

results may be summarized in the rough generalization that "precipitated phosphates soluble in acetic acid are transposed, more or less readily, by a solution of silver nitrate into silver phosphate and the corresponding nitrate, while those insoluble in acetic acid are not so transposed." Thus, the phosphates of the alkaline earths, magnesium, zinc, manganese, nickel, cobalt, copper and cadmium, are transposed, but those of iron, aluminum, lead and bismuth are not.

Quantitative examination of the action of silver nitrate on precipitated phosphates was limited to that of calcium, as this is the only phosphate that has any commercial value. It was found that precipitated calcium phosphate is quantitatively transposed into silver phosphate and calcium nitrate when it is shaken up for a few minutes with at least twice the theoretical amount of 0.1 *N* silver nitrate required. The procedure is the same as given under soluble phosphates. In case of the tri-basic phosphate, no zinc oxide is required, as there will be no acid formed. The commercial phosphate is usually a mixture of the di- and tribasic, and some acid will be formed when silver nitrate is added to it and consequently zinc oxide will have to be added. Below are given some results obtained by this method with two samples of calcium phosphate. Both contained chloride, which was determined and corrected for. The figures given in the first column were obtained gravimetrically.

	Per cent. $P_2O_5$ present.	Per cent. $P_2O_5$ found.	Error found.
1.....	47.20	47.12	-0.08
2.....	47.20	49.07	-0.11
3.....	48.52	48.36	-0.16
4.....	48.52	48.34	-0.18

The fact that the results obtained by this method are slightly lower than the gravimetric is probably due to the presence of a little iron in the phosphate.

The operation by the described method should not be performed in direct strong sunlight, as the yellow silver phosphate is liable to blacken somewhat and thus give rise to doubts as to the correctness of the procedure.

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## THE OXIDATION OF FERROUS SALTS.

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In the course of an examination of commercial oxygen, it was observed with surprise that a slightly acid solution of ferrous ammonium sulfate (Mohr's salt) was not appreciably oxidized by bubbling oxygen through it for three hours. Subsequent tests with variations were made and this communication records our findings.

1. In the following instances, there was observed no oxidation of 5 g. Mohr's salt, as shown by titration with 0.5 *N*  $\text{KMnO}_4$ :

- (a) The salt exposed to air for one week.
- (b) Stream of oxygen for 3 hours through a solution acidified with sulfuric acid.
- (c) Stream of filtered air for 3 hours through a solution acidified with sulfuric acid.<sup>1</sup> The same was observed with unfiltered air.<sup>2</sup>
- (d) Stream of air for 3 hours through a neutral solution.

2. These four experiments were repeated, using  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  instead of Mohr's salt, with the same results—no oxidation, thus showing that the presence of ammonium sulfate does not retard or accelerate the oxidation.

3. To determine the effect of the presence of substances which are ordinarily in iron ore, a hematite ore was dissolved in hydrochloric acid, precipitated by ammonium hydroxide redissolved in sulfuric acid, reduced by zinc and subjected to the following tests, no oxidation occurring in any instance:

- (a) Without filtration, allowed to stand in an open casserole for 3 hours,<sup>3</sup> all of the zinc having dissolved.
- (b) Filtered and allowed to stand in an open casserole for 3 hours.<sup>1</sup>
- (c) Without filtration, a stream of air passed through for 3 hours.
- (d) Filtered and a stream of air passed through for 3 hours.

4. The presence of other substances which are sometimes in iron ore has no effect upon the oxidation as was observed by passing air for 3 hours through solutions of Mohr's salt acidified with sulfuric acid to which had been added, in amounts corresponding to 0.1 g. of the metal, salts of these metals: Co, Cr, Cu, Mn, Mo, Ni, Ti, V, W.

5. The presence of undissolved substances was next tried. Dust in the air, glass wool, and pumice stone did not accelerate the oxidation, but when platinized asbestos was used, 5 g. of Mohr's salt in 200 cc. water, acidified with sulfuric acid, after a passage of air for 3 hours, showed about 50 per cent. oxidation, and in the absence of air no oxidation whatever.

6. Because the titration with 0.5 *N*  $\text{KMnO}_4$ , as in the experiments above does not detect small amounts of oxidation, standards of  $\text{Fe}(\text{CNS})_3$  were prepared and the solutions tested with potassium thiocyanate. In this way, it was shown that Mohr's salt (Kahlbaum), dissolved in water acidified with sulfuric acid and immediately tested, contains 0.0002 g.  $\pm$   $\text{Fe}^{+++}$  in the presence of 0.7100 g.  $\pm$   $\text{Fe}^{++}$ , and upon passing air through it for 3 hours there is a noticeable oxidation, and after 12 hours there has resulted a formation of 0.0001 g.  $\pm$   $\text{Fe}^{+++}$ . This

<sup>1</sup> No oxidation occurred after a passage of air for 12 hours and standing exposed to the air for 12 hours.

<sup>2</sup> The ventilation system of the building filters the air, but at times it is not entirely efficacious.

<sup>3</sup> After 30 hours, very little, if any, oxidation was observed.

solution, after complete reduction by zinc, is oxidized in the presence of air, but at about the same rate as the original Mohr's salt in acid solution. The point of equilibrium is probably complete oxidation, but the reaction velocity in the absence of catalyzers is very small.

7. Oxidation of  $\text{Fe}^{++}$  readily occurs in alkaline solutions; 50 per cent.  $\pm$  of the iron is oxidized upon passage of air for 3 hours.

8. All of these experiments were performed at room temperature. At a temperature slightly below the boiling point of the solution, upon passage of air for 3 hours, the  $\text{Fe}^{++}$  from the different sources was oxidized to an extent of about 2 per cent. in the acid solutions and about 5 per cent. in the neutral solutions.

*Conclusion.*—We conclude that  $\text{Fe}^{++}$  in acid and in neutral solutions, at room temperature, is so slowly oxidized, and this oxidation is so slightly affected by such substances as are apt to be present, that expulsion of air during reduction by zinc is unnecessary and the titration may be performed at leisure, in ordinary determinations of iron by titration with potassium permanganate.

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## THE RAPID DETERMINATION OF SILVER AND CADMIUM BY MEANS OF THE GAUZE CATHODE AND STATIONARY ANODE.

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The use of the gauze cathode with stationary anode, which was found to be so efficient in the determination of nickel and cobalt,<sup>1</sup> has been extended to include the metals, silver and cadmium. The range of electrolytes from which these elements could be deposited on the gauze cathode in an adherent form, when strong currents were used, was found to be much less than in the case of the metals referred to.

Several of the electrolytes, which are applicable in case of the slow electrolytic methods, did not give good deposits on the gauze cathode with high currents, but the deposits obtained for each metal with potassium cyanide as an electrolyte were entirely satisfactory.

The electrodes used in these experiments were the same as those already described in the work on nickel and cobalt.<sup>2</sup>

*Silver.*—The first determinations of silver, using the gauze cathode, were made by Stoddard<sup>3</sup> with satisfactory results. The same experiments were repeated by Price and Humphreys.<sup>4</sup> They, however, reported rather unfavorably on the use of this method for the determination of silver,

<sup>1</sup> THIS JOURNAL, 33, 493.

<sup>2</sup> *Loc. cit.*

<sup>3</sup> THIS JOURNAL, 31, 385.

<sup>4</sup> *J. Soc. Chem. Ind.*, 29, 307.