[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

The Ternary Systems Barium Hydroxide and Water with Barium Chloride, Thiocyanate, Chlorate or Acetate at 25°

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It has been shown by phase-rule methods that barium forms a basic chloride,[1] bromide and iodide[2]; and that it forms no basic nitrate.[3] The conditions for the formation of the so-called basic salt $BaOH\cdot SH\cdot 5H_2O$ have been determined by Terres and Brückner[4] but there appears to be no reason why this compound may not be more simply considered as $BaS\cdot 6H_2O$, a compound which has been known for many years. In fact, the work of these investigators shows that no basic barium sulfide exists over a wide range of temperature. Except for these cases, no systematic attempts have been made to determine to what extent barium forms basic salts. On account of the considerable solubility of the hydroxide, however, basic barium salts, if they form, can readily be determined by isothermal solubility diagrams. The results obtained on four systems at 25° are given in the present paper.

Materials and Methods

Barium hydroxide, chlorate and chloride were recrystallized before use, the first in a special apparatus which excluded carbon dioxide. We were fortunate in having samples of the thiocyanate and acetate of excellent purity which were used without further purification.[5]

Barium hydroxide was determined by titration with standard hydrochloric acid, using nitrazine yellow as indicator in the presence of the chloride, thiocyanate and chlorate; and phenolphthalein in the presence of the acetate. The acid was standardized by titrating barium hydroxide solutions whose concentration was determined by converting the hydroxide to the chloride, evaporating and drying to constant weight. This standard agreed closely with that obtained by determining the chloride gravimetrically as silver chloride. In the systems containing chloride, chlorate or acetate, total barium was determined by evaporating with hydrochloric acid, and weighing barium chloride. In the system containing thiocyanate, this radical was determined directly by the usual method with standard silver nitrate, using ferric alum as indicator.

Mixtures of the three components in suitable proportions were rotated in the thermostat at 25° for several days. In no case was difficulty experienced in obtaining equilibrium in two days. The temperature variation of the thermostat was not greater than ±0.03° which affects the results less than can be detected by analysis. Samples of solution for analysis were drawn off through asbestos or glass wool filters, or, when the solid settled properly, without filtering, and weighed. When barium hydroxide alone or a single barium salt was present in the residue, it was in most cases not analyzed as qualitative tests were sufficient to identify it. When an analysis was necessary, the residues were removed and dried almost completely between filter papers as rapidly as possible. This material, as it contained a small amount of residual solution, involved the use of the well-known Schreinemakers method for deriving the composition of the residues free of solution. By drying the residues almost completely only a short extrapolation of the results is necessary, which is of importance in the case of hydrated compounds for the accurate determination of the amount of water. On the other hand, the hydroxide, during exposure to the air, becomes slightly carbonated, which in the analysis, gives a somewhat low result for the hydroxide and a correspondingly high result for the salt present. The error from this source, however, is less important than the error from a long extrapolation as there is no difficulty in determining the ratio of the hydroxide to the salt with sufficient accuracy, and the chief difficulty is in determining the water of hydration. From the nature of the case, the composition of the solutions can be determined more accurately than the composition of the residues.

System: $Ba(OH_2)$–$BaCl_2$–H_2O.—This system has been investigated at 30° by Schreinemakers,[1] who found the basic salt $BaOHCl\cdot 2H_2O$. We have determined the solubility curve at 25° to make the results comparable with the other systems, all of which have been determined at this temperature. The data for the curves where barium chloride or barium hydroxide alone were the solid phases were obtained with considerably more care and are more numerous than was perhaps necessary for the system, as the results were needed in connection with another investigation. These determinations were made in duplicate and the titration of the hydroxide was carried out with a weight buret.

The solubility results are given in Table I. Only enough wet residues were analyzed to confirm the formula of Schreinemakers,[1] $BaOHCl\cdot 2H_2O$. All data represent percentages by weight.

The solubility data are plotted in Fig. 1 together with the composition of the three wet residues analyzed, which were in equilibrium with pure double salt. Results at univariant points were averaged. To avoid confusion, the data have been omitted along the short curve where barium chloride was the solid phase.

(1) Schreinemakers, *Z. physik. Chem.*, **68**, 83 (1910).
(2) Milikan, *ibid.*, **92**, 59, 496 (1918).
(3) Parsons and Carson, THIS JOURNAL, **32**, 1383 (1910).
(4) Terres and Brückner, *Z. Elektrochem.*, **26**, 1 (1920).
(5) Barium thiocyanate crystallizes at room temperatures as the compound $Ba(CNS)_2\cdot 3H_2O$. It was originally described incorrectly as the dihydrate and this error has been retained in many references to the compound. Whether a dihydrate is formed at a higher temperature has not been determined.

TABLE I

SYSTEM: $Ba(OH)_2$–$BaCl_2$–H_2O AT 25°

Solution % $Ba(OH)_2$	Solution % $BaCl_2$	Wet residue % $Ba(OH)_2$	Wet residue % $BaCl_2$	Residue contains:
4.489	None	..	..	$Ba(OH)_2 \cdot 8H_2O$
4.224	3.649	..	..	$Ba(OH)_2 \cdot 8H_2O$
4.100	6.788	..	..	$Ba(OH)_2 \cdot 8H_2O$
4.04	10.10	..	..	$Ba(OH)_2 \cdot 8H_2O$
4.03	12.62	..	..	$Ba(OH)_2 \cdot 8H_2O$
4.05	15.33	..	..	$Ba(OH)_2 \cdot 8H_2O$
4.06	17.05	..	..	$Ba(OH)_2 \cdot 8H_2O$
4.11	19.31	..	..	$Ba(OH)_2 \cdot 8H_2O$ $BaOHCl \cdot 2H_2O$
4.13	19.32	..	..	$Ba(OH)_2 \cdot 8H_2O$ $BaOHCl \cdot 2H_2O$
3.38	20.79	35.3	45.5	$BaOHCl \cdot 2H_2O$
3.13	22.05	34.0	44.9	$BaOHCl \cdot 2H_2O$
2.65	23.57	35.1	46.9	$BaOHCl \cdot 2H_2O$
1.94	26.69	..	..	$BaOHCl \cdot 2H_2O$ $BaCl_2 \cdot 2H_2O$
1.95	26.71	..	..	$BaOHCl \cdot 2H_2O$ $BaCl_2 \cdot 2H_2O$
1.77	26.72	..	..	$BaCl_2 \cdot 2H_2O$
1.39	26.83	..	..	$BaCl_2 \cdot 2H_2O$
0.89	26.94	..	..	$BaCl_2 \cdot 2H_2O$
None	27.16	..	..	$BaCl_2 \cdot 2H_2O$

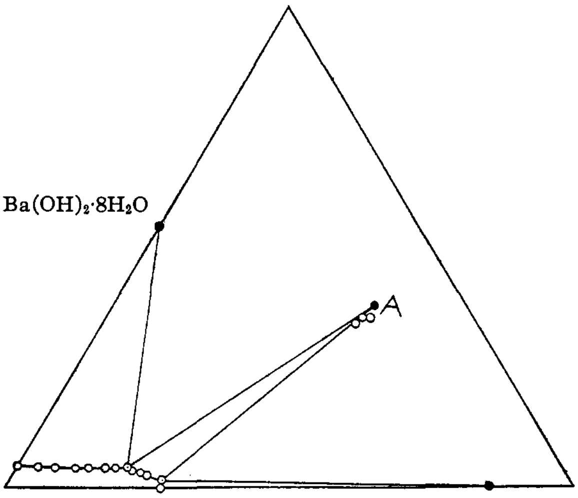

Fig. 1.—System $Ba(OH)_2$–$BaCl_2$–H_2O. Solid phases are $Ba(OH)_2 \cdot 8H_2O$, $BaCl_2 \cdot 2H_2O$ and $BaOHCl \cdot 2H_2O$ (A in diagram).

System: $Ba(OH)_2$–$Ba(CNS)_2$–H_2O.—The results are given in Table II.

The results in Table II are plotted in Fig. 2. Tie lines connecting solutions and residues are shown as dotted lines. The solid in one of the wet residues at the univariant point where basic salt and thiocyanate are in equilibrium was nearly pure basic salt and the point representing the composition of the residue has been shifted slightly to the right for clarity.

TABLE II

SYSTEM: $Ba(OH)_2$–$Ba(CNS)_2$–H_2O AT 25°

Solution % $Ba(OH)_2$	Solution % $Ba(CNS)_2$	Wet residue % $Ba(OH)_2$	Wet residue % $Ba(CNS)_2$	Residue contains:
4.489	None	..	..	$Ba(OH)_2 \cdot 8H_2O$
3.58	15.83	..	..	$Ba(OH)_2 \cdot 8H_2O$
3.44	26.54	..	..	$Ba(OH)_2 \cdot 8H_2O$
5.89	47.51	52.4	2.4	$Ba(OH)_2 \cdot 8H_2O$
8.45	50.88	44.2	24.3	$Ba(OH)_2 \cdot 8H_2O$ BaOHCNS
8.49	51.00	35.7	50.5	$Ba(OH)_2 \cdot 8H_2O$ BaOHCNS
6.16	54.49	34.7	59.7	BaOHCNS
4.75	57.34	37.7	59.0	BaOHCNS
3.18	61.61	31.8	59.9	BaOHCNS $Ba(CNS)_2 \cdot 3H_2O$
3.16	61.73	1.4	80.9	BaOHCNS $Ba(CNS)_2 \cdot 3H_2O$
2.05	61.97	0.1	81.7	$Ba(CNS)_2 \cdot 3H_2O$
None	62.63	..	..	$Ba(CNS)_2 \cdot 3H_2O$

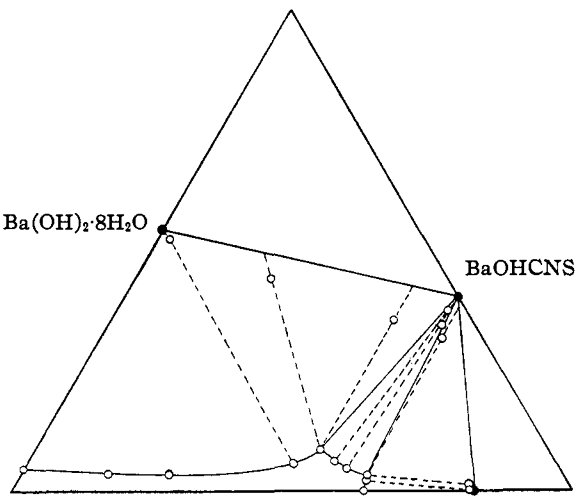

Fig. 2.—System $Ba(OH)_2$–$Ba(CNS)_2$–H_2O. Solid phases are $Ba(OH)_2 \cdot 8H_2O$, $Ba(CNS)_2 \cdot 3H_2O$ and BaOHCNS.

It was difficult to obtain the basic salt in pure condition as the crystals were very small and only formed in solutions containing a large excess of thiocyanate. A sample of the salt for analysis was prepared by crystallizing a small amount at 25° from a solution of the proper concentration. This material gave on analysis

$Ba(OH)_2$, 38.53; $Ba(CNS)_2$, 59.16; H_2O (diff.), 2.31

corresponding to the molecular ratio 1:1.04:0.57. As the material could not be dried properly, the water is undoubtedly from the solution and the result confirms the formula mentioned above.

System: $Ba(OH)_2$–$Ba(ClO_3)_2$–H_2O.—This system forms no basic salt at 25° and the only solids occurring are hydrated barium hydroxide and barium chlorate, which crystallizes as the anhydrous salt. The solubility results are given in Table III. They are plotted in Fig. 3 together with the composition of the only two wet residues which it was necessary to analyze.

TABLE III

SYSTEM: $Ba(OH)_2$–$Ba(ClO_3)_2$–H_2O AT 25°

Solution % $Ba(OH)_2$	Solution % $Ba(ClO_3)_2$	Wet residue % $Ba(OH)_2$	Wet residue % $Ba(ClO_3)_2$	Residue contains:
4.489	None	..	..	$Ba(OH)_2 \cdot 8H_2O$
4.02	8.79	..	..	$Ba(OH)_2 \cdot 8H_2O$
3.85	15.98	..	..	$Ba(OH)_2 \cdot 8H_2O$
3.77	21.85	..	..	$Ba(OH)_2 \cdot 8H_2O$
3.72	26.55	51.4	3.2	$Ba(OH)_2 \cdot 8H_2O$, $Ba(ClO_3)_2$
3.71	26.62	3.6	81.6	$Ba(OH)_2 \cdot 8H_2O$, $Ba(ClO_3)_2$
1.87	27.17	..	..	$Ba(ClO_3)_2$
None	27.58	..	..	$Ba(ClO_3)_2$

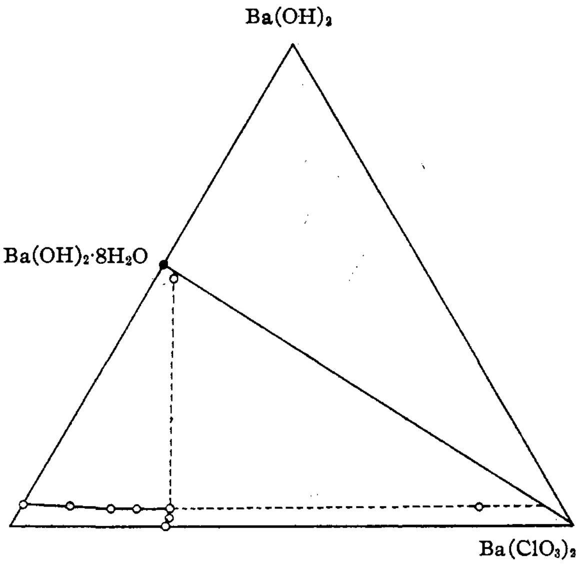

Fig. 3.—System $Ba(OH)_2$–$Ba(ClO_3)_2$–H_2O. Solid phases are $Ba(OH)_2 \cdot 8H_2O$ and $Ba(ClO_3)_2$.

System: $Ba(OH)_2$–$Ba(C_2H_3O_2)_2$–H_2O.—This system, like the previous one, forms no basic salt. At 25° the monohydrate is the stable form of barium acetate in contact with solutions. The results are given in Table IV and plotted in Fig. 4.

TABLE IV

SYSTEM: $Ba(OH)_2$–$Ba(C_2H_3O_2)_2$–H_2O AT 25°

Solution % $Ba(OH)_2$	Solution % $Ba(C_2H_3O_2)_2$	Wet residue % $Ba(OH)_2$	Wet residue % $Ba(C_2H_3O_2)_2$	Residue contains:
4.489	None	...	...	$Ba(OH)_2 \cdot 8H_2O$
3.22	16.91	52.74	1.14	$Ba(OH)_2 \cdot 8H_2O$
2.85	29.32	51.80	2.45	$Ba(OH)_2 \cdot 8H_2O$
2.64	37.97	50.31	4.73	$Ba(OH)_2 \cdot 8H_2O$
2.56	41.71	39.86	23.42	$Ba(OH)_2 \cdot 8H_2O$, $Ba(C_2H_3O_2)_2 \cdot H_2O$
2.56	41.71	27.53	43.45	$Ba(OH)_2 \cdot 8H_2O$, $Ba(C_2H_3O_2)_2 \cdot H_2O$
2.60	41.80	3.81	83.91	$Ba(OH)_2 \cdot 8H_2O$, $Ba(C_2H_3O_2)_2 \cdot H_2O$
1.35	42.40	Trace	93.71	$Ba(C_2H_3O_2O_2 \cdot H_2O$
None	43.20	None	91.72	$Ba(C_2H_3O_2)_2 \cdot H_2O$

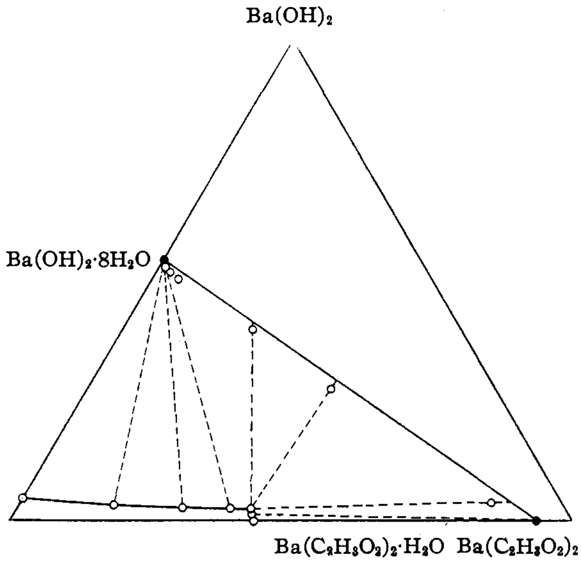

Fig. 4.—System $Ba(OH)_2$–$Ba(C_2H_3O_2)_2$–H_2O. Solid phases are $Ba(OH)_2 \cdot 8H_2O$ and $Ba(C_2H_3O_2)_2 \cdot H_2O$.

Summary

Isothermal solubility determinations (at 25°) have been made in the ternary systems composed of barium hydroxide and water with barium chloride, thiocyanate, chlorate or acetate. The basic salt $BaOHCl \cdot 2H_2O$, investigated by Schreinemakers at another temperature, has been found. A new basic salt BaOHCNS also has been found. No basic chlorate or acetate forms at this temperature, the solid phases being the same that crystallize in the binary systems with water alone.

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