(No. 127) indicates that there is a lower hydrate of CaHPO_4 . It is probable that this is the anhydrous salt and that the single point (No. 127) gives the conditions at 25° for the transition

As the KCl present in solution influences the vapor pressure of the solution, concentrations of calcium oxide and phosphoric anhydride in each case are somewhat lower than for the corresponding solution where no potassium chloride is present.

These results also show the effect of potassium chloride in concentrations of about 25–30 grams per liter upon the system $\text{CaO}-\text{P}_2\text{O}_5-\text{H}_2\text{O}$. In the accompanying diagram are given the results of Bassett, of Cameron and Seidell, and of the present paper where potassium chloride is present. These last results lie above the curves drawn through the former points. Thus the effect of the potassium chloride is to increase the lime in solution.

In this paper it has been shown that:

1. The presence of potassium chloride in solution containing calcium oxide and phosphoric anhydride increases slightly the lime content of solutions in equilibrium with dicalcium phosphate and monocalcium phosphate.
2. By the "tell-tale" method the composition of the solid phases was found to be $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ and $\text{CaH}_4(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ with a region between, which was not explored, where the composition of the solid was probably CaHPO_4 .
3. This result is in accord with Bassett's last determination of the transition interval of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O} \rightleftharpoons \text{CaHPO}_4 + 2\text{H}_2\text{O}$ but is not in accord with his direct determination of the compositions of the solid phases.

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BASIC NITRATE OF YTTRIUM.

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Of all the methods that have been published for the separation of yttrium and erbium, the classic procedure of Bahr and Bunsen¹ still serves best. It was therefore considered that a study of the system $\text{Y}_2\text{O}_3, \text{N}_2\text{O}_5, \text{H}_2\text{O}$ would be highly interesting.

The only basic nitrate mentioned by Bahr and Bunsen was given the formula (recalculated) $2\text{Y}_2\text{O}_3 \cdot 3\text{N}_2\text{O}_5 \cdot 9\text{H}_2\text{O}$, which was derived from the analysis of the air-dried salt. It is highly probable that their compound was contaminated with normal nitrate from adherent mother liquor.

¹ *Ann.*, 137, 1 (1866).

In order to study the system Y_2O_3 , N_2O_5 , H_2O , it was necessary to prepare a comparatively large amount of pure yttrium oxide, since yttrium nitrate is extremely soluble.

The Preparation of Yttria Material.—The crude yttria earths were first submitted to a long fractional crystallization by the bromate method.¹ By this procedure samarium, gadolinium, terbium, dysprosium and holmium separated in the least soluble portions. The middle fractions contained yttrium, together with a little erbium and holmium, while the most soluble portion carried nearly all the erbium and all the thulium, ytterbium, lutecium and scandium.

The middle fractions were then precipitated as the hydroxide and well washed with boiling water. The hydroxides were next converted into the nitrates and the latter subjected to fractional decomposition. This was carried out by evaporating the solution and fusing until a portion had decomposed. The evolution of red fumes was allowed to proceed until the surface acquired a peculiar steely appearance. This point was easily ascertained by experience. The decomposition was not allowed to continue until the mass became creamy.

In order to find the best method of obtaining the solution of the melt, several plans were tried. It was discovered that the simplest way was to pour the fused mass into cold water. Great care was required in order to prevent spattering. The result of this operation was a nicely granulated product, which rapidly disintegrated upon boiling.

Under the best conditions the entire mass went into solution; especially was this true of the yttrium end of the series. Upon cooling, the basic nitrates separated out in a crystalline form. At the opposite end—the least basic portion—of the fractions there always remained an insoluble basic nitrate, unless the decomposition was stopped at an earlier stage, *i. e.*, when there was a copious evolution of red fumes.

In case a precipitate remained, it was highly important that it should be well agitated by thorough boiling. After cooling, the precipitate was filtered off (Fraction II), redissolved in nitric acid and again fused. The filtrate (Fraction I) was also boiled down, and fused. This second series gives two filtrates and two precipitates. The filtrate from Fraction II was mixed with the precipitate from Fraction I with the result that the second series contained three fractions. The diagram below will readily show the manner in which the work was carried out.

About 40 series of operations were carried out, yielding two kilos of yttrium nitrate. The nitrate was dissolved in water, heated and precipitated by means of oxalic acid. The resulting oxalate was filtered off, well washed, dried and ignited.

¹ THIS JOURNAL, 30, 182.

The white oxide obtained in this way was dissolved in an excess of nitric acid, and twice crystallized from this solvent.

A saturated solution of the nitrate was then prepared by using 1 kilogram of the salt. The spectroscope showed only very faint bands of erbium and holmium when viewed through a layer 12.5 cm. thick and the solution was perfectly colorless. Therefore, it was considered sufficiently pure for the study of the basic nitrates.

Some of the remaining fractions of yttrium, which still contained a little erbium and holmium, were put through a modified chromate method. This yielded a further supply of yttrium oxide of such a purity that, when converted into a concentrated solution of the nitrate, it showed no absorption bands through a layer of about 5 cm.

Twenty-two solutions were prepared, in regularly increasing concentrations of yttrium nitrate, from great dilution to a saturated solution. These solutions together with an excess of yttrium oxide were placed in bottles of 100 cc. capacity, and rotated in a thermostat at 25° . After an interval of three months, several of the solutions were analyzed. During the analysis, it was observed that the solid phase, in those solutions having a fairly high concentration of yttrium nitrate, was composed of fine crystals. These bottles cleared in a comparatively short time so that the supernatant liquid could be readily drawn off. In the bottles, where the concentrations were not so great, the solid phases settled with difficulty, and had more the appearance of a hydroxide. After four and a half months of rotation, the system was found to be in equilibrium. The solutions were withdrawn, and the yttrium, present as the hydroxide and the total yttrium determined.

Several difficulties were encountered in carrying out these analyses, and different methods were tried in order to reduce errors to a minimum. The following methods gave the most accurate and rapid results:

A weighed amount of mother liquor was, after considerable dilution, titrated to the neutral point with standard nitric acid (approximately $\frac{1}{10}$ normal) using methyl orange as the indicator. From this, the amount of yttrium oxide, present as hydroxide, was easily calculated. Checks, which were run on several of the solutions, proved that dependence could be placed upon the results obtained.

In order to determine the total yttrium, the solutions, which had previously been titrated, were diluted to 200 cc. Aliquot portions of these diluted solutions were warmed, and treated with a slight excess of an oxalic acid solution. After being allowed to stand for some time, the precipitate was filtered off, dried, and carefully ignited to the oxide in a weighed platinum crucible.

The data obtained from the analyses of the solutions are given in Table I and shown graphically in Fig. 1.

TABLE I.

No.	Density 25°/25°.	Per cent. Y_2O_3 as $Y(NO_3)_3$.	Per cent. Y_2O_3 as $Y(OH)_3$.	Grams $Y(NO_3)_3$ in 100 grams H_2O .	Grams Y_2O_3 as $Y(OH)_3$ in 100 grams H_2O .
1.....	1.0260	1.25	0.014	3.13	0.014
2.....	1.0675	3.17	0.021	8.37	0.022
3.....	1.1106	5.01	0.033	13.87	0.034
4.....	1.1506	6.57	0.039	19.05	0.048
5.....	1.1907	8.20	0.049	24.94	0.063
6.....	1.2350	9.58	0.071	30.46	0.091
7.....	1.2517	10.19	0.121	33.02	0.160
8.....	1.2897	11.45	0.088	38.71	0.122
9.....	1.3268	12.61	0.079	44.35	0.114
10.....	1.3698	14.02	0.068	51.87	0.103
11.....	1.4104	15.17	0.060	58.61	0.095
12.....	1.4484	16.31	0.054	65.89	0.090
13.....	1.4867	17.33	0.045	73.03	0.078
14.....	1.5231	18.33	0.039	80.67	0.072
15.....	1.5587	19.34	0.039	89.06	0.074
16.....	1.5923	20.10	0.038	95.98	0.074
17.....	1.6259	20.91	0.037	103.80	0.075
18.....	1.6603	21.82	0.037	113.40	0.079
19.....	1.6931	22.59	0.036	122.40	0.080
20.....	1.7260	23.37	0.032 ¹	132.10	0.074
21.....	1.7440	23.74	0.035	137.10	0.083
22.....	1.7446	24.07	..	141.60	...

Bottle No. 21 contained an excess of both basic yttrium nitrate and yttrium nitrate. Bottle No. 22 contained only an excess of yttrium nitrate, which gave for the solubility of this compound at 25° 141.6 grams per 100 grams of water.

For the analysis of the solid phase, the sample was withdrawn, freed, as far as possible, from adhering mother liquor, by pressing between

¹ This result undoubtedly contains a slight error, but, unfortunately, the bottle was emptied before it could be checked.

filter paper, after which it was quickly transferred to a weighing bottle and carefully mixed. A known amount was then ignited in a weighed platinum crucible for total yttrium. In another portion of the same

Fig. 1.

sample the yttrium oxide as yttrium hydroxide was estimated by dissolving a weighed amount in an excess of standard nitric acid, and titrating back to neutrality with a sodium carbonate solution of known ratio. In this case methyl orange was again used as the indicator.

The results are given in Table II, and plotted on the triangular diagram in Fig. 2.

TABLE II.

Point.	Solutions.		Point.	Solids.		Bottle No.
	Y ₂ O ₃ .	N ₂ O ₅ .		Y ₂ O ₃ .	N ₂ O ₅ .	
E.....	1.26	1.79	E'	49.55	13.29	1
F.....	3.19	4.55	F'	45.20	12.96	2
G.....	5.04	7.18	G'	42.97	13.74	3
H.....	6.61	9.42	H'	47.82	14.56	4
I.....	9.65	13.74	I'	41.67	16.22	6
J.....	11.54	16.42	J'	39.78	26.98	8
K.....	12.69	18.08	K'	38.09	26.93	9
L.....	15.23	21.75	L'	38.21	27.89	11
M.....	16.36	23.39	M'	38.39	28.12	12
N.....	17.38	24.83	N'	38.19	28.70	13
O.....	18.37	26.28	O'	38.44	29.19	14
P.....	19.38	27.73	P'	37.83	29.58	15

It will be seen that the lines (EE', FF' and GG', etc., of Fig. 2) joining points represented on curve AB of Fig. 1 do not intersect at a common point; also the solids, upon examination, showed a great resemblance to yttrium hydroxide. Therefore the precipitates along this line can only

be solid solutions. Lines joining any points along the curve BC (Fig. 1) meet at a common point x, which corresponds to a definite hydrated basic nitrate of yttrium possessing the formula $3Y_2O_3 \cdot 4N_2O_5 \cdot 20H_2O$.

Fig. 2.

The basic nitrate consisted entirely of small crystals, which were rapidly decomposed by water. The compound, however, was not affected by continued washing with absolute alcohol, and, since the normal nitrate is very soluble in this liquid, it could be entirely separated from the basic nitrate. The solids from several bottles along the curve BC were filtered upon a Hirsch funnel, washed with absolute alcohol, air-dried, and analyzed. The results obtained were as follows:

Calculated	Y_2O_3	46.10	N_2O_5	29.40	H_2O	24.50
Found (bottle 10)	Y_2O_3	46.09	N_2O_5	29.55	H_2O (diff.)	24.36
Found (bottle 11)	Y_2O_3	45.96	N_2O_5	29.67	H_2O (diff.)	24.37
Found (bottle 13)	Y_2O_3	45.82	N_2O_5	29.67	H_2O (diff.)	24.51

The basic compound from still another bottle was dissolved in yttrium nitrate solution, and recrystallized after filtering. The mother liquor was separated by suction, the crystals washed with absolute alcohol, and air-dried. The analytical results obtained agreed well with the above as may be seen:

Y_2O_3	45.82	N_2O_5	29.67	H_2O	24.51
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For this compound the authors offer the following complex formula:

From the foregoing work the following conclusions are drawn:

First, that the basic compound mentioned by Bahr and Bunsen does not exist. Their results were undoubtedly due to adherent normal nitrate.

Secondly, the only basic nitrate that does exist at 25° is the one corresponding to the formula $3\text{Y}_2\text{O}_3 \cdot 4\text{N}_2\text{O}_5 \cdot 20\text{H}_2\text{O}$.

Thirdly, this compound is stable in air and can exist in contact with water containing more than 33 grams of yttrium nitrate to 100 grams of water.

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THE RATE OF EXTRACTION OF PLANT FOOD CONSTITUENTS FROM THE PHOSPHATES OF CALCIUM AND FROM A LOAM SOIL.

BY JAMES M. BELL.

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In a recent paper¹ entitled "Ein Beitrag zur Düngemittel und Boden-analyse," E. A. Mitscherlich, R. Kunze, K. Celichowski, and E. Merres, have investigated the rate of solution of two phosphates of calcium and the rate of extraction of lime from a loam soil, by water saturated with carbon dioxide. The conclusion was reached that the usual equation expressing the rate of solution does not accord with their data. In this equation, *viz.*:

$$dy/dt = k(A - y) \dots \dots \dots (1)$$

which when integrated becomes

$$\log (A - y) = \log A - kt \dots \dots \dots (2)$$

A represents the concentration of the solution when final equilibrium is reached. In applying these equations, however, the authors have mistaken the significance of A; since the value of A used by them was the total quantity of the salt which was originally mixed with the carbonated water, and not that portion of salt which the liquid was capable of dissolving. Only when the quantity of salt added to the water is just sufficient for saturation is the above procedure valid. Since in the experiments, two different original ratios of dicalcium phosphate to water were employed, *viz.*: 1 : 750 and 1 : 1500, at least in one case (and probably in both) a wrong value was assigned to A. In the case of tricalcium phosphate four different ratios of salt to water were employed, *viz.*: 1 : 1500, 1 : 2000, 1 : 3000, and 1 : 6000. So that in three of the four

¹ *Landw. Jahrb.*, 39, 299 (1910).