treated preparation which had been nearly reversibly shortened and re-extended by a heating and cooling cycle.

Throughout all manipulations that have been tried there is no apparent relation between variations in the large period and the diffractions observed at wider angles. This is interpreted to mean that the wide-angle (short) spacings are related to but a portion or portions of the entire matter constituting the macroperiod.

The long spacings of collagen promise to be more directly related to certain of the colloidal properties of this protein than are the short spacings used to study such phenomena in the past. Correlation is excellent between the X-ray information and electron microscope results regarding the large period of collagen.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NEW YORK UNIVERSITY COLLEGE OF MEDICINE]

Anomalous Effects in the Titration of Phosphoric Acid with Calcium Hydroxide

BY ISIDOR GREENWALD

In 1923, Wendt and Clarke[1] reported that the titration of a solution of phosphoric acid with one of calcium hydroxide yielded anomalous results, in that, after a little more than one equivalent of calcium hydroxide had been added, further addition *lowered* the *p*H. After shaking for two hours, this effect was lessened, and after ten days it had disappeared. They advanced the explanation that the increasing acidity upon the addition of calcium hydroxide was due to the fact that the precipitate of calcium monohydrogen phosphate first formed was changed into tri-calcium phosphate and that the amount of acid thus set free was greater than was required to neutralize the hydroxide added. Similar results were also obtained by Holt, La Mer and Chown[2] and by Farnell.[3] Holt, La Mer and Chown analyzed the precipitates obtained in one series of experiments, in which this anomalous effect had practically disappeared after ten days of continuous shaking at 38°. The ratio of calcium to phosphorus, by weight, was close to 1.94, that calculated for tricalcium phosphate. They believed these analyses confirmed the hypothesis of Wendt and Clarke. While they mentioned another series of experiments in which "a slight irregularity remained" after shaking intermittently for six months and then continuously for two months, they made no attempt to explain why this irregularity should persist for so long a time.

It should be quite obvious that, while the hypothesis of Wendt and Clarke might explain the increase in acidity during the titration, it cannot explain the subsequent *diminished* acidity in the same mixtures after six hours or ten days.

The clue to a satisfactory explanation is given by those results of Holt, La Mer and Chown, in which the anomaly persisted for eight months. In the first five columns of Table I, there are presented the pertinent data taken from the paper by Holt, La Mer and Chown. The values in the following columns are calculated from these.

TABLE I

TITRATION OF PHOSPHORIC ACID WITH CALCIUM HYDROXIDE

Data of Holt, La Mer and Chown[2] (pp. 537 and 550)

	Initial	Final			Precipitated			
Number	$\frac{[Ca^{++}]}{10^3}$	$\frac{[Ca^{++}]}{10^3}$	$\frac{[P]}{10^3}$	*p*H	$\frac{[Ca]}{10^3}$	$\frac{[P]}{10^3}$	[Ca]/[P]	[Ca]/[P]
M_4	5.89	5.30	10.65	5.06	0.59	0.15	4	0.44
M_5	6.64	5.00	10.3	5.03	1.64	0.5	3.3	1.14
M_6	7.34	4.55	10.3	4.94	2.79	0.5	5.6	2.29
M_7	8.10	4.15	8.39	4.86	3.95	2.41	1.64	1.54
M_8	8.80	4.00	7.74	4.84	4.80	3.06	1.57	1.74
M_9	9.56	3.50	6.97	4.87	6.06	3.83	1.58	2.23

It will be noted that, with the exception of M_6, the value for [Ca]/[P] in the precipitate fell regularly with the addition of $Ca(OH)_2$. This exceptional value is not determined very accurately, being derived from small differences between rather large numbers. However, it can scarcely be less than 4, unless the value for either $[Ca^{++}]$ or [P] in the liquid be in error. Examination of the fourth column indicates that this is probably the case. This is the one instance in which the addition of calcium hydroxide did not lower [P].

We believe that the failure of these particular mixtures to attain equilibrium even after six months was due to the fact that the precipitate contained no crystals having the apatite structure, but consisted entirely of $CaHPO_4$ and $Ca(OH)_2$; or of $CaHPO_4$ and some compound having Ca:P > 1.5. In the last column of the table, we have calculated the amount of precipitated $Ca(OH)_2$, upon the assumption that all the precipitated P was present as $CaHPO_4$. With the exception of M_6, the *amount* of such precipitated $Ca(OH)_2$ increases regularly, although the ratio, Ca:P, diminishes.

That precipitates of tri-calcium phosphate are apt to contain an excess of calcium hydroxide is well known, but it has been observed previously only at a *p*H above 6 or 7. Even with a large excess of calcium hydroxide, the highest Ca:P

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[1] G. A. Wendt and A. H. Clarke, THIS JOURNAL, 45, 881 (1923).

[2] L. E. Holt, V. K. La Mer and H. B. Chown, *J. Biol. Chem.*, 64, 509 (1925).

[3] R. G. W. Farnell, *J. Soc. Chem. Ind.*, *Trans.*, 45, 343 (1926).

that has yet been reported is 2.25, by Jolibois and Maze-Sencier.[4]

Because the figures in the eighth column of Table I seem to indicate the formation of precipitate with a higher ratio of Ca:P, an attempt was made to prepare precipitates having such high ratios. It seemed that this might best be accomplished by the addition of a phosphoric acid solution to a solution of calcium hydroxide (Table II). After thorough mixing in centrifuge tubes and standing for the times indicated, the tubes were centrifuged and the clear liquid was titrated with standard acid, using methyl red as indicator, and was also tested for the presence of phosphate by the method of Fiske and Subbarow.[5] None, or at most, inconsiderable traces of phosphorus were found. In a number of the mixtures, the analyses of which are not given, the precipitates could not be separated by centrifuging. This peptizing action of calcium hydroxide solution upon precipitates of calcium phosphate had previously been reported by Jolibois and Maze-Sencier.[4]

One such peptized mixture was prepared on a larger scale and was filtered through a dense paper, with almost complete exclusion of air. The first third was discarded. The filtrate subsequently obtained was crystal clear and contained no phosphate. The results of the analyses are given at the foot of Table II.

TABLE II

COMPOSITION OF PRECIPITATES OBTAINED WITH PHOSPHORIC ACID AND LARGE EXCESS OF CALCIUM HYDROXIDE

Experiment	Time, days	Initial $[Ca^{++}]$ 10^3	Initial $[P]$ 10^3	Final $[Ca^{++}]$ 10^3	Precipitate $[Ca]/[P]$
1	5	21.05	0.973	18.34	2.79
2	5	19.29	1.78	15.28	2.25
3	5	17.81	2.47	12.51	2.25
13	4	15.43	0.89	13.16	2.45
21	1	20.27	0.971	17.80	2.54
22	1	22.12	2.12	16.80	2.51

The ratios in this table are reasonably constant and are not appreciably greater than those reported by Jolibois and Maze-Sencier.[4] The higher ratios in Table I are probably erroneous. The first two deviations may very well be due to the small differences employed in the calculations: that in the third is almost certainly due to some gross error.

We may now picture the course of events as follows: after the first equivalent of calcium hydroxide has been added, the solution contains Ca^{++}, $H_2PO_4^-$ and $HPO_4^=$ ions. It also contains some undissociated $CaHPO_4$.[6] This may act as an acid and upon addition of $Ca(OH)_2$ give a precipitate of $Ca(OH)\cdot CaPO_4$, possibly occluding or adsorbing a little $Ca(OH)_2$ as well. Removal of $CaHPO_4$, lowers the value of $[H_2PO_4^=]$, of $[HPO_4^=]/[HPO_4^-]$, and, consequently, of *p*H. Upon standing, *if a crystal of $Ca_3(PO_4)_2$* or related compound is present, the precipitate will gradually change to approximate this composition, and the solution will, accordingly, become more alkaline. If no such crystal is present, the metastable condition may persist indefinitely, as appears to have been the case in series M of the experiments of Holt, La Mer and Chown.

Summary

It is believed that the anomalous results obtained by others in the titration of phosphoric acid with calcium hydroxide can be explained by the formation of a precipitate having Ca:P = 2 or more, with a subsequent slow change to the usual 1.5.

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(4) P. Jolibois and J. Maze-Sencier, *Compt. rend.*, **181**, 36 (1925).

(5) C. H. Fiske and Y. Subbarow, *J. Biol. Chem.*, **66**, 375 (1925).

(6) I. Greenwald, J. Redish and A. Kibrick, *J. Biol. Chem.*, **135**, 65 (1940).

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[CONTRIBUTION FROM THE CENTRAL EXPERIMENT STATION, BUREAU OF MINES, PITTSBURGH, PA.]

Pressure Dependence of the Rate of Gasification of Carbon[1]

BY B. R. WARNER[2]

In a previous publication[3] a mechanism of the steam-carbon reaction was postulated in which the rate of gasification was stated to be a function of an adsorption isotherm with a saturation pressure. This postulate was based on existing data[4] obtained in a system which was at a constant pressure and wherein the partial pressure of steam was varied by the change in the fraction of steam decomposed on altering the velocity of the steam passing through the carbon bed. It was found that the rate of gasification approached constancy with increase in the partial pressure of the steam. In these cases, however, the gaseous atmosphere surrounding the carbon is not pure steam but an admixture of steam and the reaction products, hydrogen, carbon monoxide, and carbon dioxide, any of which can be adsorbed in competition with the steam. A more rigorous proof can be obtained by changing the absolute pressure of the

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(2) Associate physical chemist, Central Experiment Station, Bureau of Mines, Pittsburgh, Pa. Present address: Gulf Research and Development, Harmarville, Pa.

(3) Warner, THIS JOURNAL, **65**, 1447 (1943).

(4) Brewer and Reyerson, *Ind. Eng. Chem.*, **26**, 734 (1934).