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

The Quaternary System $Ba(ClO_3)_2$–$BaBr_2$–$Ba(NO_3)_2$–H_2O at 10° and Some Isotherms of the Related Ternary Systems

BY JOHN E. RICCI AND ARTHUR J. FREEDMAN

Solubility isotherms are reported for the ternary systems $Ba(ClO_3)_2$–$BaBr_2$–H_2O at 10 and 25°, $Ba(ClO_3)_2$–$Ba(NO_3)_2$–H_2O at 10, 25 and 45° and $BaBr_2$–$Ba(NO_3)_2$–H_2O at 10 and 25°. The nitrate systems form incongruently soluble hydrated double salts stable at 10 and 25, but not at 45°. Their formulas are tentatively reported as $Ba(ClO_3)_2 \cdot 6Ba(NO_3)_2 \cdot 12H_2O$ and $BaBr_2 \cdot 8Ba(NO_3)_2 \cdot 12H_2O$. The quaternary system $Ba(ClO_3)_2$–$BaBr_2$–$Ba(NO_3)_2$–H_2O was studied at 10°; the only congruent drying-up point of the isotherm is a solution saturated with the solids $Ba(ClO_3)_2 \cdot H_2O$, $BaBr_2 \cdot 2H_2O$ and $Ba(ClO_3)_2 \cdot 6Ba(NO_3)_2 \cdot 12H_2O$.

In the course of investigations on the aqueous phase relations of the halates of barium, the ternary system $Ba(ClO_3)_2$–$Ba(NO_3)_2$–H_2O was found to form an incongruently soluble hydrated double salt involving a low molar ratio of chlorate to nitrate. The determination of the formula of such a compound is difficult whether attempted directly by analysis of isolated samples or indirectly through equilibrium phase relations. For some of the possible molar ratios requiring consideration, for example, such as 1:6, 1:7, 1:8, the weight percentage of $Ba(ClO_3)_2$ varies only little, being 16.25, 14.26, 12.71%, respectively. Also, the more unequal is the salt ratio, the more difficult is the determination of the degree of hydration of the double salt. Even for the 1:6 ratio, the weight percentage of water varies only from 8.78 to 9.57 to 10.35% for the hydrates 1·6·10, 1·6·11 and $1 \cdot 6 \cdot 12H_2O$. A further difficulty lies in the slow formation of the double salt and the slow attainment of equilibrium for its phase relations.

Since the determination of the formula had to be essentially indirect, it was decided to try, among other methods, the use of a fourth component. The range of existence of the double salt in the ternary system $Ba(ClO_3)_2$–$Ba(NO_3)_2$–H_2O is rather small, so that extrapolation of tie-lines has low significance. An additional very soluble barium salt would possibly enlarge the isothermal field, although in a third dimension of composition. If the third salt is subject to accurate analytical determination, the expansion of the field in the direction of the added component would still be useful. For this purpose, barium bromide was tried as the fourth component.

The quaternary system $Ba(ClO_3)_2$–$BaBr_2$–$Ba(NO_3)_2$–H_2O then requires study of the additional ternary systems $Ba(ClO_3)_2$–$BaBr_2$–H_2O and $BaBr_2$–$Ba(NO_3)_2$–H_2O. The first of these, $Ba(ClO_3)_2$–$BaBr_2$–H_2O, is a simple system, not adding, therefore, to the existing complications. The system $BaBr_2$–$Ba(NO_3)_2$–H_2O, however, turned out to form a hydrated double salt, incongruently soluble and with a salt ratio even more unequal than that in the chlorate–nitrate double salt the formula of which was to be clarified.

As a result, the quaternary isotherm, studied at 10° because the double salt fields are larger at that temperature than at 25°, did not aid in the determination of the formula of either of the double salts. The tentative formulas finally selected for these compounds are $Ba(ClO_3)_2 \cdot 6Ba(NO_3)_2 \cdot 12H_2O$ and $BaBr_2 \cdot 8Ba(NO_3)_2 \cdot 12H_2O$. The uncertainties in these formulas will be pointed out in connection with the presentation of the solubility measurements upon which, essentially, both of them are based.

No other double salt of barium chlorate seems to be known, although double salts both of barium bromide[1] and of barium nitrate[2] have been reported.

Materials.—A C.P. grade of barium chlorate monohydrate was used, a hydrate stable in air at room temperature. Dehydration to constant weight at 300° and determination of chlorate by the method described later gave results agreeing within one part per thousand, but the water content of one batch was somewhat high (+0.3%). The actual salt content was used in calculating total compositions. The C.P. barium nitrate was found to be 99.9% pure by determination of barium both as barium sulfate and by precipitation with excess of standard potassium iodate followed by titration of the filtrate with sodium thiosulfate.

The barium bromide was used as the dihydrate. Only one sample of the commercially available C.P. product was found on analysis (dehydration at 300° and determination of bromide by the Volhard method) to be sufficiently pure for use in solubility experiments. Most of the material used was therefore made from C.P. $Ba(OH)_2 \cdot 8H_2O$, which was first recrystallized from water solution and then neutralized with 40% aq. HBr. The resulting solution was evaporated almost to dryness and cooled in ice; then the residue was filtered and the last portion of mother liquor was discarded. The crystals were redissolved and the evaporation and filtration were repeated. The final pure white, needle-shaped crystals gave a neutral solution. The salt was dried in air for actual use. Its analysis, for water and for bromide, showed it to be pure barium bromide with a water content somewhat higher (11.14%) than the theoretical value (10.81%) for the dihydrate.

Methods.—The general procedures for the solubility determinations were those usually described for similar systems. Complexes of known compositions, enclosed in Pyrex tubes, were rotated in constant temperature water-baths. Calibrated pipets with filter paper tips were used in sampling the saturated solutions for analysis, so that approximate densities are also reported.

For the analysis, the total salt content was determined by evaporation to constant weight at 300°, and bromide was determined by the Volhard method with filtration of the silver bromide. The oxidimetric determination of chlorate by heating with excess of standard arsenite in presence of hydrochloric acid and titration of the unused arsenite with potassium bromate was found to give erratic results, evidently because of the oxidizing interference on the part of nitrate. The chlorate was therefore determined as chloride after reduction with sodium nitrite. To the sample, diluted to 100 ml., were added a measured volume, in excess, of standard silver nitrate and a solution of 2 g. sodium nitrite in 10 ml. water. The solution was warmed until the silver nitrite first precipitated had dissolved; 10 ml. of 6 *N* nitric acid was then added, with vigorous shaking. After boiling to remove oxides of nitrogen, the silver chloride was filtered off and the excess of silver nitrate was titrated by the Volhard method. The procedure was tested and found to apply without error for the combinations of

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(1) A. Benrath and K. Lechner, *Z. anorg. Chem.*, **244**, 359 (1940); F. W. Foote and H. S. Bristol, *Am. Chem. J.*, **32**, 246 (1904).

(2) S. Glasstone and E. J. Riggs, *J. Chem. Soc.*, **127**, 2846 (1925).

salts involved in the investigation. In the quaternary system, this procedure was used to determine total halogen, or the total number of equivalents of chlorate and bromide.

System $Ba(ClO_3)_2$–$BaBr_2$–H_2O.—The solutions were analyzed for bromide and total solid. Reanalysis after further stirring showed that equilibrium was reached with one day of stirring, the minimum time used. The pure solubilities and the invariant points for the two temperatures studied, 10 and 25°, are listed in Table I.[3] The only solid phases are $Ba(ClO_3)_2 \cdot H_2O$ (or A) and $BaBr_2 \cdot 2H_2O$ (or B), and the isothermal diagrams are of the simplest type, each with two simple solubility curves, one for each solid.

TABLE I

SYSTEM $Ba(ClO_3)_2$–$BaBr_2$–H_2O

Temperature, °C.	$Ba(ClO_3)_2$, %	$BaBr_2$, %	Density	Solids
10	21.22	0.00	1.198	A
(Point a)	4.32	46.02	1.724	A + B
	0.00	48.77	1.698	B
25	27.42	0.00	1.263	A
(Point a)	5.68	46.53	1.755	A + B
	0.00	50.07	1.726	B

The identity of solid phases was established indirectly by means of the tie-lines fixed by the compositions of saturated solution as determined by analysis and of total complex or mixture as prepared synthetically. When these tie-lines are extrapolated,[4] their deviations from the theoretical compositions of the solid phases may be expressed as $\%BaBr_2$ on the line representing $\%Ba(ClO_3)_2$ in A and as $\%Ba(ClO_3)_2$ on the line of $\%BaBr_2$ in B. The average extrapolation error, for both solids, is 0.22% at 10° and 0.07% at 25°, and because of the multiplying lever arm effect of the tie-line segments, these averages indicate very low operational errors if the phases are pure.

(As in Table I, all measurements are reported and plotted in terms of weight percentages. For brevity, moreover, the solid phases will be represented by the following letters throughout: A, $Ba(ClO_3)_2 \cdot H_2O$; B, $BaBr_2 \cdot 2H_2O$; C, $Ba(NO_3)_2$; D, $BaBr_2 \cdot 8Ba(NO_3)_2 \cdot 12H_2O$; E, $Ba(ClO_3)_2 \cdot 6Ba(NO_3)_2 \cdot 12H_2O$.)

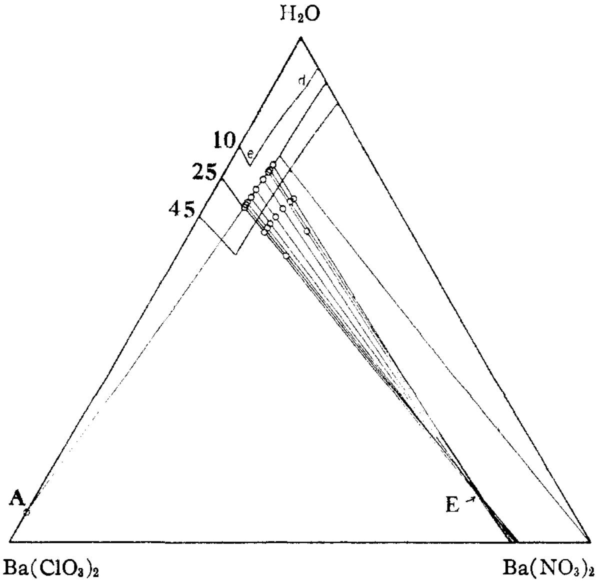

Fig. 1.—System $Ba(ClO_3)_2$–$Ba(NO_3)_2$–H_2O; stable relations only.

System $Ba(ClO_3)_2$–$Ba(NO_3)_2$–H_2O.—This system was studied at 10, 25 and 45°, with results as listed in Table II. This table gives only the invariant points and the experimental data for the determination of the composition of the hydrated double salt. The complete numerical data for the other parts of these isotherms are available on microfilm.[3] The stable relations at 25° are plotted in Fig. 1, which also shows, without tie-lines, the corresponding curves for the 10 and 45° isotherms. The range of stability of the double salt $Ba(ClO_3)_2 \cdot 6Ba(NO_3)_2 \cdot 12H_2O$(E) is wider at 10° than at 25°; at 45° the compound does not appear at all, and the only solid phases are $Ba(ClO_3)_2 \cdot H_2O$(A) and $Ba(NO_3)_2$(C). Parallel to the increasing range for the compound with decreasing temperature is the vanishing of the effect of the nitrate in decreasing the solubility of the chlorate.

TABLE II

SYSTEM $Ba(ClO_3)_2$–$Ba(NO_3)_2$–H_2O

Original complex Wt. %		Saturated solution Wt. %			
$Ba(ClO_3)_2$	$Ba(NO_3)_2$	$Ba(ClO_3)_2$	$Ba(NO_3)_2$	Density	Solid phase
Temperature, 10°					
...	0.00	21.22	0.00	1.198	A
Point e, aver.		21.38	4.52	1.249	A + E
19.70	16.99	20.97	4.56	1.245	E
17.99	16.95	18.90	4.60	1.224	E
15.99	17.83	16.55	4.67	1.197	E
13.99	17.17	14.15	4.83	1.174	E
10.02	17.05	9.51	5.18	1.128	E
5.50	17.50	4.24	6.00	1.088	E
5.01	17.57	3.95	6.03	1.084	E
3.98	17.99	3.94	6.06	1.087	E
Point d, aver.		3.47	6.16	1.083	E + C
0.00	...	0.00	6.361	1.051	C
Temperature, 25°					
...	0.00	27.42	0.00	1.263	A
Average		26.82	7.94	1.362	A + C (m)[a]
Point e, aver.		26.67	7.28	1.347	A + E
25.18	13.08	26.12	7.25	1.344	E
24.01	18.97	25.91	7.23	1.337	E
24.53	13.00	25.39	7.28	1.333	E
24.45	12.98	25.32	7.28	1.332	E
23.45	13.28	24.27	7.36	1.318	E
21.78	13.58	22.48	7.53	1.301	E
19.77	14.01	20.24	7.81	1.277	E
19.69	14.02	20.20	7.78	1.275	E
18.04	19.97	18.84	7.84	1.258	E
17.93	14.49	18.29	7.96	1.254	E
17.04	14.79	17.32	8.09	1.243	E
Point d, aver.		15.08	8.39	1.222	E + C
0.00	...	0.00	9.246	1.079	C
Temperature, 45°					
...	0.00	34.90	0.00	1.347	A
Average		32.48	10.16	1.465	A + C
0.00	...	0.00	13.60	1.110	C

[a] (m) = metastable.

All the complexes at 45° were seeded three times with the double salt, and the attainment of equilibrium was verified

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[3] For complete data for these isotherms order Document 3412 from American Documentation Institute, 1719 N Street, N.W., Washington 6, D. C., remitting $1.00 for microfilm (images 1 inch high on standard 35 mm. motion picture film) or $1.20 for photocopies (6 × 8 inches) readable without optical aid.

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

by repeated analysis after long periods of stirring, but the compound never formed as a stable solid phase. Although the final state of heterogeneous equilibrium is probably reached more rapidly at 25° than at 10°, the double salt itself formed more readily at the lower temperature. Thus the complete metastable isotherm at 25° (with only A and C as solid phases) was easily determined,[3] whereas only one point with $Ba(NO_3)_2$ as metastable saturating solid was obtained at 10°. A minimum time of two weeks of stirring (but usually much longer) was used, and this was proved sufficient for equilibrium by repeated analysis. Near the congruently saturated isothermally invariant point **e**, or the solution saturated with solids A and E, equilibrium was generally reached fairly rapidly; but near point **d**, the solution incongruently saturated with solids E and C, the process was very much slower. The same difference (between corresponding points **b** and **c**) was noted in the system $BaBr_2$–$Ba(NO_3)_2$–H_2O.

The double salt forms in minute, transparent, tetrahedral crystals of uniform size, distinct from the monoclinic $Ba(ClO_3)_2 \cdot H_2O$ and the cubic $Ba(NO_3)_2$.[5] Except in one experiment, the double salt particles were so fine that all attempts to obtain samples free of mother liquor failed; even centrifuging left much of the solution trapped in the packed crystals. Attempts were made to obtain large crystals by slow evaporation, both at 25 and at 10°, of solutions which were seeded with the double salt when their compositions were calculated to have reached saturation with this solid, but the seed apparently dissolved, and at any rate had no effect, the only solid product being $Ba(NO_3)_2$. In one such experiment at 10° the double salt did form, but as a fine crystal meal. As a variation, a complex was brought to equilibrium with the double salt as solid phase near point **d** at 25°. It was then rotated at 10°, whereupon, it was hoped, the further precipitation of double salt would occur on the crystals already formed, but again only a very fine product was obtained.

Two large complexes on the solubility curve of the double salt, one near each of the points **d** and **e** at 25°, and containing no marbles (usually enclosed to accelerate attainment of equilibrium by the grinding of the solids) were rotated for two years, with the expectation that the solid particles would grow in size. Those near point **e** were up to 2 mm. in diameter, while those near point **d** were smaller. Half of each sample was pressed once between filter papers and centrifuged before analysis; the other half was dried with filter paper until free-flowing and analyzed. The centrifuged samples again apparently retained too much mother liquor. The others (dry to the touch) indicated, on analysis, the molar proportions 1:6:12–13 for $Ba(ClO_3)_2$:$Ba(NO_3)_2$:H_2O. Specifically, those near point **e** gave 1:5.5:12.3, and those near point **d** gave 1:5.7:13.0; mother liquor included in the analysis lowers the observed nitrate/chlorate ratio.

The 1:6 salt ratio was confirmed in an experiment in which a small amount of silver nitrate was used as a tracer, according to van Bijlert's method,[6] to correct the analysis of the wet solid for the quantity of mother liquor present. The results gave 1:6 (±0.1) for the salt ratio, with ~ 9 moles of water.

Although the actual isothermal tie-lines, both those at 25°, shown in Fig. 1, and those at 10°, seem to converge best at a point on the base of the triangle, suggesting an anhydrous double salt with ~ 13.4% $Ba(ClO_3)_2$, or a molar ratio of 2:15, the experiments just mentioned indicate that the ratio is probably 1:6 and that the salt is probably hydrated. Visual inspection of a large-scale plot (20 inch triangle) of the eleven tie-lines for saturation with the double salt at 25° shows them to intersect the line representing the salt ratio 1:6 at ~ 9.8% H_2O, corresponding to 11.3 moles H_2O. Algebraic calculation of the intersection of each of the tie-lines with the 1:6 salt ratio line gives, in fact, 11.7 moles H_2O (with an average deviation from the mean of 0.9); for this average the sixth tie-line, as listed in Table II, which gives 16.7 moles H_2O, was omitted. The formula $Ba(ClO_3)_2 \cdot 6Ba(NO_3)_2 \cdot 12H_2O$ is therefore at least a possible one, and we shall accept it tentatively.

TABLE III

System $BaBr_2$–$Ba(NO_3)_2$–H_2O

Original complex Wt. %		Saturated solution Wt. %			Solid phase
$BaBr_2$	$Ba(NO_3)_2$	$BaBr_2$	$Ba(NO_3)_2$	Density	
		Temperature, 10°			
...	0.00	48.77	0.00	1.698	B
45.70	11.06	47.51	4.80	1.757	B + C (m)[a]
Point **b**, aver.		47.47	4.04	1.752	B + D
45.64	7.10	47.05	4.04	1.741	D
42.70	10.79	45.79	3.94	1.710	D
42.68	7.99	44.41	3.95	1.678	D
40.88	10.68	43.68	3.98	1.662	D
35.21	19.95	41.47	4.00		D
35.68	10.80	38.02	3.98	1.542	D
33.01	11.09	35.14	4.12	1.491	D
29.92	11.08	31.68	4.30	1.433	D
26.65	10.97	28.04	4.51	1.375	D
25.14	15.99	27.56	4.57	1.367	D
24.68	15.99	26.99	4.64	1.363	D
23.30	16.05	25.38	4.74	1.336	D
22.77	16.00	24.81	4.73	1.321	D
Point **c**, aver.		24.03	4.84	1.319	D + C
0.00	...	0.00	6.361	1.051	C
		Temperature, 25°			
...	0.00	50.07	0.00	1.726	B
Point b, aver.		48.24	5.21	1.793	B + D
40.42	19.99	47.51	5.23		D
42.21	14.84	46.75	5.20	1.757	D
42.20	15.46	47.23	5.32	1.771	C(m)[a]
41.54	14.97	46.29	5.15	1.740	C
0.00	...	0.00	9.246	1.079	C

[a] (m) = metastable.

System $BaBr_2$–$Ba(NO_3)_2$–H_2O.—Table III lists the compositions of the invariant points and the data for the determination of the composition of the double salt; the rest of the numerical data for the two isotherms is available on microfilm.[3] The stable relations at 10° are plotted in Fig. 2. The minimum time of stirring was two weeks, with equilibrium checked by later analysis.

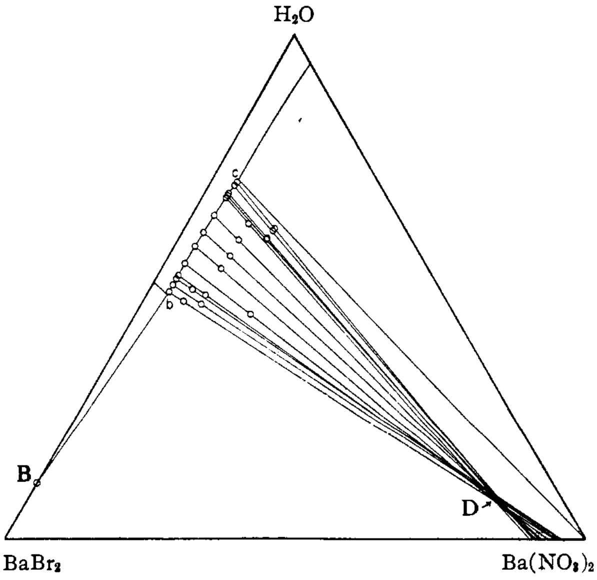

Fig. 2.—System $BaBr_2$–$Ba(NO_3)_2$–H_2O at 10°; stable relations only.

The hydrated double salt D in this system has a wide region of stability at 10° and a very small range

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[5] Barium nitrate does sometimes crystallize in a tetrahedral habit, according to A. N. Winchell, "Microscopic Characters of Artificial Minerals," John Wiley and Sons, New York, N. Y., 1931, pp. 207, 349.

[6] A. van Bijlert, *Z. physik. Chem.*, **8**, 343 (1891).

at 25°. The limits, points **b** and **c**, are clearly defined at 10°, at which temperature a complete metastable diagram was also obtained with B and C as sole solid phases. The limit **c** at 25°, for saturation with D and C, has not been determined, the D field being so small that the stable and metastable curves are almost identical.

The cubic crystals of this double salt were always so fine that no sample was obtained sufficiently free of mother liquor for a dependable direct analysis. An estimate of the formula has therefore been made entirely on the basis of the isothermal tie-lines. From a large-scale plot of all the 10° tie-lines for saturation with solid D, the best common intersection seems to be on the line representing the salt ratio 1:8, with ~ 8 (±1)% H_2O, corresponding to ~ 11.5 moles H_2O. As in the previous case, however, the analytical differences involved are small, and difficult to fix by means of tie-lines alone. The formulas 1·7·12, 1·8·12, 1·9·12 correspond to 13.87, 12.36, 11.15% $BaBr_2$, respectively, and for the 1:8 salt ratio, the formulas 1·8·11 and 1·8·12 correspond to 7.66 and 8.30% H_2O, respectively. Two complexes at 25° gave the double salt as sole solid phase. The intersections of their tie-lines with the 1:8 salt ratio line, calculated algebraically, correspond to 11.88 and 12.06 moles H_2O for the formula. For the salt ratio 1:7 they give 12.46 and 12.66 H_2O and for the ratio 1:9 they give 11.31 and 11.42.

On the basis of these combined observations, the formula of the double salt D is tentatively taken as $BaBr_2 \cdot 8Ba(NO_3)_2 \cdot 12H_2O$.

System $Ba(ClO_3)_2$–$BaBr_2$–$Ba(NO_3)_2$–H_2O at 10°.—The saturated solutions were analyzed for total solid, total halogen and bromide, so that only the components H_2O and $BaBr_2$ were determined directly and independently; the accuracy or significance of the salt percentages reported therefore varies, generally, in the order $BaBr_2 > Ba(ClO_3)_2 > Ba(NO_3)_2$.

The compositions of quaternary solutions saturated with two and with three solids are listed in Table IV, in terms of weight percentage, so that $\%H_2O = 100 - \Sigma(\%\text{salt})$. Recalculated on the basis of weight percentage of each salt relative to total salts alone, the *salt proportions* in these solutions are plotted as the points and curves of Fig. 3, as a Jänecke diagram. The ternary solutions of twofold saturation, or points **a**, b, **c**, d, **e**, are those already discussed for the 10° isotherms of the ternary systems in Tables I, II, III and Figs. 1, 2. From each of these points a curve representing quaternary liquid saturated with the two solids enters the diagram; these curves then give rise to the isothermally invariant quaternary solutions 1, 2, **3**, saturated with the three solids C + D + E, B + D + E, and A + B + E, respectively. Curve 1 → 2 therefore represents solutions saturated with the two double salts D + E, and curve 2 → **3** represents saturation with the solids B and E.

If the water content in terms, for example, of grams water per gram salt, is plotted perpendicularly upon the plane of the diagram of Fig. 3, the solubility surfaces become part of a 3-dimensional isotherm, the Jänecke prism. If the points and curves of such a diagram are then projected orthogonally upon the A–C face of the prism, the result is the Jänecke elevation drawn, somewhat schematically for clarity, in Fig. 4.

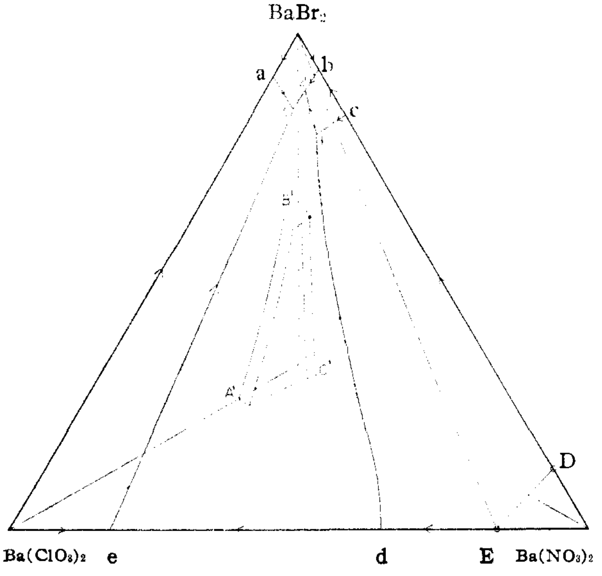

Fig. 3.—System $Ba(ClO_3)_2$–$BaBr_2$–$Ba(NO_3)_2$–H_2O at 10°, Jänecke diagram. The orthogonal diagram is enclosed, with primed letters.

TABLE IV

SYSTEM $Ba(ClO_3)_2$–$BaBr_2$–$Ba(NO_3)_2$·H_2O AT 10°

Curve or point	Weight percentage Ba(ClO₃)₂	BaBr₂	Ba(NO₃)₂	Density	Solid phase
e → 3	20.65	1.33	4.46		A + E
e → 3	19.93	2.81	4.39	1.267	A + E
e → 3	19.13	4.29	4.36	1.277	A + E
e → 3	17.18	8.26	4.25	1.307	A + E
e → 3	15.11	12.76	4.11	1.342	A + E
e → 3	15.26	13.42	4.08	1.350	A + E
e → 3	12.86	17.81	4.07	1.390	A + E
e → 3	10.61	24.08	3.82	1.456	A + E
e → 3	10.30	24.87	3.79	1.467	A + E
e → 3	7.46	33.28	3.65	1.576	A + E
e → 3	4.58	44.10	3.87	1.761	A + E
3	4.50	44.68	3.90	1.779	A + E + B
d → 1	3.34	0.61	6.14	1.085	E + C
d → 1	3.19	1.58	5.98	1.094	E + C
d → 1	3.29	2.45	6.04	1.113	E + C
d → 1	3.27	3.23	5.77	1.108	E + C
d → 1	3.25	5.00	5.55	1.127	E + C
d → 1	3.17	7.45	5.32	1.152	E + C
d → 1	3.07	10.62	5.04	1.183	E + C
d → 1	2.60	18.06	4.55	1.266	E + C
d → 1	2.17	23.66	4.27	1.335	E + C
1[a]	2.0	24.3	4.2		E + C + D
c → 1	0.40	24.10	4.80	1.326	C + D
c → 1	0.73	24.05	4.65	1.327	C + D
c → 1	0.87	23.93	4.53		C + D
c → 1	1.10	23.98	4.45	1.327	C + D
c → 1	1.45	24.05	4.36	1.333	C + D
c → 1	1.45	24.04	4.57	1.335	C + D
1 → **2**	2.07	26.58	4.15	1.377	D + E
1 → **2**	2.07	26.79	4.15	1.380	D + E
1 → **2**	2.04	30.58	4.00	1.438	D + E
1 → **2**	1.97	33.72	3.88	1.491	D + E
2	1.59	46.57	3.96	1.761	B + D + E
2	1.61	46.59	3.91	1.763	B + D + E
b → **2**	1.02	46.85	3.98	1.759	B + D
2 → 3	2.17	46.13	3.92	1.763	B + E
2 → 3	3.52	45.27	3.96	1.775	B + E
3	4.33	44.74	4.01	1.780	A + B + E
a → 3	4.49	45.66	0.88	1.738	A + B
a → 3	4.40	45.41	1.90	1.753	A + B
a → 3	4.30	45.07	3.14	1.766	A + B
3	4.39	44.69	3.98	1.779	A + B + E
3 (aver.)	4.42	44.71	3.96	1.780	A + B + E

[a] Estimated graphically from intersection of curves.

Experimentally, the equilibrium along the curve **a → 3**, for saturation with solids A and B, was readily attained. For this curve the complexes were prepared directly from the four components and rotated for a short time before analysis. For the curves originating at b, **c**, **d** or **e**, each with a double salt as one solid phase, the ternary invariant solution was first prepared by seeding and stirring for a period of time known to be sufficient for equilibrium. The fourth component was then added, and the solution was analyzed after further stirring.

The curves **e** → **3**, b → 2, and 2 → **3** were easily followed, and the point **3** was reached along each of the three curves **a** → **3**, **e** → **3**, 2 → **3**. Points on curve 2 → **3** were obtained from solution **b** by addition of $Ba(ClO_3)_2 \cdot H_2O$ and seeding with double salt E. Curves **c** → 1 and **d** → 1 were more difficult to determine because of the narrow 3-dimensional spaces within which the total quaternary composition must fall for the solution to lie on one of these curves.

Curve 1 → 2 was followed by addition of solid $BaBr_2 \cdot 2H_2O$ to solution **d** and seeding with double salt D. The first point listed in Table IV for this curve was reseeded after the first analysis, and its composition remained constant. The second was made from the last solution on curve **d** → 1 by addition of $BaBr_2 \cdot 2H_2O$. Microscopic examination showed only crystals of the double salts D and E in the solids of the first four solutions listed for curve 1 → 2; no $Ba(NO_3)_2$ could be observed. The two analyses for point 2 were obtained by addition of $BaBr_2 \cdot 2H_2O$ to the third and fourth solutions, respectively, of curve 1 → 2; the composition, falling on curve b → 2, therefore fixes the intersection of the two curves as point 2.

Point 1 itself could not be made, either from curve **c** → 1 or from curve **d** → 1. The complexes intended to give point 1 always gave solutions on the curves intersecting at point 1, because of the difficulty of preparing a total composition in the very limited volume for saturation with the three solids C + D + E. The composition of point 1 was therefore estimated by graphical extrapolation of the three curves **d** → 1, **c** → 1, and 1 → 2, to their common intersection, the Jänecke diagram of Fig. 3 being used for the salt proportions and the elevation of Fig. 4 for the water content.

The only quaternary invariant congruently saturated with its three solids is point **3**, which is therefore the vapor pressure minimum of the isotherm and the final drying-up point for isothermal evaporation of all solutions in the triangle ABE. With complete solid phase equilibrium, those in CDE dry up at point 1 and those in BDE at point 2. The phase reaction for isothermal evaporation is of the transition type along all three curves meeting at point 1: for **d** → 1, solution + C → E + H_2O ↗; for **c** → 1, solution + C → D + H_2O ↗; and for 1 → 2, solution + D → E + H_2O↗. The reactions at the incongruently saturated quaternary invariants are: solution + C → D + E + H_2O↗ at point 1, and solution + D → B + E + H_2O↗ at point 2. For practical purposes, therefore, the drying-up point for the whole system is point **3**, where the solution precipitates simultaneously the solids $Ba(ClO_3)_2 \cdot H_2O$, $BaBr_2 \cdot 2H_2O$ and "$Ba(ClO_3)_2 \cdot 6Ba(NO_3)_2 \cdot 12H_2O$" or double salt E. In Fig. 4, the point **3** is seen to be actually the solution of lowest water content for the isotherm. The arrows in Fig. 3 indicate the direction of isothermal evaporation, or, from Fig. 4, the direction of falling water content.

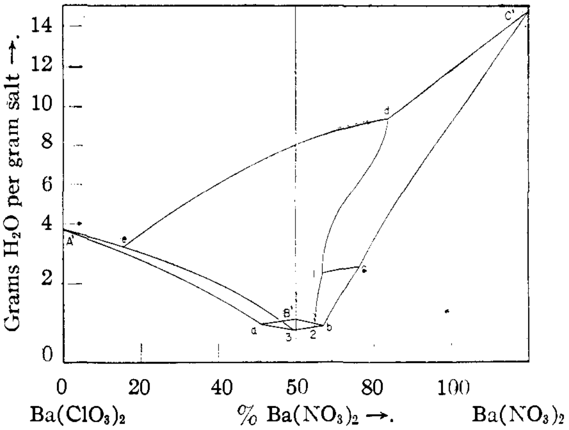

Fig. 4.—System $Ba(ClO_3)_2$–$BaBr_2$–$Ba(NO_3)_2$–H_2O at 10°; elevation (partially schematic showing water content).

Finally, the composition may be represented, in the units given in Table IV, in a regular tetrahedron with water as one of the corners. Radial projection from the water apex to the salt base gives the Jänecke diagram of Fig. 3. Orthogonal projection on the same base gives the "orthogonal diagram," which, labeled with primed letters, is plotted together with the Jänecke projection in Fig. 3. The data of Table IV may be plotted directly as an orthogonal diagram after addition of one third of the water percentage to each of the salt percentages.

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Some Aqueous Ternary Systems Involving Barium Halates

BY JOHN E. RICCI AND ARTHUR J. FREEDMAN

The system $Ba(BrO_3)_2$–$BaCl_2$–H_2O forms the incongruently soluble double salt $Ba(BrO_3)_2 \cdot BaCl_2 \cdot 2H_2O$ at each of the temperatures studied, 10, 25, 45°; its range of stability increases slightly with rising temperature. The following systems form neither compounds nor solid solutions at 25°: $Ba(ClO_3)_2$–$BaCl_2$–H_2O, $Ba(BrO_3)_2$–$BaBr_2$–H_2O, $Ba(BrO_3)_2$–$Ba(NO_3)_2$–H_2O, $Ba(IO_3)_2$–$BaBr_2$–H_2O, $Ba(IO_3)_2$–$Ba(NO_3)_2$–H_2O and $Ba(IO_3)_2$–$Mg(IO_3)_2$–H_2O. Mixtures made up from barium iodate, iodic acid and water form the incongruently soluble anhydrous compound $Ba(IO_3)_2 \cdot I_2O_5$, so that the measurements are reported as part of the system $Ba(IO_3)_2$–I_2O_5–H_2O. A few points on the 25° isotherm of the system $Mg(IO_3)_2$–HIO_3–H_2O are reported indicating a marked increase in the solublity of magnesium iodate tetrahydrate in high concentrations of iodic acid, with the formation of very dense and viscous solutions.

This is a report on some further aqueous ternary systems involving barium halates, continuing the work on these systems previously published. The material already reported includes the study of the solid solution of barium bromate monohydrate with barium chlorate monohydrate,[1] the solubility of barium iodate in the presence of foreign electrolytes[2] and in dioxane–water solvents,[3] the double salt $Ba(IO_3)_2 \cdot BaCl_2 \cdot 2H_2O$ in the system $Ba(IO_3)_2$–$BaCl_2$–H_2O[4] and the double salt $Ba(ClO_3)_2 \cdot 6Ba(NO_3)_2 \cdot 12H_2O$ in the quaternary system $Ba(ClO_3)_2$–$BaBr_2$–$Ba(NO_3)_2$–H_2O.[5]

The present work reports the double salt $Ba(BrO_3)_2 \cdot BaCl_2 \cdot 2H_2O$ and the polyiodate $Ba(IO_3)_2 \cdot I_2O_5$ as new compounds.

Most of the materials were the same as those used in similar investigations and the general procedure was also the same. Barium chlorate monohydrate, barium bromate monohydrate, barium chloride

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[1] J. E. Ricci and S. H. Smiley, THIS JOURNAL, **66**, 1011 (1944).

[2] S. Naidich and J. E. Ricci, *ibid.*, **61**, 3268 (1939).

[3] T. W. Davis, J. E. Ricci and C. G. Sauter, *ibid.*, **61**, 3274 (1939).

[4] J. E. Ricci, *ibid.*, **73**, 1375 (1951).

[5] J. E. Ricci and A. J. Freedman, *ibid.*, **74**, 1765 (1952).