Summary

1. The value of the equilibrium constant $K_4 = P_{H_2O}/P_{H_2}$ for the reaction $FeO + H_2 = Fe + H_2O$ has been determined by a flow method at 600, 700, 800, 900 and 1000° to be 0.332, 0.422, 0.499, 0.594 and 0.669, respectively.

2. The value of the equilibrium constant $K_6 = P_{H_2O}/P_{H_2}$ for the reaction $Fe_3O_4 + H_2 = 3FeO + H_2O$ has been determined by a flow method at 700 and 800° to be 1.18 and 2.37, respectively.

3. Combination of these values with the "best values" of Eastman for the Fe–C–O system gives values for the water gas equilibrium in good agreement with the water gas values determined directly by Neumann and Köhler.

4. The so-called "surface effect" is presented as a probable reason for the discrepancies between the water gas values as obtained indirectly by other workers and the directly determined values.

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[CONTRIBUTION FROM THE UNIVERSITY OF NORTH CAROLINA]

A STUDY OF THE QUANTITATIVE PRECIPITATION OF CALCIUM OXALATE IN THE PRESENCE OF THE ARSENATE ION

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A study of the quantitative precipitation of calcium oxalate in the presence of the phosphate ion by Dobbins and Mebane[1] showed that the calcium ion could be quantitatively precipitated from a solution containing an excess of phosphate ions. Since the usual method of estimating calcium in calcium arsenate involves the same difficulties met in the phosphate analysis, a similar study was made of the quantitative precipitation of calcium in the presence of the arsenate ion. As the phosphate ion and the arsenate ion are chemically similar, the same method of study was used.

The study was based on the assumption that the so-called tertiary calcium arsenate, which forms on the addition of ammonium hydroxide to the solution, having a much greater solubility product than calcium oxalate would go into solution and thus the calcium oxalate form. Consequently, if the solution be allowed to stand long enough for this metathesis to be complete, it should be possible to precipitate calcium oxalate in the presence of the arsenate ion. In order to determine the most favorable conditions under which to carry out the precipitation, several series of analyses were made to determine the time required for complete

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[1] Dobbins and Mebane, THIS JOURNAL, **52**, 1469 (1930).

transformation of calcium arsenate to calcium oxalate and the effect of temperature and alkalinity of solution at time of precipitation.

After first having found the minimum time necessary for the complete precipitation, determinations were made to determine the difference in results, if any, caused by adding the precipitating agent before and after the solutions were made alkaline with ammonium hydroxide and by varying the alkalinity of solution at time of precipitation. These series were run at 30 and 100°. An excessive amount of ammonium hydroxide, when added first to the solution, appeared to hinder the formation of calcium oxalate. Consequently two series were made using a slight excess of ammonia in one case and 10-cc. excess of concentrated ammonium hydroxide solution in the other, in order to determine the effect of the concentration of ammonium hydroxide on the solution.

Procedure.—A 0.1 *N* solution of calcium chloride was prepared by dissolving a weighed quantity of Iceland spar in hydrochloric acid. Approximately 0.1 *N* solutions of disodium arsenate and potassium permanganate were made. As the precipitating agent, a saturated solution of ammonium oxalate was used.

Twenty cc. of the standard solution was taken for each analysis. To this solution 25 cc. of the disodium arsenate was added to give an excess of arsenate ions, and then an excess of ammonium oxalate. The total volume of solution at this point was 80–100 cc. The precipitates were filtered, washed by decantation with distilled water containing a small amount of ammonium hydroxide and transferred on the filter paper to the precipitation beaker. The precipitates were dissolved in dilute sulfuric acid, the solution was brought almost to boiling temperature, and titrated rapidly with the 0.1 *N* permanganate solution in the usual way. As the precipitate was very finely divided, an inferior grade of filter paper could not be used in this determination. It was found that as accurate results were obtained by titrating the precipitate first formed as by following the usual procedure of dissolving and reprecipitating the calcium oxalate. The losses involved in redissolving the precipitate were as great as the error caused by the adsorption of ammonium oxalate by the precipitate.

TABLE I

EFFECT OF TIME OF STANDING

Twenty cc. of *N*/10 calcium solution used in all cases, made alkaline with ammonia before addition of oxalate

Time, hours	30° *N*/10 $KMnO_4$, cc.	100° *N*/10 $KMnO_4$, cc.
0.25	20.10	20.00
0.5	19.95	20.00
1	20.10	19.95
1.5	20.10	20.00
2	20.10	20.00

TABLE II

EFFECT OF TEMPERATURE, CONCENTRATION OF AMMONIA AND ORDER OF ADDITION OF REAGENTS

Ammonium hydroxide added to the solution before ammonium oxalate. One hour allowed for reaction

30°		100°	
Slight excess NH_4OH $N/10$ $KMnO_4$, cc.	10 cc. excess NH_4OH $N/10$ $KMnO_4$, cc.	Slight excess NH_4OH $N/10$ $KMnO_4$, cc.	10 cc. excess NH_4OH $N/10$ $KMnO_4$, cc.
20.60	21.90	20.00	20.10
20.20	20.30	20.05	20.10
20.20	19.95	20.00	20.15
Twenty-four hours allowed for reaction			
20.00	20.05	20.05	20.00
20.00	19.95	20.00	19.95
20.00	20.00	19.95	20.00
Ammonium hydroxide added to the solution after ammonium oxalate. One hour allowed for reaction			
20.00	20.95	20.00	20.30
20.15	19.85	20.00	20.20
19.80	20.10	20.00	20.35
Twenty-four hours allowed for reaction			
19.95	19.95	19.95	20.00
20.00	19.95	19.95	20.00
20.00	20.00	20.00	20.00

Discussion

The formation of calcium oxalate in the presence of the arsenate ion was not as rapid as in the presence of the phosphate ion. Especially was this true at low temperature. Judging from other reactions of arsenates and phosphates, this was to be expected. Due possibly to adsorption of ammonium oxalate by calcium arsenate, the results of the titration were apt to be high if insufficient time were allowed for complete transformation of the calcium arsenate into calcium oxalate. This was also shown by the fact that good results were obtained in all cases where the precipitates were allowed to stand twenty-four hours before filtration or had been formed in solutions only faintly alkaline with ammonium hydroxide and digested at the boiling temperature for one hour. This heating seemed to destroy the flocculent nature of the previously precipitated calcium arsenate and made filtration very difficult, but good results were obtained by this method. The time of addition of ammonium hydroxide made no material difference in the analysis where the higher temperature was used. A large excess of ammonia gave high results in most of the analyses which were allowed to stand for an hour. This is possibly explained upon the difference in the adsorptive power of calcium arsenate which was formed in high concentrations of ammonium hydroxide and that which was formed in solutions only faintly alkaline. Those precipitates which were allowed to stand over for a twenty-four hour period gave uniformly good results. This was due to the complete transformation of the arsenate into the oxalate during this period of standing.

Recommended Procedure

Accurate results were obtained from the following procedure. The solution was made alkaline with ammonium hydroxide and a few drops excess added. After the addition of an excess of ammonium oxalate to the boiling solution, it was kept at incipient boiling temperature and occasionally stirred for ten minutes. After standing for an hour the precipitate was filtered off, washed with distilled water containing a small amount of ammonium hydroxide, transferred on the paper to the precipitation beaker, dissolved in 30 cc. of dilute sulfuric acid, diluted to 100 cc. and titrated rapidly with a 0.10 *N* potassium permanganate solution.

Summary

1. Calcium oxalate may be precipitated quantitatively in the presence of the arsenate ion.
2. The solution may be made alkaline either before or after the addition of ammonium oxalate, and a small excess of ammonium hydroxide added.
3. The best temperature for precipitation is 90–100°

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THE PHOTOCHEMICAL FORMATION OF CHLORINE DIOXIDE FROM CHLORINE MONOXIDE IN CARBON TETRACHLORIDE SOLUTION

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That chlorine monoxide, Cl_2O, is sensitive toward light has long been recognized. In recent years several quantitative investigations of the photochemistry of this compound have been undertaken. Bowen[1] studied the effect of light in the region 4100–4700 Å. on carbon tetrachloride solutions of chlorine monoxide; apparently on the assumption that the products of the reaction were simply chlorine and oxygen, he found from 0.81 to 1.02 molecules of the monoxide decomposed per quantum absorbed. He later measured[2] the effect of light on gaseous chlorine monoxide and concluded that in the gaseous state apparently two molecules of monoxide were decomposed for each quantum of blue and violet light absorbed.

[1] E. J. Bowen, *J. Chem. Soc.*, **123**, 1199 (1923).

[2] Bowen, *ibid.*, **123**, 2330 (1923).