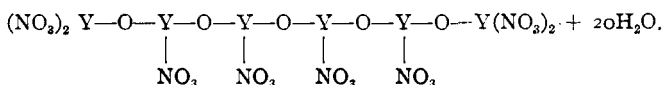


For this compound the authors offer the following complex formula:



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 paper<sup>1</sup> entitled "Ein Beitrag zur Düngemittel und Bodenanalyse," 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

<sup>1</sup> *Landw. Jahrb.*, 39, 299 (1910).

series, and probably also in the fourth, incorrect values were assigned to A.

As the above equations under these conditions failed to accord well with the data, a modified form of equation (2) has been proposed by the above authors,

$$\log (A - y) = \log A - ct^n \dots \dots \dots (3)$$

in which A represents the total quantity of the salt and  $c$  and  $n$  are constants. It seems to me proper, therefore, to recalculate the results, in order to determine whether equations (1) and (2) are really out of accord with the data.

Before discussing the recalculated results, several features of solution phenomena should be recalled. It is obvious that the rate of solution of any substance depends upon its exposed surface. Where the substance is in grains of widely different sizes, it is not possible to deduce any *rational* equation representing the rate of solution of such an aggregation of particles. And further, if any *empirical* equation is found to conform with the data for material in one mechanical condition, that equation will not, in general, describe the rate of solution of material which is chemically the same but mechanically different. Consequently experiments on rate of solution have usually been carried out with large crystals of low solubility, the surface changing but slightly during the course of the experiment. It is apparent also that an aggregation of crystals of uniform size and of low solubility may be considered as of constant surface during the solution.

In the experiments of Mitscherlich, Kunze, Celichowski, and Merres powdered material was probably used, but no statement is made as to its mechanical condition. The data indicate that the surface exposed must have altered considerably, for in the experiments with dicalcium phosphate over half of the phosphoric anhydride was extracted, and in the experiments with tricalcium phosphate, at least 45 per cent. of the phosphoric anhydride was extracted. Consequently, even if the proper value of A (the total quantity of phosphoric anhydride in solution at equilibrium) had been used in the calculations, the usual equation for rate of solution might have failed because of the great changes in the extent of surface.

In the tables the first figures give the concentration of the solution one hour after the salt and water were mixed. In my recalculated results, this has been taken as the starting point of the reaction, for the following reasons: In every case more phosphoric anhydride passed into solution within the first hour (within which no determinations were made) than in the remaining time of the reaction (23-47 hours). Thus, calculated on the basis of 45.55 per cent. phosphoric anhydride in dicalcium phosphate, in one case the increase was from 20.16 per cent. after 1 hour to

only 23.03 per cent. after 47 hours more, and in the other case the variation was between 35.09 per cent. and 39.67 per cent. Similarly for tricalcium phosphate with 43.22 per cent. phosphoric anhydride, the increases for four experiments were as follows: From 14.92 per cent. after 1 hour to 19.83 per cent. after 47 hours more; from 17.24 per cent. after 1 hour to 24.69 per cent. after 24 hours; from 20.99 per cent. after 1 hour to 34.55 per cent. after 48 hours; and from 21.46 per cent. after 1 hour to 42.14 per cent. after 24 hours. Thus, for most of the cases, the solution has been very close to equilibrium, and the extent of surface has probably changed but little. For the last two cases given (Tables V and VI) however, the changes in surface have been considerable. In the recalculated results this surface factor has been assumed constant, a legitimate assumption in all but two cases (Tables V and VI). Even in these two cases, in spite of this objection to the application of the usual equation, it will be seen that the equation describes the facts at least as well as the empirical equation proposed by the above authors.

TABLE I.—RATE OF SOLUTION OF DICALCIUM PHOSPHATE IN WATER SATURATED WITH CO<sub>2</sub>. RATIO OF SALT TO WATER, 1 : 750. TEMP. 30° C.

Original.			Recalculated.			
<i>t</i> .	<i>y</i> found.	<i>y</i> calc. from eqn. (4).	$T = t - 1.$	$Y = y - 20.16.$	<i>Y</i> calc. from eqn. (5).	<i>y</i> calc. = $Y + 20.16.$
1	20.16	20.05	0	0	0	20.16
2	20.80	20.56	1	0.64	0.23	20.39
4	21.15	21.10	3	0.99	0.64	20.80
8	21.42	21.63	7	1.26	1.29	21.45
12	21.53	21.94	11	1.37	1.76	21.92
24	22.78	22.47	23	2.62	2.53	22.69
48	23.03	23.02	47	2.87	2.93	23.09

$$\log (45.55 - y) = 1.6585 - 0.252 \sqrt{t} \dots \dots \dots (4)$$

$$\log (3.00 - Y) = \log 3.00 - 0.035 T \dots \dots \dots (5)$$

TABLE II.—RATE OF SOLUTION OF DICALCIUM PHOSPHATE IN WATER SATURATED WITH CO<sub>2</sub>. RATIO OF SALT TO WATER, 1 : 1500. TEMP. 30° C.

Original.			Recalculated.			
<i>t</i> .	<i>y</i> found.	<i>y</i> calc. from eqn. (6).	$T = t - 1.$	$Y = y - 35.09.$	<i>Y</i> calc. from eqn. (7).	<i>y</i> calc. = $Y + 35.09.$
1	35.09	35.00	0	0	0	35.09
2	35.82	36.05	1	0.73	0.68	35.77
4	37.09	37.06	3	2.00	1.76	36.85
8	38.29	38.02	7	3.20	3.11	38.20
12	38.67	38.56	11	3.58	3.82	38.91
24	39.31	39.45	23	4.22	4.49	39.58
48	39.67	40.21	47	4.58	4.60	39.69

$$\log (45.55 - y) = 1.6585 - 0.635 \sqrt{t} \dots \dots \dots (6)$$

$$\log (4.60 - Y) = \log 4.60 - 0.70 T \dots \dots \dots (7)$$

TABLE III.—RATE OF SOLUTION OF TRICALCIUM PHOSPHATE IN WATER SATURATED WITH CO<sub>2</sub>. RATIO OF SALT TO WATER, 1 : 1500. TEMP. 30° C.

<i>t.</i>	Original.		Recalculated.			
	<i>y</i> found.	<i>y</i> calc. from eqn. (8).	<i>T</i> = <i>t</i> - 1.	<i>Y</i> = <i>y</i> - 14.92.	<i>Y</i> calc. from eqn. (9).	<i>y</i> calc. <sub>15</sub> <i>Y</i> + 14.92.
1	14.92	17.29	0	0	0	14.92
2	16.31	17.78	1	1.39	1.03	15.95
4	18.15	18.23	3	3.23	2.49	17.41
8	18.92	18.71	7	4.00	4.00	18.92
12	18.96	18.99	11	4.04	4.60	19.52
18	19.05	19.27	17	4.13	4.90	19.82
24	19.68	19.48	23	4.76	4.97	19.89
48	19.83	19.97	47	4.91	5.00	19.92

$$\log(43.22 - y) = 1.6357 - 0.222\sqrt{t} \dots \dots \dots (8)$$

$$\log(5.00 - Y) = \log 5.00 - 0.100T \dots \dots \dots (9)$$

TABLE IV.—RATE OF SOLUTION OF TRICALCIUM PHOSPHATE IN WATER SATURATED WITH CO<sub>2</sub>. RATIO OF SALT TO WATER, 1 : 2000. TEMP. 30° C.

<i>t.</i>	Original.		Recalculated.			
	<i>y</i> found.	<i>y</i> calc. from eqn. (10).	<i>T</i> = <i>t</i> - 1.	<i>Y</i> = <i>y</i> - 17.24.	<i>Y</i> calc. from eqn. (11).	<i>y</i> calc. <sub>15</sub> <i>Y</i> + 17.24.
1	17.24	21.51	0	0	0	17.24
2	20.19	22.20	1	2.95	2.19	19.43
4	20.75	22.92	3	5.51	4.84	22.08
8	23.68	23.59	7	6.44	6.83	24.07
12	23.90	24.04	11	6.66	7.33	24.57
24	24.69	24.77	23	7.45	7.50	24.74

$$\log(43.22 - y) = 1.6357 - 0.299\sqrt{t} \dots \dots \dots (10)$$

$$\log(7.50 - Y) = \log 7.50 - 0.150T \dots \dots \dots (11)$$

TABLE V.—RATE OF SOLUTION OF TRICALCIUM PHOSPHATE IN WATER SATURATED WITH CO<sub>2</sub>. RATIO OF SALT TO WATER, 1 : 3000. TEMP. 30° C.

<i>t.</i>	Original.		Recalculated.			
	<i>y</i> found.	<i>y</i> calc. from eqn. (12).	<i>T</i> = <i>t</i> - 1.	<i>Y</i> = <i>y</i> - 20.99.	<i>Y</i> calc. from eqn. (13).	<i>y</i> calc. <sub>15</sub> <i>Y</i> + 20.99.
1	20.99	24.78	0	0	0	20.99
2	24.35	26.60	1	3.36	3.19	24.18
4	28.55	28.44	3	7.56	5.60	26.59
8	30.66	30.28	7	9.67	9.67	30.56
12	31.30	31.34	11	10.31	11.46	32.45
24	33.71	33.06	23	12.72	13.01	34.00
48	34.15	34.70	47	13.16	13.20	34.19

$$\log(43.22 - y) = 1.6357 - 0.370\sqrt{t} \dots \dots \dots (12)$$

$$\log(13.20 - Y) = \log 13.20 - 0.080T \dots \dots \dots (13)$$

TABLE VI.—RATE OF SOLUTION OF TRICALCIUM PHOSPHATE IN WATER SATURATED WITH CO<sub>2</sub>. RATIO OF SALT TO WATER, 1 : 6000. TEMP. 30° C.

Original.			Recalculated.			
<i>t</i> .	<i>y</i> found.	<i>y</i> calc. from eqn. (14).	<i>T</i> = <i>t</i> - 1.	<i>Y</i> = <i>y</i> - 21.48.	<i>Y</i> calc. from eqn. (15).	<i>y</i> calc. = <i>Y</i> + 21.48.
1	21.48	28.31	0	0	0	21.48
2	30.30	32.59	1	8.82	6.40	27.88
4	36.71	36.44	3	15.23	13.85	35.33
8	39.67	39.48	7	18.19	19.13	40.61
12	40.88	40.77	11	19.40	20.34	41.82
24	42.14	42.22	23	20.66	20.70	42.18

$$\log (43.22 - y) = 1.6357 - 0.462 \sqrt{t^2} \dots \dots \dots (14)$$

$$\log (20.70 - Y) = \log 20.70 - 0.160T \dots \dots \dots (15)$$

TABLE XXI.—RATE OF SOLUTION OF LIME FROM A LOAM SOIL BY WATER SATURATED WITH CO<sub>2</sub>. RATIO OF SOIL TO WATER, 1 : 10. TEMP. 30° C.

Original.			Recalculated.			
<i>t</i> .	<i>y</i> found.	<i>y</i> calc. from eqn. (16).	<i>T</i> = <i>t</i> - 2.	<i>Y</i> = <i>y</i> - 0.1087.	<i>Y</i> calc. from eqn. (17).	<i>y</i> calc. = <i>Y</i> + 0.1087.
2	0.1087	0.1069	0	0	0	0.1087
4	0.1199	0.1232	2	0.0112	0.0107	0.1194
8	0.1342	0.1378	6	0.0257	0.0264	0.1351
11.5	0.1461	0.1450	9.5	0.0374	0.0360	0.1447
16	0.1520	0.1511	14	0.0433	0.0436	0.1523
24	0.1572	0.1578	22	0.0485	0.0512	0.1599
32	0.1631	0.1620	30	0.0544	0.0544	0.1631

$$\log (0.18 - y) = (0.2553 - 1) - 0.315 \sqrt{t^3} \dots \dots \dots (16)$$

$$\log (0.057 - Y) = \log 0.057 - 0.045T \dots \dots \dots (17)$$

From the above tables it is evident that the results calculated by the usual velocity equation are in as good accord with the observed values, as are the results calculated by the empirical equation (3) proposed by the above authors.

Finally it should be observed that A, which is the maximum quantity of phosphoric anhydride which the liquid can extract, is not identical in Tables I and II, or in Tables III to VI. If the phenomenon being measured were one of solution only, this would of course, be a legitimate objection to these calculations. But it has been shown that when water acts on dicalcium phosphate or tricalcium phosphate a decomposition results, the solution having a higher ratio, P<sub>2</sub>O<sub>5</sub>:CaO, than the remaining solid.<sup>1</sup> The same sort of hydrolysis undoubtedly takes place when carbonated water is used as a solvent. With a hydrolysis whose extent depends on the original ratio of salt to water, the quantity of phosphoric anhydride in solution at equilibrium depends on the quantity of salt originally employed, and hence A will vary with the conditions of the experiments.

<sup>1</sup> Cameron and Bell, *Bull.* 41, Bureau of Soils, U. S. Dept. Agr.

In this paper it has been shown that notwithstanding the conditions militating against the use of the ordinary equation for rate of solution, *viz.*: the variable extent of surface and the fact that the phenomenon observed is not one of solution only but also of hydrolysis, this equation describes the data at least as well as the empirical equation proposed by Mitscherlich, Kunze, Celichowski, and Merres.

The usual equation for rate of solution also describes very well the extraction of lime from a loam soil by carbonated water.

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### NOTES.

*Red Lines for a Balance Scale.*—Having occasion recently to purchase a balance, it occurred to me that, as color contrast is an aid to vision, it might be of assistance in reading the variations of the needle on a balance scale, and I therefore instructed the makers to equip the balance with an ivory scale having *red* lines, instead of the usual black ones.

This was done, and the result has justified my anticipations. The contrast between the black needle and the red lines on a white background is restful and pleasing to the eyes, and enables a close weighing with less eye-strain than with the black lines.

No extra expense was incurred in making the change from black lines to red, and I would recommend such innovation to those contemplating the purchase of a balance.

C. M. CLARK.

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*Rack for Holding Reagents in Bulk.*<sup>1</sup>—The bottle rack that we designed for our building to store the common stock solutions in five-gallon quantities is a framework of two-inch square material. Each row holds thirteen bottles, which are held apart, both in front and back, by uprights of the same material. For each bottle there is, therefore, a frame compartment. The bottles are kept from the wall by a three-inch board, nailed to the floor of each shelf at the rear of the rack. Along the front of each tier runs a board with a "V" shaped cut in the middle of each compartment on the sides of which the bottles rest. This prevents them from rolling. It also allows the bottles to be placed in the rack on their sides, at an angle which gives the maximum room for the solution and uses up the minimum amount of space. A glass siphon runs to the lowest portion of the bottle through a notched cork or rubber stopper, and is closed at the outer end by means of a rubber tube and a pinch clamp. Smaller bottles can thus be neatly and quickly filled without lifting the heavy, cumbersome stock bottles.

The solutions are made concentrated, according to a formula, and then

<sup>1</sup> Published by permission of Dr. Charles Baskerville, Director of the Chemical Laboratory, College of the City of New York.