# CATALYSIS IN VOLUMETRIC ANALYSIS.

## PART VI. IODIMETRIC ESTIMATION OF VANADATE WITH FERROUS SULPHATE AS CATALYST.

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In Part II of this series Gopala Rao and Ramanjaneyulu (1945) have reported an iodimetric method for the estimation of vanadate using oxalic acid as catalyst. We have now found that ferrous sulphate has a marked catalytic effect on the reaction between vanadate and hydriodic acid and that it can be made use of in the iodimetric estimation of vanadate.

### EXPERIMENTAL.

A solution of sodium vanadate was prepared from a pure sample of ammonium vanadate, Merck. The concentration of this solution was determined by the method of Furman. The iodimetric estimations were carried out in an atmosphere of carbon dioxide in the following manner: 20 ml. of the vanadate solution was taken in a narrow cylindrical gas washing bottle, fitted with fused-in glass inlet and outlet tubes, 20 ml. of 0·25 molar potassium iodide solution was then added, followed by the addition of the requisite quantity of the ferrous salt (0·02 molar). A current of carbon dioxide washed with water was passed through briskly for about thirty minutes to ensure the complete elimination of oxygen. A trap containing potassium iodide solution was also attached to the outlet tube. This was intended to catch any iodine carried off by the stream of carbon dioxide in the later part of the experiment. After elimination of dissolved air, the stream of carbon dioxide was somewhat slowed down, the stopper of the reaction vessel was removed

TABLE I.

15 ml. of vanadate solution (0·05008N) + 20 ml. of 0·25 molar potassium iodide + 5 ml. of sulphuric acid (4N) + water to make up the volume to 50 ml.

| Time in minutes. | AMOUNT OF IODINE LIBERATED IN ML. OF HYPO-SOLUTION | |
|---|---|---|
| | Without catalyst. | With 2 c.c. of $FeSO_4$ solution. |
| 5 | 2·95 | 9·90 |
| 10 | 4·90 | 14·70 |
| 15 | 6·85 | 15·05 |
| 20 | 7·85 | 15·05 |
| 30 | 9·50 | 15·15 |
| 40 | 10·95 | 15·25 |
| 60 | 12·80 | 15·25 |

for a while and 5 ml. of sulphuric acid (4N) was run in quickly. The stopper was replaced and a slow current of carbon dioxide passed through for five minutes, then the entrances and exits were all closed airtight. After standing thus for the requisite interval of time, the trap solution was added to the main reaction mixture and the whole quickly titrated with standard sodium thiosulphate solution. The results recorded in Table I show the catalytic action of ferrous sulphate.

Experiments were made with a view to find the optimum concentration of ferrous sulphate that will secure the quantitative liberation of iodine in 15 minutes. The results were recorded in the following table:—

TABLE II.

10 ml. of vanadate + 20 ml. of 0·25 molar potassium iodide + 5 ml. of sulphuric acid (4N) + water to make up the volume to 50 ml.

| Time in minutes. | Amount of iodine liberated in ml. of hypo-solution. | | | | | | |
|---|---|---|---|---|---|---|---|
| | Without catalyst. | Catalyst 0·5 ml. | Catalyst 1·0 ml. | Catalyst 2·0 ml. | Catalyst 3·0 ml. | Catalyst 5·0 ml. | Catalyst 7·0 ml. |
| 5 | 2·05 | 4·04 | 6·70 | 9·30 | 9·25 | 9·20 | 9·05 |
| 10 | 3·50 | 7·35 | 9·60 | 9·65 | 9·60 | 9·50 | 9·40 |
| 15 | 4·65 | 9·35 | 9·65 | 9·65 | 9·60 | 9·50 | 9·50 |
| 20 | 5·60 | 9·65 | 9·65 | 9·70 | 9·70 | 9·60 | 9·60 |
| 30 | 6·80 | 9·75 | 9·70 | 9·70 | 9·70 | 9·75 | 9·70 |
| 40 | 7·70 | 9·75 | 9·70 | 9·75 | 9·75 | 9·75 | 9·75 |
| 60 | 8·75 | 9·70 | 9·70 | 9·70 | 9·75 | 9·75 | 9·75 |

From the results recorded above, it can be easily seen that the amount of iodine liberated in the first five minutes increases with the increase of the amount of the catalyst up to a limit and then remains steady with a further increase in the concentration of the catalyst. The optimum amount of catalyst to be used depends upon the concentration of the vanadate in the solution, as can be seen from the following tables :—

TABLE III.

15 ml. of vanadate (0·05006N) + 20 ml. of 0·25 molar potassium iodide + 5 ml. of sulphuric acid (4N) + water to make up the volume to 50 ml.

| Time in minutes. | Amount of iodine liberated in ml. of hypo-solution. | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | Without catalyst. | Catalyst 0·5 ml. | Catalyst 1·0 ml. | Catalyst 2·0 ml. | Catalyst 3·0 ml. | Catalyst 5·0 ml. | Catalyst 7·0 ml. | Catalyst 10·0 ml. |
| 5 | 2·95 | 5·10 | 7·10 | 9·90 | 12·70 | 14·15 | 14·00 | 13·60 |
| 10 | 4·90 | 8·45 | 11·50 | 14·70 | 14·95 | 14·80 | 14·67 | 14·40 |
| 15 | 6·85 | 11·00 | 14·80 | 15·05 | 14·95 | 14·95 | 14·70 | 14·60 |
| 20 | 7·85 | 12·65 | 15·00 | 15·05 | 15·15 | 15·00 | 14·90 | 14·65 |
| 30 | 9·50 | 15·00 | 15·25 | 15·15 | 15·15 | 15·15 | 15·05 | 14·95 |
| 40 | 10·95 | 15·20 | 15·20 | 15·25 | 15·20 | 15·20 | 15·20 | 15·10 |
| 60 | 12·80 | 15·30 | 15·30 | 15·25 | 15·30 | 15·20 | 15·30 | 15·30 |

TABLE IV.

20 ml. of vanadate (0·05008N) + 20 ml. of 0·25 molar potassium iodide + 5 ml. of sulphuric (4N) + water to make up the volume to 60 ml.

| Time in minutes. | AMOUNT OF IODINE LIBERATED IN ML. OF HYPO-SOLUTION. | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | Without catalyst. | Catalyst 0·5 ml. | Catalyst 1·0 ml. | Catalyst 2·0 ml. | Catalyst 3·0 ml. | Catalyst 5·0 ml. | Catalyst 7·0 ml. | Catalyst 10 ml. |
| 5 | 2·00 | 3·25 | 4·65 | 6·60 | 7·75 | 12·55 | 13·75 | 16·55 |
| 10 | 3·45 | 5·95 | 7·55 | 10·30 | 1·51 | 18·40 | 18·40 | 18·40 |
| 15 | 4·85 | 7·25 | 9·55 | 16·05 | 19·05 | 19·20 | 19·00 | 18·80 |
| 20 | 6·75 | 11·35 | 15·05 | 19·40 | 19·45 | 19·40 | 19·10 | 18·90 |
| 30 | 9·15 | 14·45 | 18·55 | 19·65 | 19·55 | 19·70 | 19·40 | 19·05 |
| 40 | 10·70 | 16·80 | 19·55 | 19·65 | 19·65 | 19·40 | 19·50 | 19·40 |
| 60 | 13·15 | 19·80 | 19·75 | 19·75 | 19·75 | 19·65 | 19·60 | 19·60 |

*Estimation of vanadate.*

We have made a large number of estimations of vanadate using the optimum volume of 0·02 molar ferrous sulphate solution as catalyst in a total volume of about 50 ml. Some typical results are given in the following table :—

TABLE V.

| AMOUNT OF VANADATE IN MILLIMOLES. | |
|---|---|
| Furman's method. | Authors' iodimetric method. |
| 0·483 | 0·483 |
| 0·747 | 0·746 |
| 1·002 | 0·999 |
| 0·966 | 0·967 |

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## REFERENCE.

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