THE SYSTEM, LIME, NITRIC ACID AND WATER[1]

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Recently mixtures composed of lime and nitric acid have become prominent in ·agriculture as proposed fertilizers. Cultural tests[2] have indicated that these mixtures have probably a great value, and at least the one produced under the patents of Birkeland and Eyde[3] is now assuming considerable commercial importance. Consequently, it has been deemed advisable to determine the solubility curves and corresponding solid phases for the system, lime (CaO), nitric oxide (N_2O_5) and water. The data here presented were obtained at a temperature of 25° C, and refer to that part of the system only in which lime is present in excess of its equivalent of nitric acid. The solutions were all alkaline to phenolphthalein.

The calcium nitrate used, contained some calcium carbonate, though otherwise quite pure. To free from carbonates, a saturated solution of this preparation was boiled, a slight but decided excess of nitric acid having first been added. A series of solutions of varying concentrations was then prepared by the addition of boiled distilled water and to each solution an excess of freshly prepared lime was added in excess. The solutions were kept in 8-ounce sterilizer bottles, tightly stoppered, and constantly rotated in a water-bath which was maintained at 25° C.

From time to time small portions of the solutions were withdrawn and titrated with a standard solution of nitric acid, until successive titrations showed that equilibrium had been reached. Upwards of a month and a half was required to bring the whole series to a constant state.

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[2] See, for example, Bellenoux : Comptes rendus, 140, 1190 (1905); and Schloesing : Ibid., 141, 745 (1905).

[3] Among the many descriptions, which have appeared, that of O. N. Witt, Chemische Industrie, 28, 699 (1905), will be found very complete and satisfactory.

At the end of this period the precipitates in the bottles were allowed to settle and the clear solution drawn off and analyzed for total calcium and calcium in excess of that required for the formation of the normal nitrate with the nitric acid present. As this quantity never exceeded more than four-tenths of 1 percent of the solution and was in most cases less than two-tenths of 1 percent, the experimental difficulties of the analysis are obviously great.

Two methods were possible. First, one might determine the total calcium and the nitric acid and calculate the calcium as calcium hydroxide by difference. It was found that the experimental error in such a proceeding might easily amount to a hundred percent in the final results and so this method had to be given up. The second method was to estimate the calcium present as hydroxide by titrating the solution to the neutral point with a standard nitric acid solution. This second method is open to two objections. No two indicators give quite the same neutral point and for the same indicator no two widely different concentrations of the same solution give strictly comparable titration figures, owing to the hydrolysis which takes place with a salt of this character. If, however, the solutions be titrated at the same dilution and using the same indicator (in this case phenolphthalein), the results are comparable and dependence can be placed upon them as far as breaks in the solubility curve are concerned. The data obtained are given in Table I, and are shown graphically in Fig. 1.

From inspection of the chart it will be seen that there are four distinct curves with three inversion points. As this is a three-component system there can be only one stable solid phase in equilibrium with solutions along each of the branches of the isotherm and the triangular diagram method, or the method of residues may be used to determine the solid phases.[1] Accordingly, the solution was freed as completely as possible from certain precipitates along the different curves and the

[1] Schreinemakers: Zeit. phys. Chem., 11, 81 (1893); Bancroft: Jour. Phys. Chem., 6, 181 (1902).

TABLE I

| Density $\frac{25^\circ}{25^\circ}$	CaO as Ca(OH)$_2$		Ca(NO$_3$)$_2$	
	In 100 cc	In 100 g H$_2$O	In 100 cc	In 100 g H$_2$O
1.0249	0.095	0.096	3.35	3.38
1.0484	0.105	0.109	8.18	8.52
1.0940	0.120	0.125	12.91	13.42
1.1383	0.170	0.181	19.43	20.73
1.1840	0.171	0.187	26.49	28.98
1.2101	0.180	0.198	29.82	32.84
1.2287	0.190	0.212	32.97	36.83
1.2290	0.191	0.213	33.27	37.55
1.2541	0.200	0.224	35.87	40.25
1.2581	0.203	0.230	37.04	41.98
1.2826	0.226	0.260	40.88	47.00
1.2905	0.229	0.263	41.08	47.16
1.3337	0.277	0.332	48.99	58.67
1.3735	0.346	0.429	50.88	69.40
1.4195	0.440	0.545	63.93	83.03
1.4840	0.331	0.449	73.58	99.70
1.5330	0.263	0.371	81.91	115.50
1.5809	0.203	0.303	90.38	135.30
1.5842	0.000	0.000	91.84	139.30
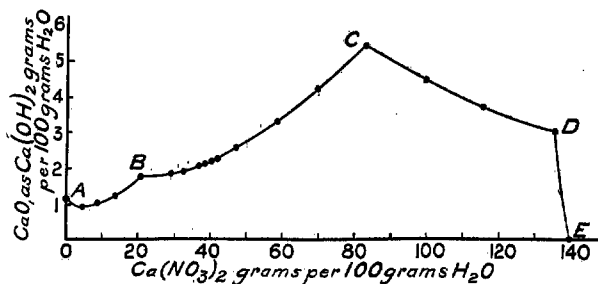
Fig. 1

points obtained by charting the analytical results, Table II, were joined with those of their respective solutions as plotted on the triangular diagram, Fig. 2.

In the analysis of the precipitate with adhering mothei-liquor the total calcium was determined gravimetrically and the free calcium hydroxide was determined by titration with
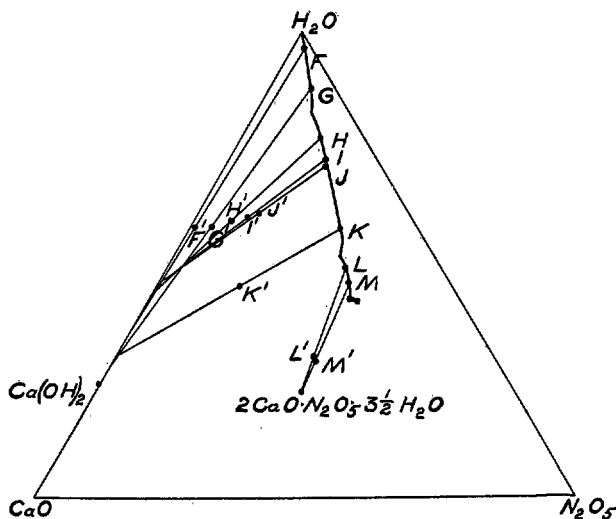
Fig. 2

standard nitric acid. The following table gives the compositions of the solutions and of the corresponding precipitates with adhering mother-liquor.

TABLE II

Point	Solution		Point	Precipitate with adhering solution	
	CaO Percent	N₂O₅ Percent		CaO Percent	N₂O₅ Percent
F	1.21	2.15	F′	40.85	1.00
G	4.16	7.80	G′	37.70	4.09
H	7.77	14.70	H′	33.26	7.20
I	9.34	17.84	I′	29.73	9.87
J	9.83	18.77	J′	27.49	11.60
K	14.21	26.87	K′	38.59	15.71
L	17.20	33.32	L′	31.64	36.36
M	18.50	35.33	M′	31.72	37.21

From the diagram it will be seen that the extension of the lines F F′ and G G′ meet in a point corresponding to solid calcium hydroxide. This substance therefore was the solid phase in contact with the solutions represented by the curve A B.

The following experiment shows conclusively that calcium hydroxide and not a solid solution containing calcium hydroxide, nitric acid and water, is the stable solid phase along this portion of the curve. A mixture was made up containing 20 grams of calcium nitrate to 100 grams water and after shaking a few days with lime the solid was washed several times by decantation and finally by suction, excluding the carbon dioxide of the air. No nitrates were found in the precipitate when treated in this way. If it were the solid solution no amount of washing would completely free it from nitric acid.

It is evident that the lines joining the points representing the composition of the solutions and their corresponding precipitates for the second branch of the curve, when extended, do not meet at a common point. The precipitate is therefore of variable composition and since there can be only one phase present it must be a series of solid solutions containing calcium oxide, nitric oxide, and probably water.

The residues along the third branch of the curve proved to be a substance occurring in long acicular crystals. As scaled off from the diagram its percentage composition is CaO, 39.5; N_2O_5, 38.0; and 22.5 H_2O, corresponding to the compound, $2CaO.N_2O_5.3\frac{1}{2}H_2O$, and is identical with the one described by Werner.[1]

Crystals of this basic nitrate were freed from adhering mother-liquor by pressing between filter-papers. On standing exposed to the air, or more quickly by washing with alcohol, the crystals gradually lost water, but retained their external forms.

It would seem that this more or less completely dehydrated residue corresponds pretty closely to the product of the Birkeland and Eyde process. Owing to the fact that it is absolutely opaque under the microscope it is not possible to say whether it be a definite compound or a mixture, but it is probably the latter. It is obvious that the basic nitrate of calcium is stable at 25° C, only when in contact with an aqueous solution containing between 83 and 135 grams of

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[1] Ann. Chim. Phys., 27, 570 (1892).

calcium nitrate—$Ca(NO_3)_2$—to 100 grams of water, and cannot therefore persist in the dry form.

The solid phase in contact with the solutions along the fourth branch of the curve was undoubtedly the well-known normal nitrate $Ca(NO_3)_2.4H_2O$, and no further attempt was made to determine its composition.

Finally, the data for the "constant solutions" have been brought together in Table III.

TABLE III

Points	Solid phases in contact with solution	Concentration of solutions, grams per 100 grams H_2O	
		CaO as $Ca(OH)_2$	$Ca(NO_3)_2$
A	$Ca(OH)_2$...................	0.118	0.0
B	$Ca(OH)_2$, and solid solution $CaO.xN_2O_5.yH_2O$.............	0.170	20.73
C	Solid solution $CaO.xN_2O_5.yH_2O$ and $CaO.N_2O_5.3\frac{1}{2}H_2O$..........	0.440	83.03
D	$CaO.N_2O_5.3\frac{1}{2}H_2O$ and $Ca(NO_3)_24H_2O$	0.203	135.3
E	$Ca(NO_3)_2.4H_2O$................	0.0	139.30

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