THE ALKALINITY OF MAGMA MAGNESIÆ AS DETERMINED BY THE HYDROGEN ELECTRODE. II.*

BY R. B. SMITH AND P. M. GIESY.

In a previous investigation[1] the authors reported on determinations of the p_H of pure Magma Magnesiæ, concluding that its p_H was 10.51. But in one experiment milk of p_H 13.31 was washed free from alkali, when the p_H, instead of remaining constant at 10.51, continued to fall to 10.20. Since this was rather unsatisfactory, we have continued this work, determining the p_H of samples of Magma Magnesiæ washed free from excesses of magnesium sulphate and sodium hydroxide. The results corroborate our earlier conclusions; they show that the p_H of pure Magma Magnesiæ lies between 10.51 and 10.54. Distilled water was used in all washings recorded in this work.

SAMPLE NO. 3.

Original milk	p_H = 10.33
After four washings, boiling, and cooling	p_H = 10.37
After four more washings, boiling, and cooling	p_H = 10.51

SAMPLE NO. 4.

This was prepared by adding slowly, with constant stirring, 56 Gm. of 45% NaOH solution to 100 Gm. of $MgSO_4.7H_2O$ in 500 cc. of water. Its original p_H was 9.48.

After three washings	p_H = 10.20
After two more washings	p_H = 10.41
After two more washings	p_H = 10.47
After two more washings	p_H = 10.57
After two more washings	p_H = 10.57
After two more washings	p_H = 10.50

It is probable that the p_H over the period of the last six washings was constant and that the above variations were due to temperature effects.

SAMPLE NO. 5.

This was prepared by adding a solution of 100 Gm. of $MgSO_4.7H_2O$ in 200 cc. of water slowly, with constant stirring, to 45 Gm. of sodium hydroxide in 355 cc. of water. Original p_H = 13.24.

After four washings	p_H = 11.10
After three more washings	p_H = 10.56
After two more washings	p_H = 10.65
After two more washings	p_H = 10.53
After two more washings	p_H = 10.53 (T = 25.3° C.)

SAMPLE NO. 7.

This sample was prepared as follows:

125 Gm. $MgCO_3$ in 500 cc. H_2O.

85.5 Gm. NaOH in 405 cc. H_2O.

The amount of NaOH used was calculated to give a slight excess to insure the decomposition of all of the $MgCO_3$. The NaOH was added slowly with stirring to the suspension of $MgCO_3$ and after the NaOH had been added the whole was stirred mechanically for $1^1/_2$ hours.

* Scientific Section, A. Ph. A., Buffalo meeting, 1924.

[1] J. A. PH. A., 12, 955 (Nov., 1923).

This material was diluted to 4 liters and allowed to settle over Sunday. It was then drained down to about 2 liters and transferred to a 4-gallon cylinder and 2 gallons of water added. It was washed in this cylinder, using 2 gallons of water per washing, until it passed the U. S. P. test for free alkali. It was again transferred to a 4-liter beaker and after it had settled sufficiently to a 2-liter cylinder, where it was allowed to settle for six days. It was then drained off and bottled and then had a volume of 1300 cc.

This had a p_H of 10.58 at 22.4° C. It therefore contained only an extremely slight amount of alkali, about 0.00004 N. Nevertheless, a U. S. P. test for free alkali required nine drops of $N/10$ acid instead of five, the upper limit. This shows the unreliability of the U. S. P. test, and the much greater delicacy of the electrometric p_H determination.

THE ALKALINITY OF MAGMA MAGNESIÆ. III. THE EFFECT OF MAGNESIUM CARBONATE.

BY R. B. SMITH AND P. M. GIESY.

In previous investigations by the same authors[1] the p_H of pure milk of magnesia was determined. Samples were prepared by mixing solutions of $MgSO_4$ and NaOH in such proportions that in some samples there was an excess of $MgSO_4$ and in the others an excess of NaOH. The p_H of the pure milk was determined by washing these samples with distilled water to constant p_H.

It was determined as a result of these experiments that the p_H of pure milk of magnesia was 10.52. During the course of this work several samples washed from high p_H values did not come to the p_H which we had reason to believe was that of pure Magma Magnesiæ; their p_H values continued to fall off, so that values as low as 10.03 were obtained. We were unable to explain this at the time.

A later investigation was made on the washing of milk of magnesia in which p_H and soluble matter determinations were made to follow the washing. During the washing of several samples which had had an initial p_H of above 10.52, it was noticed that the p_H continued to drop even after a p_H of 10.52 was attained, while the soluble matter shortly became constant.

A consideration of the solubilities of $MgCO_3$ and $Mg(OH)_2$ which are given by Seidell, "Solubilities of Inorganic and Organic Compounds," Second Edition, as $MgCO_3$ = 0.18 Gm. per liter, solution in equilibrium with air at 20° C.; $Mg(OH)_2$ = 0.009 Gm. per liter, gave us the idea that the p_H of a $Mg(OH)_2$ suspension might be considerably affected by the presence of $MgCO_3$. This $MgCO_3$ could be introduced into the solution by the carbonate impurities of the NaOH used for precipitation, by CO_2 in the distilled water, or by absorption of CO_2 from the air by the alkaline solutions as they were being washed. Since magnesium carbonate is relatively insoluble, its removal by washing would be a slow process and a saturated solution of it would always be present until all the solid $MgCO_3$ was washed out. This dissolved magnesium carbonate would be expected to depress the solubility and therefore the p_H of the magnesium hydroxide suspension by its mass action effect.

[1] J. A. PH. A., 12, 955 (Nov., 1923).