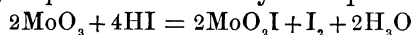


ART. XIX.—*The Iodometric Estimation of Molybdic Acid*;  
by F. A. GOOCH and CHARLOTTE FAIRBANKS.

[Contributions from the Kent Chemical Laboratory of Yale University—LII.]

I. *The Digestion Method*.—Mauro and Danesi have shown\* that under carefully regulated conditions, hydrochloric acid, potassium iodide and a soluble molybdate interact so definitely that the iodine set free from an excess of potassium iodide may be taken as a measure of the molybdic acid, assuming that every molecule of molybdic acid sets free an atom of iodine. They explain this action by the equation :



These results are obtained by acting upon a soluble molybdate containing from 0.1 to 0.5 gram. of molybdic acid with 1.5 gram. of potassium iodide in 1.5<sup>cc</sup> of water and 2.5<sup>cc</sup> of strong hydrochloric acid, in an atmosphere of carbon dioxide, the whole being heated an hour and a half in a sealed tube. The authors point out that with prolonged heating the action proceeds a little farther, and in the cold, under conditions otherwise similar, not quite so far as the theory of the equation would indicate.

Upon following out exactly the directions of Mauro and Danesi we obtained results similar in general to theirs. The digestion in sealed tubes under the conditions indicated gave results closely comparable with theirs, and these were in fairly good accord with the theory of the reduction. Our results obtained by digesting in the cold and in small volumes for a long time, according to the second method of Mauro and Danesi, were not equally favorable, and these results, as well as those obtained by varying the treatment, indicated an increasing difficulty in the reduction of the molybdic acid as its amount increased. As will be seen from the table, the method of Mauro and Danesi was varied in two ways: instead of only treating in small volumes (4<sup>cc</sup>) at 100° C., we used larger volumes (20<sup>cc</sup> to 30<sup>cc</sup>) at 100° C. with weaker acid and smaller amounts of the iodide; and instead of their treatment in the cold of only small volumes (4<sup>cc</sup>), large volumes (50<sup>cc</sup> to 100<sup>cc</sup>) with stronger acid were used.

*Treatment in sealed tubes at 100° for 1½ hours.*

(Method of Mauro and Danesi.)

| MoO <sub>3</sub> , as ammonium |                   |       |            |                         |        |
|--------------------------------|-------------------|-------|------------|-------------------------|--------|
| HCl.                           | H <sub>2</sub> O. | KI.   | molybdate. | MoO <sub>3</sub> found. | Error. |
| cc.                            | cc.               | gram. | gram.      | gram.                   | gram.  |
| 2.5                            | 1.5               | 1.5   | .1010      | .1007                   | .0003— |
| 2.5                            | 1.5               | 1.5   | .3015      | .3004                   | .0007— |
| 2.5                            | 1.5               | 1.5   | .5006      | .4795                   | .0031— |
| 2.5                            | 1.5               | 1.5   | .5020      | .4924                   | .0096— |

\* Zeitschr. für Anal. Chem., 1881.

*Treatment 18–22 hrs. in cold.*

(Method of Mauro and Danesi.)

| HCl.<br>cc. | H <sub>2</sub> O.<br>cc. | KI.<br>gram. | MoO <sub>3</sub> as above.<br>gram. | MoO <sub>3</sub> found.<br>gram. | Error.<br>gram. |
|-------------|--------------------------|--------------|-------------------------------------|----------------------------------|-----------------|
| 2·5         | 1·5                      | 1·5          | ·0986                               | ·0982                            | ·0004—          |
| 2·5         | 1·5                      | 1·5          | ·0982                               | ·0979                            | ·0003—          |
| 2·5         | 1·5                      | 1·5          | ·2041                               | ·2024                            | ·0017—          |
| 2·5         | 1·5                      | 1·5          | ·2059                               | ·2043                            | ·0016—          |
| 2·5         | 1·5                      | 1·5          | ·2063                               | ·2040                            | ·0023—          |
| 2·5         | 1·5                      | 1·5          | ·3116                               | ·3059                            | ·0057—          |
| 2·5         | 1·5                      | 1·5          | ·3098                               | ·3011                            | ·0087—          |
| 2·5         | 1·5                      | 1·5          | ·4080                               | ·4011                            | ·0069—          |
| 2·5         | 1·5                      | 1·5          | ·4087                               | ·4015                            | ·0072—          |
| 2·5         | 1·5                      | 1·5          | ·5210                               | ·5102                            | ·0108—          |
| 2·5         | 1·5                      | 1·5          | ·5172                               | ·5023                            | ·0149—          |

*Treatment at 100° for 1 hour.*

(Amounts of liquid and iodide different from those of Mauro and Danesi.)

| HCl.<br>cc. | H <sub>2</sub> O.<br>cc. | KI.<br>gram. | MoO <sub>3</sub> taken.<br>gram. | MoO <sub>3</sub> found.<br>gram. | Error.<br>gram. |
|-------------|--------------------------|--------------|----------------------------------|----------------------------------|-----------------|
| 15          | 15                       | ·5           | ·0893                            | ·0897                            | ·0004 +         |
| 15          | 15                       | ·5           | ·0824                            | ·0813                            | ·0011—          |
| 15          | 15                       | ·5           | ·0828                            | ·0813                            | ·0015—          |
| 15          | 15                       | ·5           | ·0990                            | ·0982                            | ·0008—          |
| 10          | 10                       | ·5           | ·0841                            | ·0842                            | ·0001 +         |
| 10          | 10                       | ·5           | ·1683                            | ·1591                            | ·0092—          |
| 10          | 10                       | ·5           | ·1706                            | ·1536                            | ·0170—          |
| 20          | 20                       | ·5           | ·1695,                           | ·1633                            | ·0062—          |

*Treatment 18 hours in cold.*

(Amounts of liquid different from those of Mauro and Danesi.)

| HCl.<br>cc. | H <sub>2</sub> O.<br>cc. | KI.<br>gram. | MoO <sub>3</sub> taken.<br>gram. | MoO <sub>3</sub> found.<br>gram. | Error.<br>gram. |
|-------------|--------------------------|--------------|----------------------------------|----------------------------------|-----------------|
| 40          | 10                       | 1·5          | ·5018                            | ·4847                            | ·0171—          |
| 90          | 30                       | 1·5          | ·5005                            | ·4910                            | ·0095—          |
| 75          | 25                       | 1·5          | ·5035                            | ·4934                            | ·0101—          |
| 75          | 25                       | 1·5          | ·5022                            | ·4920                            | ·0102—          |

The explanation of these experimental results we were inclined to believe lay in a tendency on the part of the iodine, set free in the process, to reverse the action. If this is so, the obvious remedy should be found in the removal of the iodine from the sphere of action, and this idea led us to experiment upon a process of distillation in which the iodine should be collected and estimated in the distillate; but before our work was completed, Friedheim and Euler published\* the results of their investigation along the same line.

II. *Distillation Process.*—These investigators have shown that if molybdic acid is treated with potassium iodide and

\* Berichte d. d. Chem. Gesell., xxviii, 2066.

hydrochloric acid, one atom of iodine is distilled for every molecule of molybdic acid present. The process according to their directions consists in treating in the Bunsen apparatus from 0.2 to 0.3 grm. of a soluble molybdate, or molybdic acid dissolved in sodium hydroxide, with 0.5 grm. to 0.75 grm. of potassium iodide and enough hydrochloric acid (sp. gr. 1.12) to two-thirds fill the flask. The solution is warmed for some time and only heated to boiling when the flask is wholly filled with the heavy vapor of iodine. It is boiled until no more iodine is visible and the liquid is of a clear green color. The iodine, collected in a receiver previously charged with a solution of potassium iodide, is then titrated with a standard thiosulphate solution. Results, varying between .05 per cent and 1.3 per cent on amounts, ranging from 0.2 grm. to 0.4 grm., of the molybdic acid present, were obtained by them.

Our experience fully confirms the usefulness of the method of Friedheim and Euler, but we have found it necessary to define more exactly the conditions of distillation. It is not sufficient to say that the boiling shall be stopped when a clear green color appears and when the steam is no longer colored by iodine; for the green color comes very gradually and we have repeatedly found iodine in the residue after the green color had developed distinctly. We have found it safer and more convenient to start the distillation with a definite volume of liquid and boil until the volume is reduced to a definite point.

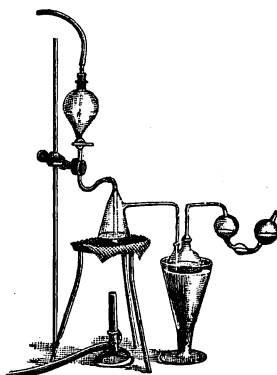
Our work has shown that if the initial volume is about 40<sup>cc</sup>, no iodine remains in the flask after the liquid has been boiled down to 25<sup>cc</sup>, and that at that degree of concentration the molybdic acid shows the theoretical reduction; but if the concentration is pushed beyond this point, a tendency to further reduction of the molybdic acid becomes evident.

We find it necessary to carry on the distillation in an atmosphere of carbon dioxide, inasmuch as the hydriodic acid freed by the action of hydrochloric acid of the strength employed upon the potassium iodide, is decomposed by distillation in contact with air, with liberation of iodine. As even a trace of oxygen will immediately set free iodine from boiling hydriodic acid, the carbon dioxide must be as free as possible from oxygen. The carbon dioxide which we used was evolved from boiled marble by the action of boiled acid to which a little cuprous chloride had been added, and was finally passed through a solution of iodine in potassium iodide to free it from any reducing substance which might be present.

The apparatus which we found most satisfactory was constructed with sealed and ground joints exclusively, and is shown in the accompanying figure. The distillation takes place in the first flask, and the iodine collects in the second flask and trap, which hold a solution of potassium iodide kept cool by immersion of the flask in cold water.

Before making the test experiments, a stream of the purified carbon dioxide was passed through the whole apparatus for some minutes and the stop-cock in the funnel was closed.

Ammonium molybdate, from 0.1 to 0.4 grm., dissolved in 10<sup>cc</sup> of boiled water, was put in the stoppered funnel and almost all of it allowed to run into the first flask. It was necessary that a few drops be left in the funnel or the liquid to follow would carry down bubbles of air. This precaution is necessary to the attainment of good results. Ten cubic centimeters of boiled water containing 0.5 grm. of potassium iodide were introduced similarly and finally 20<sup>cc</sup> of strong hydrochloric acid (sp. gr. 1.20). Before the acid was allowed to run in wholly, the stoppered funnel was again filled with carbon dioxide and finally left connected with the generator so that carbon dioxide might be passed into the apparatus at any time.



The liquid in the first flask, which at that time held the ammonium molybdate, 0.5 grm. of potassium iodide, 20<sup>cc</sup> boiled water and 20<sup>cc</sup> of hydrochloric acid (sp. gr. 1.20), was boiled until the volume decreased to 25<sup>cc</sup>. Under these conditions we do not find it necessary to digest the mixture before boiling. The iodine in the second and third flasks was titrated with standard thiosulphate.

The ammonium molybdate which we used in all the experiments was prepared by twice recrystallizing presumably pure molybdate. This salt was proved to contain 81.55 per cent of molybdic acid by the fact that a given weight of the molybdate was found to liberate 81.55 per cent of the amount of iodine set free by the same weight of pure molybdic anhydride dissolved in sodium hydroxide and treated similarly.

We have found it to be a matter of importance that the potassium iodide present shall never exceed the theoretical requirement by more than half a gram; otherwise the reducing action on the molybdic acid will be forced too far. When the amount of molybdic acid present is less than 0.3 grm. it is safer to restrict the potassium iodide used to half a gram.

| MoO <sub>3</sub> as ammonium<br>molybdate taken. | KI.  | MoO <sub>3</sub> found. | Error.  |
|--------------------------------------------------|------|-------------------------|---------|
| grm.                                             | grm. | grm.                    | grm.    |
| •2585                                            | 0.5  | •2580                   | •0005 — |
| •2995                                            | 0.5  | •2991                   | •0004 — |
| •2524                                            | 0.5  | •2513                   | •0011 — |
| •2446                                            | 0.5  | •2457                   | •0011 + |
| •2903                                            | 0.5  | •2914                   | •0011 + |
| •2798                                            | 0.5  | •2808                   | •0010 + |
| •2656                                            | 0.5  | •2663                   | •0007 + |

| MoO <sub>3</sub> dissolved<br>in NaOH.<br>gram. | KI.<br>gram. | MoO <sub>3</sub> found.<br>gram. | Error.<br>gram. |
|-------------------------------------------------|--------------|----------------------------------|-----------------|
| ·2273                                           | 0·5          | ·2281                            | ·0008 +         |
| ·2052                                           | 0·5          | ·2062                            | ·0010 +         |
| ·3474                                           | 0·5          | ·3467                            | ·0007 —         |

III. *Reoxidation Process.*—It was noticed during our experiments upon the method of Mauro and Danesi, as has been remarked previously, that large amounts of iodine in the digestion flask seemed to react upon the reduced product. In the process of Friedheim and Euler, too, it was discovered that, when the iodine which had collected in the second flask was drawn back into the first flask and mixed with the hot reduced product, the iodine found by titration was deficient in amount. It was found also that small amounts of standard iodine, introduced into the flask containing the reduced molybdic acid in an atmosphere of carbon dioxide, were absorbed slowly when this mixture was heated. This slow disappearance of the iodine in acid solution suggested the possibility of effecting the complete oxidation of the reduced molybdic acid in an alkaline solution, containing a tartrate or other salt of an organic acid to prevent precipitation. Several experiments were made in this direction upon the residues left in the process of Friedheim and Euler, the distillate having been titrated as usual with sodium thiosulphate to make sure that the reduction had proceeded properly. These residues were treated in each case with 1 gram. of tartaric acid, neutralized by acid sodium carbonate and left standing for an hour or two with an excess of standard iodine. Upon determining, by means of standard arsenious acid, the iodine left over, it was found that the amount of it which had disappeared corresponded very closely with that set free in the distillation, which is of course the same as that necessary to reoxidize the molybdic acid completely.

The conditions necessary to complete oxidation being known, experiments were made to see whether the process could not be successfully carried on in an open flask. Naturally under these conditions the air present must, as in the previous experiments, tend to set free some iodine at the outset, but, inasmuch as the hydriodic acid gradually diminishes in strength as the molybdenum is reduced and all iodine is ultimately driven from the flask, which is filled with steam during the boiling, it seemed possible that the danger from the action of atmospheric oxygen might be so far reduced as not to interfere essentially in the estimation of the molybdenum in the residue, provided the contents of the flask is diluted and cooled at the end of the boiling. Ammonium molybdate containing from 0·1 to 0·3 gram. molybdic acid, 0·5 gram. of potassium iodide,

20° of water and 20° of hydrochloric acid (sp. gr. 1.20)—the same proportions as those used in the process of Friedheim and Euler—were put into a 100° flask or narrow-based Erlenmeyer, and boiled from a total volume of 40° to exactly 25°, a point carefully marked on the flask. At this point of concentration, tests, repeated in many cases, have shown no free iodine in the reduced solution. If the solution is boiled below 25°, there is a tendency for the reducing action to go too far.

The residue was diluted at once, neutralized with acid sodium carbonate, and treated with an excess of standard iodine.

For a trap to prevent loss during boiling, a two-bulbed calcium chloride tube, cut off as shown in the figure four centimeters below the larger bulb, was fitted loosely inside the neck of the flask. Too violent boiling was prevented by the addition of two or three small pieces of pumice stone. While still acid the reduced solution, diluted and containing at this time little hydriodic acid, is not appreciably reoxidized in the air for some time; but when once made alkaline, it is very easily changed. Therefore the iodine for reoxidation must either be added before the solution is made alkaline or great care must be taken while neutralizing to stir the solution as little as possible and to draw in the iodine immediately. Less chance for error is introduced if the reduced solution is put, with an excess amounting to at least 8° of decinormal iodine and with a gram of tartaric acid, to prevent precipitation, in a liter flask, corked and then neutralized with acid sodium carbonate. The flask was fitted with a paraffined rubber stopper, carrying a funnel with a stop-cock for introducing the acid sodium carbonate and a Will and Varrentrapp trap for catching in a solution of potassium iodide any iodine thrown off during the effervescence. In some of the test experiments normal potassium carbonate, as causing less effervescence, was substituted for the acid sodium carbonate during the first part of the neutralization; the solution, however, must always finally be made alkaline with the acid carbonate.



The simpler method of neutralization is to put the reduced solution and a gram of tartaric acid in a liter flask, adding enough sodium hydroxide to nearly neutralize the solution, and finally making the solution surely alkaline with acid sodium carbonate. An excess of the standard iodine must be drawn in at once or atmospheric oxidation will take place and the error of the process be great.

If the solution has been properly neutralized according to either method, the iodine color should perceptibly fade within

fifteen minutes, but for complete oxidation the trapped or corked bottle should be set aside out of sunlight for an hour and a half or two hours. The iodine which was not used for reoxidation was then titrated with a standard arsenic solution. Since there is a slight tendency, especially when sodium hydroxide and acid sodium carbonate are used for neutralization, toward the formation of a little iodate, it is wise to acidulate the solution in each case slightly with dilute hydrochloric acid and then to determine by sodium thiosulphate the iodine which has taken the form of iodate. The ratio 126.85:144 expresses the relation of the total amount of iodine used in the reoxidation process to the calculated amount of molybdic acid present. The table given below shows the amount of molybdic acid taken in the form of ammonium molybdate and the molybdic acid found calculated from the iodine used in reoxidation.

| MoO <sub>3</sub> as<br>ammonium<br>molybdate,<br>gram. | KI.<br>gram. | MoO <sub>3</sub><br>found,<br>gram. | Error.<br>gram. | Neutralized by                                      |
|--------------------------------------------------------|--------------|-------------------------------------|-----------------|-----------------------------------------------------|
| 1640                                                   | .5           | .1639                               | .0001 —         | K <sub>2</sub> CO <sub>3</sub> + NaHCO <sub>3</sub> |
| 1692                                                   | .5           | .1681                               | .0011 —         | “ “                                                 |
| 1666                                                   | .5           | .1661                               | .0005 —         | “ “                                                 |
| 1517                                                   | .5           | .1517                               | .0000           | NaHCO <sub>3</sub>                                  |
| 2530                                                   | .5           | .2537                               | .0007 +         | “                                                   |
| 1636                                                   | .5           | .1637                               | .0001 +         | “                                                   |
| 1702                                                   | .5           | .1702                               | .0000           | “                                                   |
| 1520                                                   | .5           | .1518                               | .0002 —         | “                                                   |
| 1642                                                   | .5           | .1652                               | .0010 +         | “                                                   |
| 4560                                                   | .75          | .4560                               | .0000           | “                                                   |
| .1690                                                  | .5           | .1683                               | .0007 —         | NaOH + NaHCO <sub>3</sub>                           |
| .0507                                                  | .5           | .0519                               | .0012 +         | “ “                                                 |
| .1663                                                  | .5           | .1666                               | .0003 +         | “ “                                                 |
| .0101                                                  | .5           | .0095                               | .0006 —         | “ “                                                 |
| .1639                                                  | .5           | .1632                               | .0007 —         | “ “                                                 |
| .1636                                                  | .5           | .1625                               | .0011 —         | “ “                                                 |
| .0507                                                  | .5           | .0510                               | .0003 +         | “ “                                                 |
| .1685                                                  | .5           | .1683                               | .0002 —         | “ “                                                 |
| .1514                                                  | .5           | .1512                               | .0002 —         | “ “                                                 |
| .1649                                                  | .5           | .1646                               | .0003 —         | “ “                                                 |

Average error in the experiments, — .0001 gram.

The results given in the foregoing table show that molybdic acid can be determined with accuracy and convenience by boiling it with hydrochloric acid and a small excess of potassium iodide to a definite concentration in an ordinary flask, then neutralizing the residue with acid sodium carbonate, and reoxidizing the reduced molybdic acid with standard iodine.