THE DECOMPOSITION OF PHOSPHATES BY SODIUM BISULPHATE.

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In giving an explanation of the circumstances under which the examination forming the subject of this paper was suggested and undertaken, I intend to show, by way of introduction, how a manufacturer is sometimes embarrassed by accumulations of by-products, which, though of intrinsic value, and capable of technical uses, remain on his hands, and compel him to study the location and the situation in general, in order to dispose of them.

Ten or more years ago the manufacture of strong nitric acid was, in America, a very limited one. I was compelled to manufacture it myself, being largely interested in the production of nitroglycerine. The consequence was, that in the years 1874 to 1878 I had gradually accumulated considerable plant at my works in Ontario, Canada; and with this also a very large amount of "nitre cake," or sodium bisulphate.

There was then no conceivable use for this salt in Canada; it would not admit of any expensive handling or costly transportation, and so it was heaped up, month after month and year after year.

The amount which thus had collected I cannot now even approximately estimate; but an idea may be formed by considering that for several years, during seven or eight months of each year, ten thousand pounds of nitric acid per week, or thirty thousand pounds of mixed acid were made. The resulting sodium bisulphate formed quite a large, hill-like prominence on the shores of the St. Lawrence river.

I had for a year or two been looking in vain for a customer to take it away for nothing. Then it came to my notice that larger quantities of apatite—the Canadian phosphate—were mined in different localities of Ontario and Quebec, and I then made the first trials of the effects of the bisulphate upon the apatite. I supposed at that time, *a priori*, that one half of the acid would certainly act upon the mineral, and the first experiment verified this opinion. However, any practical result which might then have been reached was counteracted by other circumstances, among which were equally large accumulations of sulphuric acid and certain commercial relations, which there and then decided against the carrying out of any project for the practical use of the bisulphates in the decomposition of the Canadian phosphates.

As I have already indicated, the working of the process was merely tentative. The bisulphates were taken from the heap, without any examination, and thus used; the mineral phosphate was also taken as found upon the docks, indiscriminately picked up, crushed and mixed with the bisulphate, and melted with it. The molten mass was poured into cold water, the white precipitate of calcium sulphate washed by decantation, and in the solutions the amount of phosphoric acid was determined.

As I had ground several hundred pounds of the phosphates, from which the samples for trial were taken, and as we knew the average amount of phosphoric acid contained in the whole, the mineral, after grinding and mixing, having been analyzed several times, a comparison in each could be exactly made in each trial. Phosphate and bisulphate were, in all cases, intimately mixed together and melted in Battersea crucibles. The result was, that in no single case was more than one per cent. of phosphoric acid left undissolved. Of course, the product in solution was sodium pyrophosphate. The experiments at the works rested at this stage but the matter had interested me so much that I undertook, not long after, the additional investigation in the laboratory.

The apatite came from mines near Perth, in the province of Ontario. Several pounds of it had been finely pulverized, and phosphoric acid determined.

I abstained from deducting anything on account of water or any volatile substance, because I had a number of trials to make; the powder was left in a large beaker, and as it had been well shaken together, it could be safely supposed that samples taken from it had the same amount of phosphoric acid.

Three determinations were made; in each case 1 grm. of the mineral was dissolved in nitric acid; the undissolved residue amounted to:

I. 0.1110. II. 0.1130. III. 0.1110.

The phosphoric acid determinations were all made with molybdate.

I. 0.3338712 phosphoric acid.
II. 0.3334100 " "
III. 0.3338800 " "

which would indicate for the mineral 33.4 per cent. of phosphoric acid.

The nitre cake, or sodium bisulphate, originated from my own works, from the Brockville Chemical Works, and from the Lodi Chemical Works. In this instance I deemed it of importance to determine in each material the amount of water and of free and combined sulphuric acid.

1. *Determination of Water.*—For this purpose a combustion tube of 24 inches length was used, in which were introduced 5 grms. of the bisulphate. The combustion-tube was placed in a trough of sheet copper, filled with paraffine and heated to 120° C. A current of air, dried over calcium chloride, passed over it and through three calcium chloride tubes. The figures obtained in this manner showed considerable differences. I then selected a sample of each of these three different salts, disintegrated it, to facilitate mixing, and thus obtain a uniform sample, and made three water determinations in the manner above indicated.

The results were: In 5 grms.

Brockville Chemical Works: $\left.\begin{array}{l}0.110\\0.112\\0.112\end{array}\right\} = 2.2\%.$

Lodi Chemical Works: $\left.\begin{array}{l}0.175\\0.169\\0.173\end{array}\right\} = 3.5\%.$

My own manufacture: $\left.\begin{array}{l}0.501\\0.500\\0.500\end{array}\right\} = 6\%.$

This great difference may be accounted for by the manner of charging the retorts, and of distilling nitric acid, and also by the storing of the nitre cake; the last, for instance, was mostly exposed to wind and rain. To ascertain the amount of free acid, 5 grms. of the three different materials were dissolved and treated volumetrically with normal caustic soda solution, with the following results:

$$\text{Brockville Chemical Works: } \left.\begin{array}{l}0.020\\0.020\\0.021\end{array}\right\} = 0.4\%.$$

$$\text{Lodi Chemical Works: } \left.\begin{array}{l}0.035\\0.032\\0.035\end{array}\right\} = 0.7\%.$$

$$\text{III. My own works. } \left.\begin{array}{l}0.150\\0.150\\0.148\end{array}\right\} = 3\%.$$

In the first series of investigation 1 grm. of phosphate mineral and 1.8 grm of bisulphates were thoroughly mixed and melted in porcelain crucibles, heated until white vapors appeared, and, after cooling, dissolved in water. The solution was filtered from the residue, which was invariably white and mostly calcium sulphate; then brought to 100 c.c. and of this 20 c.c. were used in each case for determination of phosphoric acid.

This course was followed with all of the samples of nitre cake on hand.

The results with the three different bisulphates were:

$$\text{I.—}\left.\begin{array}{l}0.064\\0.069\\0.065\end{array}\right\} \text{Loss : 0,0007.}$$

$$\text{II.—}\left.\begin{array}{l}0.065\\0.063\\0.067\end{array}\right\} \text{Loss : 0.0017.}$$

$$\text{III.—}\left.\begin{array}{l}0.064\\0.067\\0.067\end{array}\right\} \text{Loss : 0.0007.}$$

In regard to conversion of diphosphate into triphosphate, I found it necessary to leave the liquid containing sodium pyrophosphate for at least three days with nitric acid in excess, before the molybdate determination could be successfully employed. Considering the results, I cannot account for the discrepancy between I. and II.; that between I. and III. might possibly be found in the greater amount of free acid in bisulphate III., and in the consequent easier decomposition of the mineral.

The idea suggested itself to obtain an idea of the temperature by which these decompositions commenced and could be carried out.

Several trials were made with boiling solutions of bisulphates and the same mineral; also mixtures of bisulphate and mineral were melted together in a paraffine bath, where the temperature could then easily be ascertained.

In all cases considerable quantities of phosphoric acid were found in solution, and when long enough heated, always very nearly the amount contained in the minerals.

It is certain that such phosphates will be decomposed—that is, the total amount of phosphoric acid will be found in solution as sodium phosphate, when boiling solutions of the bisulphates are used; and I have reason to believe that under pressure, and consequently at a higher temperature, this could be done in a comparatively short time.

In a very similar way all phosphoric acid contained in slags from the Bessemer or Thomas processes can be brought into solution as sodium phosphate; my investigation of this has not been finished, as the material was exhausted, and as I found it somewhat difficult to obtain slags of the desired kind in this country.

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(To be continued.)