of a solid solution extending from pure $AgBrO_3$ to the compound $AgBrO_3 \cdot NaBrO_3$, with a distribution, between liquid and solid phases, such that ordinary recrystallization of $AgBrO_3$ would not lead to purification with respect to any contaminating $NaBrO_3$. The system $AgBrO_3$–$KBrO_3$–H_2O, here reported, shows, on the other hand, no solid solution at all at 25°, so that the reaction of $AgNO_3$ with $KBrO_3$ should give a product easily purified.

Silver chlorate is apparently best prepared[2] by the reaction of $AgNO_3$ and $NaClO_3$ in solution, sodium nitrate being much more soluble than silver chlorate. The final product is obtained pure after a few recrystallizations, despite the formation of solid solution between $AgClO_3$ and $NaClO_3$, which has long been known.[3] The purpose of the present study was to investigate the distribution at room temperature between the solid and the liquid solutions.

As in similar reported investigations, ternary complexes of known composition were made to come to equilibrium at 25°, whereupon the saturated liquid solution was filtered and sampled for analysis. In the bromate system the solution was simply evaporated to dryness for its $KBrO_3$ content, since the solubility of $AgBrO_3$ in presence of $KBrO_3$ was

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[1] J. E. Ricci and J. J. Aleshnick, THIS JOURNAL, **66**, 980 (1944).

[2] D. G. Nicholson and C. E. Holley, "Inorganic Syntheses," Vol. II, W. C. Fernelius, Editor, McGraw-Hill Book Co., Inc., New York, N. Y., 1946, p. 4.

[3] J. W. Retgers, *Z. physik. Chem.*, **5**, 436 (1890).

found to be negligible from the point of view of general phase relations. In the chlorate system one sample was titrated for silver with standard KCNS solution and one was evaporated to dryness for total salt content, whereupon $NaClO_3$ was calculated by difference. Tests on known mixtures of $AgClO_3$ and $NaClO_3$ showed the residue to be stable at 110–125°, the temperature range used for evaporation to constant weight.

The available commercial sample of C.P. $AgBrO_3$ was found to contain only 94.7% $AgBrO_3$ by gravimetric determination of silver as AgBr after reduction in acid solution with $NaNO_2$ in presence of a small amount of NaBr.[1] A quantity of the salt for use in the ternary solubility determinations was therefore made from Ag_2CO_3 and aq. $HBrO_3$. The silver carbonate was made (since the commercial material looked obviously impure) by addition of Na_2CO_3 to excess of aq. $AgNO_3$, the precipitate being washed with dil. $AgNO_3$ on a Büchner funnel. The bromic acid solution was made from dil. H_2SO_4 and solid $Ba(BrO_3)_2 \cdot H_2O$ in slight excess, the excess being removed, together with the precipitated $BaSO_4$, by filtration. The solid Ag_2CO_3 was then added slowly, in slight excess, with stirring, to the dilute solution of bromic acid; the presence of excess of Ag_2CO_3, mixed with the white $AgBrO_3$ being precipitated, is revealed by the yellow color of the carbonate. Some concd. HNO_3 was then added to dissolve any carbonate and oxide of silver, and then some bromic acid to precipitate the silver completely as $AgBrO_3$. After some heating and digestion the solid was washed with water, through decantation and filtration, and finally dried at 110° before and after powdering. The bromate content was determined gravimetrically as AgBr, after reduction in dil. HNO_3 with $NaNO_2$ in presence of some $AgNO_3$.[1] On this basis the two batches prepared gave 99.93 and 99.75% $AgBrO_3$, respectively. Similar analysis gave 99.97% purity for the C.P. $KBrO_3$ used.

The data for this ternary isotherm are listed in Table I, in terms of weight percentage. The liquid compositions, determined after two weeks of stirring, remained constant in every case after 3–6 weeks of further stirring. The tie-lines through liquid composition and total complex, examined both graphically and algebraically, show that the solid $AgBrO_3$ does not contain any $KBrO_3$ in solid solution, within the experimental error of this indirect method. The algebraic extrapolation[4] gives −0.05, +0.16 and +0.15% $KBrO_3$, respectively, for the three tie-lines involved. The solubility of the $AgBrO_3$ used was 0.193%, a little lower than the value previously reported[1]; for other literature references, see ref. (1).

Silver chlorate was made according to the procedure described by Nicholson and Holley,[2] from C.P. $AgNO_3$ and C.P. $NaClO_3$. After three recrystallizations the product was 99.72% pure on the basis of gravimetric determination of silver as AgCl after reduction with $NaNO_2$ in presence of some NaCl.

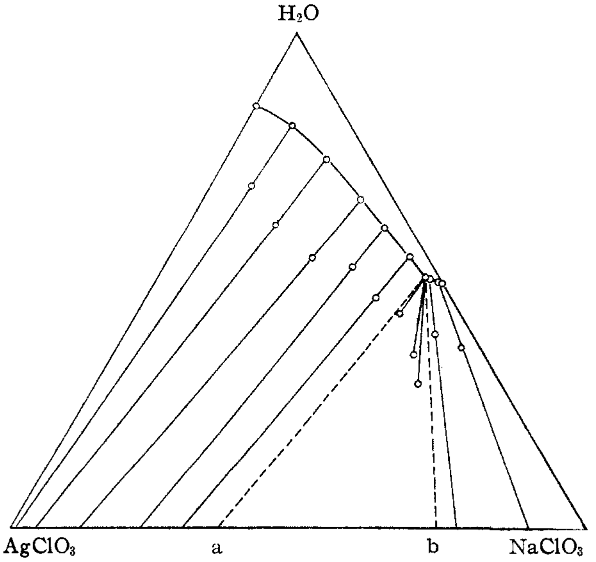

Fig. 1.—Ternary system: $AgClO_3$–$NaClO_3$–H_2O at 25°.

TABLE I

SYSTEM $AgBrO_3$–$KBrO_3$–H_2O AT 25°

Total complex % $AgBrO_3$	Total complex % $KBrO_3$	Liquid solution % $KBrO_3$	Density	Solid phase
...	0.00	(0.19% $AgBrO_3$)	0.9983	$AgBrO_3$
9.56	2.90	3.21	1.022	$AgBrO_3$
9.82	5.16	5.70	1.049	$AgBrO_3$
15.22	5.98	7.03	1.050	$AgBrO_3$
9.38	7.12	7.52	1.054	$AgBrO_3$ + $KBrO_3$
15.33	8.97	7.57	1.052	$AgBrO_3$ + $KBrO_3$
12.02	9.97	7.56	1.053	$AgBrO_3$ + $KBrO_3$
6.99	15.31	7.55	1.054	$AgBrO_3$ + $KBrO_3$
0.00	...	7.52	1.053	$KBrO_3$

The equilibrium measurements for the ternary system $AgClO_3$–$NaClO_3$–H_2O are listed in Table II, in weight percentage, and plotted in Fig. 1. The composition of the liquid solution, first analyzed after two weeks of stirring, was unchanged in every case after 1–3 weeks of further stirring. The solubility found for $AgClO_3$ at 25°, 14.46% by weight, determined by Volhard titration with KCNS, is somewhat lower than the value 14.56% calculated from Noonan's values[5] determined by evaporation. The value for $NaClO_3$, and that for $KBrO_3$ in Table I, agree well with previously reported figures.

TABLE II

SYSTEM $AgClO_3$–$NaClO_3$–H_2O AT 25°

Total complex % $AgClO_3$	Total complex % $NaClO_3$	Liquid solution % $AgClO_3$	Liquid solution % $NaClO_3$	Liquid solution Density	Solid phase % $AgClO_3$	Solid phase
...	0.00	14.46	0.00	1.126	100.00	$AgClO_3$
23.19	7.04	10.02	8.11	1.143	99.1	S.S.I
23.00	15.17	7.48	17.49	1.194	95.7	S.S.I
20.10	24.95	5.56	27.53	1.270	86.9	S.S.I
14.03	32.80	4.23	34.39	1.317	77.4	S.S.I
13.03	39.97	2.85	41.78	1.375	70.1	S.S.I
14.15	55.98	2.14	46.57	1.415	S.S.I + S.S.II	
12.01	52.43	2.15	46.54	1.413	S.S.I + S.S.II	
10.24	45.71	2.15	46.55	1.417	S.S.I + S.S.II	
6.18	54.01	1.66	47.52	1.419	22.5	S.S.II
3.04	60.11	0.56	49.23	1.428	9.9	S.S.II
0.00	...	0.00	50.04	1.424	0.0	$NaClO_3$

The disposition of the tie-lines in Fig. 1 shows two series of solid solutions, one of $NaClO_3$ in $AgClO_3$ and one of $AgClO_3$ in $NaClO_3$. The first, or S.S.I, forms tetragonal prisms and the second, S.S.II, is cubic in crystal form, according to Retgers.[3] The composition of the saturating solid solution in equilibrium with the liquid solution was calculated by algebraic extrapolation of the tie-line fixed by liquid composition and total complex, to the base of the diagram. The limiting compositions of the two solid solutions (points a and b of Fig. 1) were estimated graphically from a Roozeboom type of distribution diagram, Fig. 2, in which the percentage of $NaClO_3$ in the dissolved salts is plotted against its percentage in the solid phases. The limits thus found are ~37% $NaClO_3$ in S.S.I and ~26% $AgClO_3$ in S.S.II. The composition of the isothermally invariant liquid saturated with these two limiting solid solutions is 2.15% $AgClO_3$ and 46.55% $NaClO_3$.

The limiting composition of S.S.I is close to the equi-molar ratio, at 35.7% $NaClO_3$. The tie-lines,

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(4) A. E. Hill and J. E. Ricci, THIS JOURNAL, **53**, 4305 (1931).

(5) E. C. Noonan, *ibid.*, **70**, 2915 (1948).

however, show no tendency to converge at this point, and hence do not suggest, as they do in the corresponding system of the bromates,[1] a tendency for compound formation between the components in the solid state. It is to be expected, therefore, that the limit (point a) will probably vary with temperature.

Since the percentage of $NaClO_3$ in the dissolved salts is always higher than it is in the solid solution, the system is an example of type V in the Roozeboom classification.[6] Evaporation at this temperature therefore always leads, under equilibrium conditions, to a solid richer in $AgClO_3$ than were the dissolved salts. This means that a sample of $AgClO_3$ containing $NaClO_3$ can be purified by a sufficient number of recrystallizations at this temperature. Moreover, since the tie-lines near the $AgClO_3$ side converge markedly toward the $AgClO_3$ corner, or since the solid phase at equilibrium is almost pure $AgClO_3$ for an appreciable concentration of $NaClO_3$ in the aqueous solution, this purification by recrystallization is rapid and efficient. In contrast, $NaClO_3$ containing some $AgClO_3$ could not thus be purified by recrystallization, since the solid obtained would be still richer in $AgClO_3$.

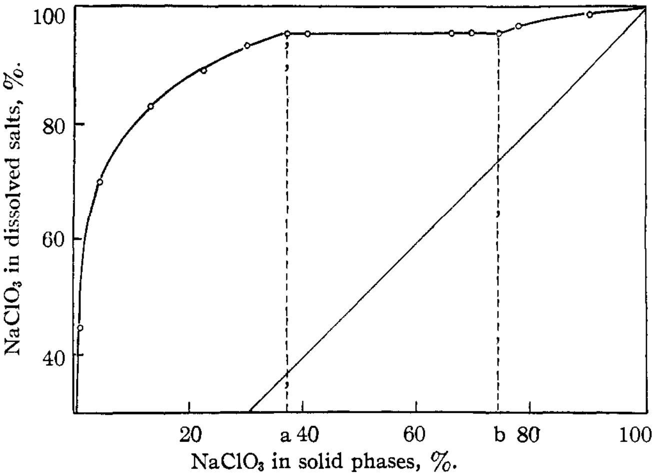

Fig. 2.—System $AgClO_3$–$NaClO_3$–H_2O at 25°; distribution diagram.

NEW YORK, N. Y.

RECEIVED OCTOBER 18, 1950

[6] B. Roozeboom, *Z. physik. Chem.*, **8**, 521 (1891).

[CONTRIBUTION FROM THE DIVISION OF INDUSTRIAL CHEMISTRY, COMMONWEALTH SCIENTIFIC AND INDUSTRIAL RESEARCH ORGANIZATION]

Barium Chloride Metaphosphate

BY F. R. HARTLEY AND A. D. WADSLEY

Barium chloride metaphosphate $Ba_4P_4O_{12}Cl_4$ has been prepared in a crystalline condition by the passage of chlorine over barium orthophosphate–carbon briquettes heated to 800°. As the result of a chemical method designed to distinguish the different classes of phosphate ion in insoluble compounds, this substance is considered to be an association of barium, chloride and metaphosphate radicals. Unit cell dimensions and possible space groups, together with some optical properties, have been determined.

The preparation of chlorophosphates has been claimed by several workers[1,2,3] but their claims are not supported by chemical or microscopical evidence. No anion of the type $(PO_3Cl)^=$ has been described hitherto, though there are well defined series of salts containing the complex anions $(PO_3F)^=$ and $PO_2F_2{}^-$ as intermediates in the series $(PO_4)^{\equiv}$ to POF_3.[4]

While investigating the mechanism of reaction of chlorine with a barium orthophosphate–carbon mixture at an elevated temperature, some crystals were isolated which had an empirical formula $BaPO_3Cl$ equivalent to barium chlorophosphate. In view of the lack of evidence for a compound of this nature, it was felt to be worthy of further investigation.

Experimental

Reagents.—Barium orthophosphate was prepared from Reagent Grade chemicals by the simultaneous addition of 500 ml. each of 1 *M* $BaCl_2$ and 0.67 *M* $(NH_4)_2HPO_4$ to 1 liter of a solution of 80 ml. of NH_4OH (sp. gr. 0.880) and 30 g. of NH_4Cl heated to 70°. After 1 hour the precipitation was complete, and the barium orthophosphate was washed by decantation, filtered, dried and ignited at 800°.

Anal. Found: Ba, 68.3; PO_4, 31.5. Calcd. for $Ba_3(PO_4)_2$: Ba, 68.5; PO_4, 31.5.

Barium "polyphosphate" was precipitated from a cold solution of barium chloride at *p*H 2.3 by the slow addition of an equivalent amount of commercial Graham salt.[5] After washing with water the dried cryptocrystalline material was heated to 800° and the melt allowed to cool slowly to below 400°. Prepared by this method, barium metaphosphate is a vitreous crystalline compound, insoluble in water. Analysis indicated that it contained only minor amounts of residual polyphosphate radicals.

Anal. Found: Ba, 46.7; PO_3, 52.5. Calcd. for $Ba(PO_3)_2$: Ba, 46.5; PO_3, 53.5.

Intensities and spacings from its powder pattern have been measured and are available in microfilm.[6]

Phosphorus oxychloride had been prepared as a by-product in some earlier work.[7] It was distilled before use, the fraction boiling between 104.5° and 105.5° being retained.

Chlorination of Barium Orthophosphate.—Barium orthophosphate and charcoal in the ratio 4.5 to 1 by weight were formed into briquettes with starch as bonding agent. These were heated at 800° in a current of chlorine in an apparatus which has been previously described.[7] A charge consisted of sufficient briquettes to contain 40 g. of ortho-

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[1] A. Ditte, *Compt. rend.*, **99**, 791 (1884).

[2] L. V. R. Ouvrard, *Ann. chim. phys.*, [6] **16**, 289 (1889).

[3] M. Berthelot, *ibid.*, [7] **25**, 197 (1902).

[4] W. Lange, *Ber.*, **62B**, 793 (1929).

[5] L. T. Jones, *Ind. Eng. Chem., Anal. Ed.*, **14**, 536 (1942).

[6] For detailed material supplementary to this article order Document 3030 from American Documentation Institute, 1719 N Street, N. W., Washington 6, D. C., remitting $0.50 for microfilm (images 1 inch high on standard 35 mm. motion picture film) or $0.50 for photocopies (6 × 8 inches) readable without optical aid.

[7] F. R. Hartley and A. W. Wylie, *J. Soc. Chem. Ind.*, **69**, 1 (1950).