COMPOSITION OF DIFFUSATE.

| Period. | M. mols $(NH_4)_2SO_4$. | M mols $Cr_2(SO_4)_3$. | $\frac{(NH_4)_2SO_4}{Cr_2(SO_4)_3}$. |
|---|---|---|---|
| 1 | 2.28 | 0.426 | 5.35 |
| 2 | 1.26 | 0.810 | 1.55 |
| 3 | 0.90 | 0.720 | 1.25 |
| Solution in cell after conclusion of experiment. | | | |
| | 0.05 | 0.13 | 0.039 |

## Diffusion of Ammonium Aluminium Alum.

Solutions same as previously used. Periods 24 hours each.

COMPOSITION OF DIFFUSATE.

| Period. | M. mols $(NH_4)_2SO_4$. | M. mols $Al_2(SO_4)_3$. | $\frac{(NH_4)_2SO_4}{Al_2(SO_4)_3}$. |
|---|---|---|---|
| 1 | 1.62 | 0.585 | 2.77 |
| 2 | 1.26 | 0.792 | 1.28 |
| Solution in cell after conclusion of experiment. | | | |
| | 0.70 | 0.138 | 0.507 |

The results of these experiments with agar-agar show in the same way as with parchment that the constituents of the alums diffuse independently.

## Conclusions.

When alums are dissolved in water they are decomposed into the simple sulphates, which can be separated from each other by diffusion. The chrome alums separate more readily than the aluminium alums. This is in entire accord with previous researches.

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# THE SOLUBILITY OF BARIUM NITRATE AND BARIUM HYDROXIDE IN THE PRESENCE OF EACH OTHER.

BY C. L. PARSONS AND H. P. CORSON.

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The work of Cameron and Robinson upon the system lime, nitric acid and water[1] proves the existence of a basic nitrate of calcium having a composition represented by $2CaO.N_2O_5.3\frac{1}{2}H_2O$. Their work suggested the possibility of the existence of similar compounds of barium, but in a careful search of the literature we were unable to find any record of such work upon barium. Hence the present investigation was undertaken.

A specially prepared barium nitrate obtained for this research was carefully tested for impurities. The salt was found to be very pure, no foreign substance being detected except a small amount of carbonate. A saturated solution of the nitrate was prepared and made slightly, yet distinctly, acid with nitric acid and boiled to remove carbon dioxide.

The barium hydroxide obtained for the work was found to be quite

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[1] *J. Physic. Chem.*, **2**, 273 (1907).

pure except for the presence of carbonate, which was eliminated by filtering a hot concentrated solution with careful exclusion of the carbon dioxide of the air. Upon cooling this solution, crystals of pure hydroxide separated out. This solid was dipped out with adhering solution and added to the solutions of nitrate.

Bottles were made up in regular steps of concentration from pure water to a saturated solution of barium nitrate, using freshly boiled distilled water for dilution. Barium hydroxide was then added until sufficient solid persisted. One bottle also had excess of solid nitrate added and two were made alkaline with barium hydroxide, but short of saturation, and excess of solid nitrate added. The bottles were sealed and constantly rotated in a water thermostat maintained at 25° until equilibrium was reached. The bottles were not opened for four months, although equilibrium was undoubtedly complete much earlier, since no reaction occurred and subsequent analysis of all bottles showed no change.

Previous experiment had shown that the gravimetric estimation of barium could be made more accurately in these pure salt solutions by weighing barium nitrate than by the usual sulphate method. Consequently the *total* barium oxide present was determined by this method. Portions of the solutions amounting to about 5 cc. were drawn off and weighed in a weighing bottle, transferred to a platinum dish, acidified with nitric acid and evaporated in an air bath at 100°. After the solution had come down to dryness, the temperature was increased to 115° to remove the last traces of free acid and moisture. The samples were then cooled and weighed as barium nitrate.

Barium oxide present as *hydroxide* was determined volumetrically by titrating a weighed portion of the solution with tenth normal nitric acid, using phenolphthalein as indicator.

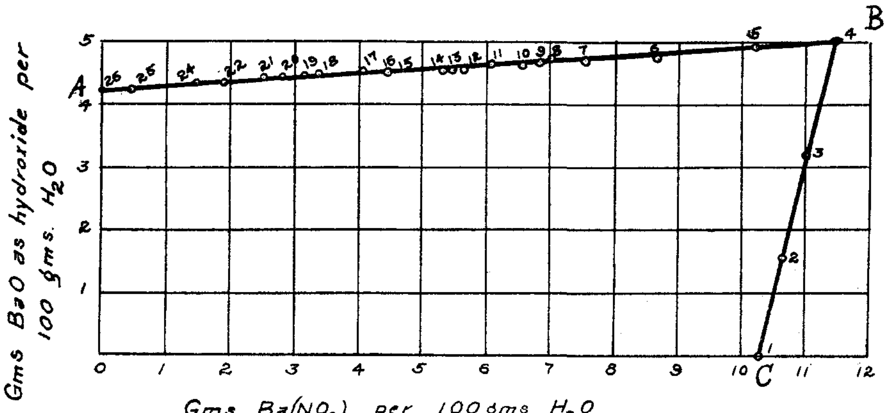

Fig. 1.

The data obtained are given in Table I, which shows (Nos. 4–26) the solubility of barium hydroxide in solutions of barium nitrate of various concentrations and (Nos. 1–4) the solubility of barium nitrate in solutions of barium hydroxide. No. 4 represents the composition at the invariant point where both solids are present in excess.

The results are expressed graphically in Fig. 1.

From an inspection of this chart, it will be seen that there are two distinct branches, AB and BC, to the isotherm. As this is a three-component system, along each of these two branches there can be only one solid phase in equilibrium with the solution.

TABLE I.

| Serial No. | Density 25°/25°. | Grams BaO as $Ba(OH)_2$ in 100 $H_2O$. | Grams $Ba(NO_3)_2$ in 100 $H_2O$. |
|---|---|---|---|
| 1 | 1.0797 | none | 10.30 |
| 2 | 1.1002 | 1.55 | 10.66 |
| 3 | 1.1210 | 3.22 | 11.04 |
| 4 | 1.1448 | 5.02 | 11.48 |
| 5 | 1.1371 | 4.93 | 10.21 |
| 6 | 1.1288 | 4.83 | 8.66 |
| 7 | 1.1220 | 4.72 | 7.55 |
| 8 | 1.1133 | 4.72 | 7.01 |
| 9 | 1.1062 | 4.65 | 6.82 |
| 10 | 1.1044 | 4.61 | 6.55 |
| 11 | 1.1010 | 4.64 | 6.08 |
| 12 | 1.0975 | 4.60 | 5.66 |
| 13 | 1.0949 | 4.55 | 5.46 |
| 14 | 1.0937 | 4.54 | 5.32 |
| 15 | 1.0885 | 4.52 | 4.44 |
| 16 | 1.0864 | 4.53 | 4.41 |
| 17 | 1.0840 | 4.52 | 4.04 |
| 18 | 1.0790 | 4.48 | 3.47 |
| 19 | 1.0774 | 4.46 | 3.14 |
| 20 | 1.0731 | 4.40 | 2.79 |
| 21 | 1.0711 | 4.42 | 2.53 |
| 22 | 1.0651 | 4.35 | 1.88 |
| 23 | 1.0626 | .... | .... |
| 24 | 1.0640 | 4.35 | 1.45 |
| 25 | 1.0538 | 4.29 | 0.43 |
| 26 | 1.0512 | 4.29 | none |

Several of the solids in contact with the solutions were analyzed. Along branch BC of the curve (Fig. 1) the solids were dipped from the solutions with a platinum spoon, no attempt being made to free them from mother liquor save by decantation. They were analyzed in exactly the same manner as the liquids, namely, titration of a weighed portion with nitric acid, then evaporation and weighing as nitrate.

The solids along branch AB of the curve (Fig. 1) were pure hydroxide and when pressed between filter paper contained so small a quantity of $N_2O_5$ that it was not practical to determine the exact amount. Table II gives the percentage composition of all the solutions, together with some of the corresponding residues.

TABLE II.

| No. | Solutions. | | | Residues with adhering solution. | | |
|---|---|---|---|---|---|---|
| | BaO. Per cent. | $N_2O_5$. Per cent. | $H_2O$. Per cent. | BaO. Per cent. | $N_2O_5$. Per cent. | $H_2O$. Per cent. |
| 1 | 5.48 | 4.86 | 89.66 | 50.21 | 35.38 | 14.41 |
| 2 | 6.95 | 3.92 | 89.13 | 51.44 | 36.22 | 12.34 |
| 3 | 8.46 | 3.98 | 87.56 | 50.29 | 35.12 | 14.59 |
| 4 | 10.05 | 4.06 | 85.89 | 56.44 | 35.20 | 8.36 |
| 5 | 9.43 | 3.63 | 86.94 | ..... | ..... | ..... |
| 6 | 8.80 | 3.21 | 87.99 | ..... | ..... | ..... |
| 7 | 8.12 | 2.78 | 89.10 | ..... | ..... | ..... |
| 8 | 7.94 | 2.64 | 89.42 | ..... | ..... | ..... |
| 9 | 7.72 | 2.52 | 89.76 | ..... | ..... | ..... |
| 10 | 7.57 | 2.42 | 90.01 | ..... | ..... | ..... |
| 11 | 7.38 | 2.26 | 90.56 | ..... | ..... | ..... |
| 12 | 7.15 | 2.11 | 90.74 | ..... | ..... | ..... |
| 13 | 7.01 | 2.04 | 90.95 | ..... | ..... | ..... |
| 14 | 6.92 | 1.98 | 91.10 | ..... | ..... | ..... |
| 15 | 6.57 | 1.71 | 91.72 | ..... | ..... | ..... |
| 16 | 6.50 | 1.66 | 91.84 | ..... | ..... | ..... |
| 17 | 6.32 | 1.54 | 92.14 | ..... | ..... | ..... |
| 18 | 5.96 | 1.29 | 92.75 | ..... | ..... | ..... |
| 19 | 5.83 | 1.20 | 92.97 | ..... | ..... | ..... |
| 20 | 5.65 | 1.08 | 93.27 | ..... | ..... | ..... |
| 21 | 5.49 | 0.97 | 93.54 | ..... | ..... | ..... |
| 22 | 5.13 | 0.74 | 94.13 | ..... | ..... | ..... |
| 23 | 4.88 | 0.56 | 94.54 | ..... | ..... | ..... |
| 24 | 4.92 | 0.58 | 94.50 | ..... | ..... | ..... |
| 25 | 4.32 | 0.17 | 95.51 | ..... | ..... | ..... |
| 26 | 4.10 | none | 95.90 | ..... | ..... | ..... |

Along the other branch, BC of the curve, the composition of the solid, evidently the nitrate, was proved by plotting the results of analyses on a triangular diagram.[1] When plotted in this manner the lines connecting the points representing liquids with other points representing their corresponding solids meet in a point which as scaled off on the diagram has the composition BaO 58.7, $N_2O_5$ 41.3. This solid, then, is represented by the formula $BaO.N_2O_5$. The analysis of the solid in bottle No. 4, which lies at the intersection of the two branches of the isotherm, shows, of course, that it consists of both $Ba(OH)_2.8H_2O$ and $Ba(NO_3)_2$. Examination of the residues by the microscope is entirely in agreement with the conclusions arrived at by analysis.

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[1] Schreinemakers, *Z. physik. Chem.*, 11, 81 (1893); Bancroft, *J. Physic. Chem.*, 6, 181 (1902).

## Conclusions.

The solubility of barium hydroxide in solutions of barium nitrate increases as the concentration of the latter increases. This fact is interesting, for in most cases a common ion tends to decrease the solubility of substances in solution in a common solvent.

The solid in equilibrium with any solution along curve AB, Fig. 1, is $Ba(OH)_2.8H_2O$, and along curve BC, is $Ba(NO_3)_2$.

Consequently, we conclude that basic nitrates of barium do not exist at 25°.

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# THE SOLUBILITY OF STRONTIUM NITRATE AND STRONTIUM HYDROXIDE IN THE PRESENCE OF EACH OTHER.

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In connection with the work described in the preceding paper on the solubility of barium nitrate in solutions of barium hydroxide it was decided to make a similar study of the strontium compounds and for the same reason. No basic nitrates of strontium have been described in the literature, but there was no certainty that a search along equilibrium lines might not reveal them.

A specially pure lot of strontium nitrate was prepared by separating the barium from a salt purchased as pure and containing no other contamination. Strontium hydroxide was prepared from pure strontium oxide by dissolving it in boiling water and filtering hot. Upon cooling the solution strontium hydroxide crystallized out and was preserved under the mother liquor. It was protected from the formation of carbonate by a sodium hydroxide seal.

A saturated solution of the nitrate was prepared and boiled with a slight excess of nitric acid to assure the absence of all carbonates. From this a series of solutions was made by diluting with freshly boiled, distilled water in varying amounts and adding the solid hydroxide until a solid phase persisted in sufficient quantity for analysis. One bottle also had excess of solid nitrate added and two bottles similarly prepared were made to contain hydroxide short of saturation. The solutions were placed in tightly stoppered bottles, the glass stoppers of which had been carefully ground, and rotated in a thermostat kept at 25° for more than a month before any analyses were made. Subsequent trials proved that equilibrium had already been attained.

Previous experimentation having shown that the methods used for barium in the research already referred to were applicable here, they were, accordingly, used. Definite portions of the solution were drawn off, weighed, acidified with nitric acid, evaporated to complete dryness