temperature–composition curve decreases or increases without limit with decreasing concentration in dilute solutions of a dissociating component, and only of a dissociating component.

4. The term "isobaric temperature" is proposed for the temperature at which the vapor pressures of the pure components are equal. The slope of the azeotropic temperature–composition curve is steep at the isobaric temperature if the deviations from Trouton's rule are small for both components.

5. If the azeotropic temperature–composition curve of a maximum (minimum) vapor pressure system extends to a pure component, this component is the more (less) volatile one. The rule holds both for upper and lower limits of the azeotropic temperature range. In connection with the fact that this range includes the isobaric temperature, the rule conveniently indicates the direction of the curve.

PULLMAN, WASHINGTON
NEW YORK, N. Y.

RECEIVED FEBRUARY 12, 1944

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

The Ternary System Barium Bromate–Barium Chlorate–Water at 25°

BY J. E. RICCI AND S. H. SMILEY

Introduction.—During various attempts to determine bromate in the presence of chlorate by precipitation with excess of barium chloride, it became apparent that the precipitated barium bromate was repeatedly and almost reproducibly contaminated with barium chlorate, despite all precautions for its proper formation in the pure state. The weight of the solid obtained, after the usual drying, was always too high, and its oxidizing equivalent, determined by iodometry, was also too high, indicating the presence of some chlorate. It was consequently suspected that the two salts, barium bromate and barium chlorate, isomorphous and both mono-hydrated, were forming solid solutions from their aqueous solutions. This was verified by a phase rule study of the ternary system involved. Since the resulting solid solution turned out to be a continuous one, the data were therefore used in testing the applicability of a semi-empirical relationship previously reported as describing the distribution of such isomorphous salts in solubility equilibrium between liquid and solid phases.[1]

Experimental Procedure.—The barium bromate used was a C. P. grade of the monohydrate, the purity of which was checked, with the following results: by iodometry, 95.73% $Ba(BrO_3)_2$, and by dehydration to constant weight at 110°, 95.53%. The theoretical value is 95.60%. A C. P. grade of $Ba(ClO_3)_2 \cdot H_2O$ also was used, found to contain 5.69% of water (by drying at 110°) as compared with the theoretical 5.60%. A qualitative test for bromate or other strong oxidizing agents proved negative (<0.001% as $Ba(BrO_3)_2$).

The experimental procedure for the solubility determinations has been described in similar publications. The temperature of the determinations was 24.95 ± 0.02°. Equilibrium was approached from two directions, in about half of the experiments from undersaturation, *i. e.*, lower temperature, and in the others from higher temperature. In most cases equilibrium was proved by the constancy of the composition of the liquid on repeated analysis. In other cases, although such direct proof was not possible since the solution was all consumed in repeated analyses before actual constancy was established, it is felt that the systems must have been very close to if not at true equilibrium, because care was taken to keep the relative amount of solid phase in the complexes very low, and because of the long period of stirring generally used (one to six, averaging three and one-half, months).

The liquid solution was analyzed after sampling by means of calibrated pipets fitted with filtering tips. The wet residues were either pressed between coarse filter paper or centrifuged briefly, before weighing and analysis.

Water was determined by drying at 110° and bromate was determined iodometrically (in the presence of chlorate) by a procedure already described[2] for a similar investigation on the system sodium bromate–sodium chlorate–water. The correction there reported for the effect of relatively high concentrations of chlorate was verified and applied in the present case. These two determinations allowed the calculation of the percentage of each salt in the various solutions and residues.

A slight complication arose from the fact that final traces of water were not easily driven off at 110°, but required a brief treatment at about 300°. Since this temperature would also cause a slight decomposition of the two salts, especially of the barium bromate, experiments were made to determine the rate of loss of weight of each salt at 300°. The results indicated that after the initial expulsion of traces of water, barium chlorate suffered no measurable loss of weight in one or two hours, while barium bromate lost almost 4 mg. per gram per hour at this temperature, a correction which was then applied in the actual analyses.

Results.—The results are tabulated in Table I, which lists all compositions in weight per cent. The density of the saturated liquid solution was not always measured. Some of the values listed were read from a plot of the density, d, against c, the total percentage of salt in the saturated solution; the dependence was in fact found to be roughly linear, with an average error of about 0.002, according to the expression

$$d = 0.993 + 0.00935c \quad (1)$$

The solubility of barium chlorate here found is the same as the accepted value in the literature.[3] The solubility of barium bromate here reported, 0.791%, also agrees well with the important literature values: 0.788%, by Trautz and Anschütz,[3a] and 0.796%, by Harkins.[4]

---

[1] Hill, Durham and Ricci, THIS JOURNAL, 62, 2723 (1940).

[2] Swenson and Ricci, *ibid.*, 61, 1974 (1939).

[3] (a) Trautz and Anschütz, *Z. physik. Chem.*, 56, 238 (1906); 27.53%; (b) Foote and Hickey, THIS JOURNAL, 59, 648 (1937); 27.58%.

[4] Harkins, *ibid.*, 33, 1807 (1911).

Table I

System $Ba(BrO_3)_2$–$Ba(ClO_3)_2$–H_2O at 25°

No.	Liquid solution Wt. % $Ba(BrO_3)_2$	Liquid solution Wt. % $Ba(ClO_3)_2$	Density[a]	C:Original complex R:Wet residue Wt. % $Ba(BrO_3)_2$	C:Original complex R:Wet residue Wt. % $Ba(ClO_3)_2$	Solid phase by extrapolation[b] Wt. % $Ba(BrO_3)_2$	Solid phase by extrapolation[b] Wt. % $Ba(ClO_3)_2$
1	0.791 (±0.001)	....	1.001				
2	.609	1.292	1.011	C:2.270	1.274	95.2	0.26
3	.553	2.304	1.016	C:2.829	2.258	95.1	.40
4	.491	4.850	(1.043)	C:2.94	4.74	94.9	.61
5	.446	7.019	1.060	C:3.00	6.90	92.4	3.1
				R:74.9	4.10		
6	.423	9.370	(1.085)	C:1.908	9.302	90.2	5.3
7	.402	10.50	(1.095)	C:5.84	10.47	84.6	10.8
				R:64.6	11.4		
8	.347	14.41	(1.131)	C:6.79	14.65	78.0	17.3
9	.347	14.56	(1.132)	C:2.92	14.81	73.5	21.9
				R:53.8	20.0		
10	.310	16.83	1.151	C:1.97	16.99	71.5	23.7
11	.282	18.07	1.165	C:2.47	18.74	59.2	36.0
12	.249	19.53	(1.178)	C:3.31	20.84	52.0	43.2
				R:38.5	37.6		
13	.235	20.50	1.186	C:1.92	21.53	46.4	48.6
14	.207	21.72	1.202	C:2.07	23.39	39.2	55.7
				R:29.3	47.8		
15	.176	22.91	(1.209)	C:2.93	25.56	32.5	62.4
				R:17.6	46.2		
16	.145	23.85	(1.217)	C:2.27	28.03	24.0	70.7
				R:16.8	58.7		
17	.112	24.87	(1.227)	C:2.93.	31.67	19.2	75.5
				R:15.5	61.7		
18	.078	25.87	1.242	C:2.28	36.02	13.0	81.6
				R:9.15	66.8		
19	.057	26.51	(1.241)	C:1.00	37.82	5.7	88.8
				R:5.66	85.3		
20		27.54	1.249				

[a] Densities in parentheses are interpolated. [b] Average of two extrapolations, where wet residue analysis is reported; otherwise extrapolation through liquid solution and original complex.

The composition of the solid solution in equilibrium with the saturated liquid solution was calculated by the algebraic extrapolation,[5] to the line joining the compositions of the two separate monohydrates, of appropriate tie-lines through the liquid composition and the original complex, and also through the liquid composition and that of the wet residue whenever the latter was analyzed.

Figure 1 is the usual graphical representation of the isothermal relations of the ternary system, showing principally the disposition of the tie-lines for the distribution of the two isomorphous salts between the two continuous conjugate solutions. The shape of the solubility curve itself cannot be shown on such a scale. It is therefore presented separately on Fig. 2, which brings out an inverted S-shape similar to that of the 25° isotherm of the corresponding system sodium bromate–sodium chlorate–water.[2] The dip in the curve near the chlorate end, accompanied with divergence of the tie-lines in the direction of the solid solution, indicates, as in the sodium salt system, a tendency toward discontinuity of the solid solution and the formation of an isothermally invariant liquid. This is borne out by the mathematical analysis of the distribution of the salts between liquid and solid phases, in which it is inferred that the solid solution involves positive deviations from Raoult's law.

Distribution between the Aqueous and the Solid Solutions.—According to a relation already shown to hold with at least approximate correctness in a number of cases of pairs of isomorphous salts, the distribution of the salts of the present investigation, at equilibrium between their solid solutions, is given by the expression

$$\log R_l = \log K + m \log R_s \qquad (2)$$

in which R_l is the mole ratio of chlorate to bromate in the liquid solution, R_s is the same ratio in the solid solution, K represents the square root of the ratio of the thermodynamic solubility product of barium chlorate to that of barium bromate, and m is an empirical constant characteristic of the particular pair of salts and representing some measure of the degree of non-ideality of the solid

---

(5) Hill and Ricci, This Journal, 53, 4305 (1931).

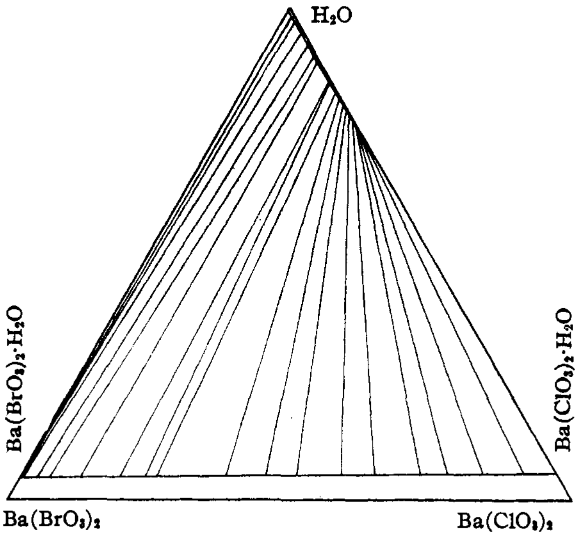


Fig. 1.—System $Ba(BrO_3)_2$–$Ba(ClO_3)_2$–H_2O at 25°.

solution formed by them. With ideal relations, $m = 1$. The equation has been found to apply to a number of systems both of alums and of picromerites.[1]

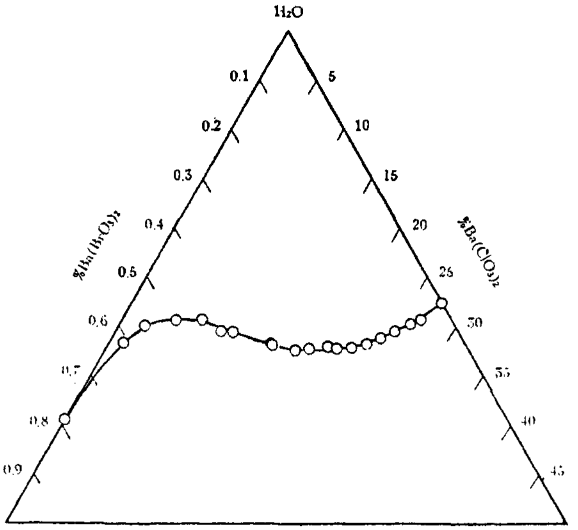


Fig. 2.—Solubility curve: $Ba(BrO_3)_2$–$Ba(ClO_3)_2$–H_2O at 25°.

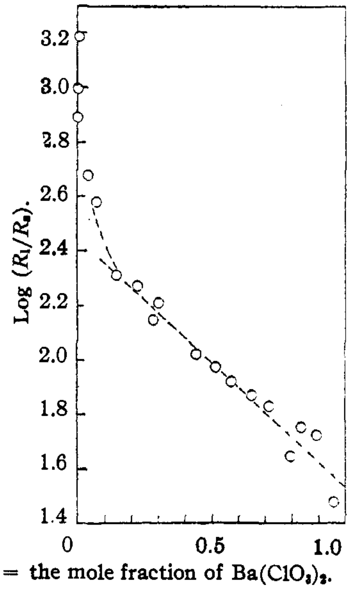
The quantities required for testing this distribution equation in the present system are listed in Table II. Here R_l and R_s are the ratios already explained, and x and y are the mole fractions of barium chlorate in the solid and in the liquid phases, respectively, excluding water.

These quantities were first plotted to see whether the solid solution of these salts constituted a "regular" solution in the Hildebrand sense.[6] This would require a linear relation between log (R_l/R_s) and x, the mole fraction of one of the salts in the solid. Figure 3 shows that while the relation is linear for values of x above 0.2, it is distinctly non-linear at lower mole fractions of the chlorate.

TABLE II

DISTRIBUTION BETWEEN LIQUID AND SOLID SOLUTIONS

No.	Log R_l	Log R_s	y	x
1			0	0
2	0.4380	−2.4523	0.733	0.00352
3	.7309	−2.2648	.843	.00541
4	1.1059	−2.0807	.927	.00824
5	1.3082	−1.3708	.954	.0408
6	1.4567	−1.1229	.967	.0701
7	1.5283	−0.7827	.971	.142
8	1.7297	− .5428	.982	.223
9	1.7342	− .4145	.984	.278
10	1.8460	− .3683	.986	.300
11	1.9180	− .1047	.988	.440
12	2.0058	+ .0308	.990	.518
13	2.0520	+ .1314	.991	.575
14	2.1322	+ .2639	.993	.648
15	2.2258	+ .3946	.994	.713
16	2.2274	.5805	.995	.792
17	2.4578	.7059	.996	.836
18	2.6320	.9091	.998	.890
19	2.7790	1.3038	.999	.953
20			1	1



x = the mole fraction of $Ba(ClO_3)_2$.

Fig. 3.—Test of "regularity" of the solid solution.

Figure 4 shows the data plotted to test equation (2). The over-all linearity of the relation between log R_l and log R_s is evident, especially with respect to intermediate values of the ratios. The scattering from linearity toward the extreme values is not necessarily significant, since the ratios at either end are more sensitive to experimental errors in the analytical determinations. Since the percentage of $Ba(ClO_3)_2$ is calculated by difference the error in the determination of R_s is relatively high when the solid phase approaches

---

(6) Hildebrand, "Solubility of Non-Electrolytes," Reinhold Publishing Company, New York, N. Y., 1936, p. 65.

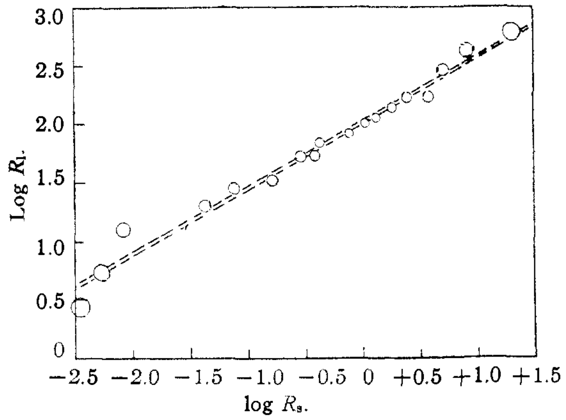


Fig. 4.—Distribution curve according to equation [4].

pure $Ba(BrO_3)_2 \cdot H_2O$. At the other extreme R_l becomes uncertain because of the decreasing precision of the determination of the small solubility of the bromate. Fortunately the important region of the plot of Fig. 4 is that near $\log R_s = 0$, and here the precision of the measurement of the ratios is high and the linearity is definite, giving a value of $m = 0.58$. At $\log R_s = 0$, $\log R_l = \log K = 2.0_0$.

This "observed" value of log K is to be compared, if possible, with that calculated from the activity products of the separate salts in their respective saturated solutions. K_a for $Ba(BrO_3)_2 \cdot H_2O$ was calculated from its ordinary solubility product, K_m, assuming the activity of water to be one, and applying the Debye–Hückel expression for the ionic activity coefficient, namely

$$\log K_a = \log K_m - \frac{6(0.510)(\mu)^{1/2}}{1 + 0.329a(\mu)^{1/2}} \qquad (3)$$

In this expression a was given the value of 2.5 Å., assuming an average ion size equal to that for the analogous salt $Ba(IO_3)_2 \cdot H_2O$.[7] This gives $K_a = 7.74 \times 10^{-6}$ at 25°.

Data for the calculation of the activity coefficient of the soluble salt, $Ba(ClO_3)_2 \cdot H_2O$, were not available. An approximate value was therefore estimated from information on barium nitrate. By plotting the activity coefficient of barium nitrate, as reported by Randall and Scott[8] from freezing point measurements, and by Ratner[9] from vapor pressure lowerings, at 70°, of solutions up to 1 M in concentration, against the square root of the ionic strength, and extrapolating to the solubility of the chlorate, (1.13 M), a value of $f_{\pm} = 0.18$ was obtained. The applicability of the estimate is subject to uncertainty both because the two salts differ in respect to hydration and because an extrapolation was involved to a concentration somewhat beyond the range of Ratner's measurements. At any rate, using this value for the ionic activity coefficient, K_a for $Ba(ClO_3)_2 \cdot H_2O$ is calculated as

$$K_a = K_m a_{H_2O}(f_{\pm})^3 \qquad (4)$$

For this calculation the activity of water in the saturated aqueous solution of barium chlorate was estimated as 0.95 from published data on the vapor pressures of barium chlorate solutions at 100°.[10] K_a thus equals 3.2×10^{-2}, whence log K for the distribution equation should equal $(3.2 \times 10^{-2}/7.7 \times 10^{-6})^{1/2} = 1.8_1$, whereas the "observed" value, as read from Fig. 4, is $\log K = 2.0_0$.

This may be considered as fair agreement, but it is not as good as that generally found for the alum and picromerite systems studied.[1] In view of the good linearity, seen in Fig. 4, in conformity with the equation, and of the approximate agreement between the observed and calculated values of log K, it is felt that the discrepancy is probably caused principally by the uncertainty in the value of the activity coefficient of the soluble salt, $Ba(ClO_3)_2 \cdot H_2O$, which had to be estimated by analogy only. Since the equation probably does describe the actual relations, it may be suggested that the observed value of log K can be used to estimate the unknown activity coefficient of $Ba(ClO_3)_2 \cdot H_2O$ in its pure saturated aqueous solution at 25°. The value thus calculated, from $\log K = 2.00$, using the solubility of the chlorate and the activity product of the bromate, is 0.24, as compared to the value 0.18 estimated from the measurements on barium nitrate. At any rate this calculation suggests the possibility of calculating the activity coefficient of a soluble salt in its saturated solution from such a phase rule study of a system involving isomorphous salts forming a continuous solid solution.

Finally, as has already been shown,[1] a value of m smaller than 1 indicates positive deviation from ideality. This is brought out in the plot of y (mole fraction in the liquid) against x (mole fraction in the solid) shown in Fig. 5. Here the sys-

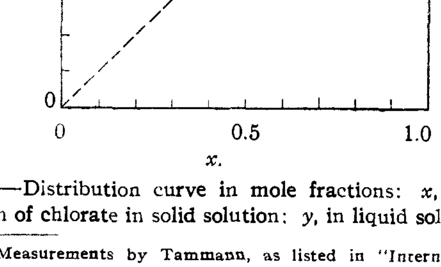


Fig. 5.—Distribution curve in mole fractions: x, mole fraction of chlorate in solid solution; y, in liquid solution.

---

[7] Ricci and Nesse, THIS JOURNAL, **64**, 2305 (1942).

[8] Randall and Scott, *ibid.*, **49**, 647 (1927).

[9] Ratner, *J. Phys. Chem., U. S. S. R.*, **9**, 257 (1937).

[10] Measurements by Tammann, as listed in "International Critical Tables," Vol. III, 1926, p. 296.

tem is seen to belong to Type II of the Roozeboom classification of such distributions between liquid and solid solutions. Although the experimental points do not actually cross the diagonal as x and y approach 1, as is demanded by Roozeboom's Type II, it may be calculated that with $m = 0.6$ and $K = 100$ in the equation

$$\frac{y}{1-y} = K\left(\frac{x}{1-x}\right)^m \qquad (5)$$

which is derivable from equation (2), the curve of Fig. 5, plotting y against x, will cross the diagonal at $x = 0.99999$, a value beyond experimental handling.

Summary

1. The solubility equilibrium relations in the system $Ba(BrO_3)_2$–$Ba(ClO_3)_2$–H_2O were studied at 25°.

2. The formation of a continuous solid solution of the monohydrates of the two salts at this temperature explains the difficulties in the attempted analytical determination of bromate in the presence of chlorate by precipitation with excess of some barium salt such as barium chloride.

3. The system is found to belong to Type II of Roozeboom's classification of solid solutions, involving positive deviations from ideality.

4. The distribution constant for the two isomorphous salts between their aqueous solutions and the saturating solid solution was determined from a plot of the data. Log K so found $= 2.0_0$, in fair agreement with the value calculated from the separate aqueous solubilities of the two salts, namely, $\log K = 1.8_1$.

5. The disagreement between calculated and observed distribution constants is attributed chiefly to the uncertainty of the value of the activity coefficient for $Ba(ClO_3)_2 \cdot H_2O$, and it is suggested that the distribution constant derived from this type of equilibrium study may be used for the calculation of such an activity coefficient.

NEW YORK, N. Y. RECEIVED MARCH 1, 1944

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

The Systems $NaClO_3$–NaBr–H_2O, $NaClO_3$–NaI–H_2O and $NaClO_3$–$NaNO_3$–H_2O, at 25°C.

BY J. E. RICCI

The solubility measurements here reported[1] have been made as additions to the systematic study of the equilibrium relations in aqueous systems involving sodium halates, particularly sodium chlorate.[2]

The experimental procedure was that already described for similar investigations. The salts were all C. P. or "reagent" materials, used without further purification. Equilibrium was established in representative instances by constancy of composition upon repeated analysis. Complexes were stirred for at least two days in every case, at a temperature of 25 ± 0.05°.

In the first two systems (I, $NaClO_3$–NaBr–H_2O; II, $NaClO_3$–NaI–H_2O) the analysis of the saturated aqueous solution involved argentometric titration of the halide salt, with eosin as adsorption indicator, determination of water in a separate sample by evaporation, and calculation of the sodium chlorate by difference. A few of the halide determinations for the isothermally invariant points were verified by the Volhard method. In the third system (III, $NaClO_3$–$NaNO_3$–H_2O) the chlorate was determined independently by treatment with standard arsenite solution and, after heating with hydrochloric acid, titration of the excess of arsenite by means of standard potassium bromate solution, using indigosulfonic acid as indicator; the sodium nitrate was then calculated by difference, after determination of water by evaporation. The solubilities of the individual salts (with the exception of sodium nitrate) were determined both volumetrically and by evaporation, with very close agreement between the two methods throughout.

The solid phases were in each case the pure separate salts or their respective hydrates stable at 25°, and were easily identified by means of tie-lines, on the ternary diagrams, drawn through the compositions of the original complex and of the corresponding saturated solution. The algebraic extrapolation of these tie-lines shows deviations from the points representing the pure salts or their hydrates, averaging 0.20, 0.21 and 0.34% in the three systems, respectively. This indicates, on the average, a relatively much smaller error in the total experimental procedure involving preparation of complexes, establishment of equilibrium and sampling and analysis of saturated solutions.

The numerical results are listed in Tables I, II and III, in terms of weight per cent. Densities were determined for the whole range of concentration only for the sodium nitrate system. These densities were obtained by using calibrated

---

[1] The greater part of the experimental work here reported was performed by A. C. Campbell (system $NaClO_3$–NaBr–H_2O), P. Mockridge (system $NaClO_3$–NaI–H_2O) and G. J. Moore (system $NaClO_3$–$NaNO_3$–H_2O), as candidates for the Bachelor's degree at New York University.

[2] Ricci and Yanick, THIS JOURNAL, **59**, 491 (1937); Ricci, **60**, 2040 (1938); Swenson and Ricci, **61**, 1974 (1939); Ricci and Weltman, **64**, 2746 (1942).