rected by the addition of 0.07 mv. for Group 1 or 0.16 mv. for the other cells, these being the corrections made at 25°. The values of E^0 at the various temperatures are shown in Table II.

TABLE II

E^0_t FOR THE CELL H_2/HI ($a = 1$)/AgI, Ag

Group no.	No. of cells	E^0_{10}	E^0_{15}	E^0_{20}	E^0_{25}
1a	2	−0.14769	−0.14894	−0.15038	−0.15195
4a	2	− .14767	− .14890	− .15037	− .15191
Calcd., Eq. 2		− .1476	− .1489	− .1503	− .1519
		E^0_{25}	E^0_{30}	E^0_{35}	E^0_{40}
1b	2	−0.15182	−0.15350	−0.15553	−0.15731
3	1	− .15189	− .15350	− .15544	− .15720
4b	2	− .15192	− .15367	− .15551	− .15724
Calcd., Eq. 2		− .1519	− .1536	− .1555	− .1575

The equation

$$E^0_t = 0.1519 + 0.000328\,(t - 25) + 0.0000028\,(t - 25)^2 \qquad (2)$$

fits the data. The constant of the t term is the same as the corresponding constant in Owen's equation, while the second constant is a little smaller.

Summary

Measurements have been made at several temperatures of the electromotive force of the cell $H_2/HI/AgI$, Ag, with an acetate buffer containing potassium iodide as the electrolyte, and the values of E^0 calculated.

DURHAM, NORTH CAROLINA RECEIVED APRIL 8, 1940

[CONTRIBUTION FROM THE DEPARTMENT OF ANALYTICAL CHEMISTRY, UNIVERSITY OF WISCONSIN]

Color Phenomena Associated with Quinquevalent Molybdenum Solutions. I. Absorption Spectra in Solutions of Various Hydrochloric Acid Concentration

BY C. F. HISKEY* AND V. W. MELOCHE

Historical

The work reported herein was begun in connection with a series of studies designed to determine the best conditions under which rhenium and molybdenum could be separated from each other. In one group of experiments attempts were made to separate the quinquevalent molybdenum with butyl acetate by preferential extraction from concentrated hydrochloric acid solutions. During the preparation of this solution as well as in a previous study[1] pronounced color changes were observed in the quinquevalent molybdenum solution as the concentration of hydrochloric acid was altered. Such phenomena had been observed by Chilesotti,[2] who studied the electro-reduction of molybdates. Later a more detailed study of the molybdate reduction was made by Foerster and Fricke[3] and by Foerster, Fricke and Hausswald,[4] who showed that on addition of one equivalent of reductant a solution was formed whose color depended on the acid concentration. In 2 N hydrochloric the solution was amber, but in 8 N hydrochloric it was green.

From solutions of a high hydrochloric acid concentration they succeeded in isolating alkali salts of the general formula M_2MoOCl_5, leading them to believe that this green color was due to $MoOCl_3$ dissolved in the solution. Somewhat earlier Barbieri[5] also had observed that Klason's salt $(NH_4)_2MoOCl_5$, when treated with ammonium hydroxide, would precipitate an insoluble molybdenum penta-hydroxide which dissolved in dilute hydrochloric acid to form amber solutions. By concentrating this solution and saturating it with hydrogen chloride he was able to re-separate green crystals of Klason's salt. This would seem to indicate that the compound $MoOCl_3$ plays a basic role in all of the color phenomena involved in these studies.

From a study of Klason's salt Scagliarini[6] concluded that when one added successive portions of water to green quinquevalent molybdenum solutions the resulting color changes could be explained by ascribing to hydrolysis. Since the products formed were too soluble to be crystallized, he was not able to isolate any of the hydrolytic substances formed. From precipitations made with hexamethylenetetramine he obtained compounds in which he believed the acidic nucleus of $(NH_4)_2Mo(OH)_4Cl_3$ existed. Later James and Wardlaw[7] isolated salts of the type of $R(MoOCl_4{\cdot}H_2O)$, and $R(MoO_2Cl_2{\cdot}H_2O)$. These investigations, however, do not give any clear indication of the nature of the color transition.

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[1] Hiskey and Meloche, THIS JOURNAL, **62**, 1565 (1940).

[2] Chilesotti, *Z. Elektrochem.*, **12**, 146, 173, 197 (1906).

[3] Foerster and Fricke, *Z. angew. Chem.*, **36**, 458 (1923).

[4] Foerster, Fricke and Hausswald, *Z. physik. Chem.*, **A146** 81, 171 (1930).

[5] Barbieri, *Atti. accad. Lincei*, **25**, I, 775 (1916).

[6] Scagliarini, *ibid.*, **6**, 676 (1905).

[7] James and Wardlaw, *J. Chem. Soc.*, 2145 (1927).

Recent developments in photo-electric colorimetry have afforded an additional tool for the study of solutions. Since this system does not readily lend itself to the separation of the colored constituents, a colorimetric approach, although limited in scope, is uniquely fitted for such problems and has been applied in this work.

General Discussion

Once the quinquevalent molybdenum is formed it was found possible to induce the amber to green color change by altering the hydrochloric acid concentration. Thus as it was raised above 5 N the change to the green form was favored and conversely, on progressively adding water to an 8 N acid solution of molybdenum, the green color was progressively shifted to the amber form. These characteristics indicate that the transition is reversible.

Not only did hydrochloric acid induce this reaction but such widely differing substances as neutral salts and organic solvents had a similar effect. The temperature, too, has a pronounced effect on this equilibrium. Although the nature of these effects will be discussed in some detail in later papers, it is necessary to give a general consideration of the temperature effect here in order to develop the special arguments of this paper.

When the amber molybdenum solutions are heated there is a gradual transition to the green form. If a 2 N hydrochloric acid solution of the molybdenum is heated to the boiling point a pronounced darkening of the solution is observed, but not a clear transition to the green form. As the acid concentration is raised, however, the effect produced by a given temperature increment increases correspondingly. With a 3.5 N acid concentration, transition to the green form may be induced by heating the solution to the boiling point and at 4 N it is only necessary to warm the solution mildly in order to produce the same effect. The influence of the hydrochloric acid on the temperature effect seems to differ only in degree from that of lithium chloride or magnesium chloride.

On cooling a 1 N hydrochloric acid–molybdenum solution below room temperature, it was found that the amber color gradually disappeared. As a result the solution was virtually colorless at the freezing point. A most striking contrast of colors may be demonstrated with two test-tubes to which equal amounts of molybdenum and hydrochloric acid are added. If one is cooled to the freezing point while the other is heated to its boiling point the resulting change will cause the cold solution to seem colorless while the hot one will be almost black. On allowing the two tubes to return to room temperature the colors within them will become identical. These peculiarities led us to seek an explanation by means of these studies. In this paper it is intended to introduce the preliminary studies begun on this problem. These consist of establishing the variables involved in the colorimetric determination of quinquevalent molybdenum, followed by a study of the absorption spectrum of quinquevalent molybdenum solutions.

Experimental

A. The Colorimetric Determination of Quinquevalent Molybdenum

In earlier work it had been shown that quantitative reductions of hexavalent molybdenum to the quinquevalent state could be performed with stannous chloride if reductions were carried out in moderately acidic solutions.[8,9] Solutions formed in this manner are amber in color and although the color density is not particularly pronounced it was felt that the requisite analytical measurements could be made colorimetrically.

Since the apparent color density of the quinquevalent molybdenum was altered by the electrolyte concentration it was necessary to determine the effect of the reagents which were to be used in the proposed determination. The intended procedure was to consist of taking the molybdate into solution with hydrochloric acid, reducing with stannous chloride and measuring the color density of the s tion.

For this study an Evelyn colorimeter was used. The light passed through the solution was made partially monochromatic by using a filter manufactured by the Rubicon Company. From studies presented below it was observed that the amber component of the quinquevalent molybdenum had absorption maxima at 460 mμ. Their filter no. 420 being available was chosen for this particular work.

In the first experiments the effect of the stannous chloride and the hydrochloric acid concentrations were determined. For this purpose fixed amounts of quinquevalent molybdenum and variable amounts of these reagents were mixed and diluted to a constant volume. The color density was then determined.

The quinquevalent molybdenum was prepared according to the technique of Birnbaum and Walden (and was approximately 0.0107 N).[10]

The data obtained are plotted in Figs. 1 and 2. These data reveal a very pronounced effect on the color of the solutions as the concentrations of these two electrolytes are increased. Since the effectiveness of the hydrochloric acid is not so great at the lower concentrations it seemed

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[8] Lang and Gottlieb, *Z. anorg. Chem.*, **49**, 148 (1906).

[9] Stěhlik, *Collection Czechoslov. Chem. Commun.*, **4**, 1418 (1932).

[10] Birnbaum and Walden, This Journal, **60**, 64 (1938).

desirable to operate in 2 *N* solutions. Lower acid concentrations are not desirable because of the possibility of molybdenum-blue formation. It is clear that the concentration of these reagents must be rigidly fixed if accurate analyses are to be made.

Procedure.—The procedure finally adopted consisted of taking a molybdate into solution with water and diluting it with an equal volume of 4 *M* hydrochloric acid. The resulting solution was then treated with 1.0 ml. of 1 *N* stannous chloride (2 *M* with hydrochloric acid). After mixing, the solution was diluted with 2 *M* hydrochloric acid to 50 ml. in a volumetric flask and mixed a second time. The sample was then placed in the colorimeter and the galvanometer deflection noted. The calibration curve as well as the entire procedure is intended to cover the range of molybdenum concentrations between 0.00025 and 0.008 *M* and amounts varying from 0.3 to 12 mg. of molybdenum. Smaller amounts of molybdenum could be used by simply reducing the volumes employed in the process as a whole. Above 0.008 *M* the results deviate from a straight line and show a tendency to curve upward. Listed in Table I are a representative group of analyses picked at random showing the accuracy with which results can be determined. In all of the determinations listed here, the correct value was unknown to the operator. From these results it is apparent that in the hands of a careful person, relatively accurate results can be obtained.

TABLE I

MoO$_4$, taken ml.	2.45	3.02	4.03	4.50	5.40	5.44	5.95
Found	2.50	3.02	4.03	4.50	5.40	5.40	6.00
MoO$_4$, taken, ml.		6.30	6.50	7.02	8.98	10.12	12.16
Found		6.30	6.50	7.00	8.98	10.12	12.10

B. Effect of Hydrochloric Acid Concentration on the Spectra of Quinquevalent Molybdenum

From some of the earlier discoveries mentioned above, it seemed as though the color changes in solution involved some kind of hydrolysis mechanism and that the amber color transition simply involved a two-component equilibrium. If this were so it would seem logical to expect that as the amber component was gradually transformed into the green one, the galvanometer deflection obtained using the no. 420 filter should decrease as the equilibrium was shifted. In the study of the effect of the hydrochloric acid on this equilibrium (Fig. 1), it was observed that instead of the galvanometer deflection decreasing as the hydrochloric acid concentration was raised, quite the reverse actually took place. This discrepancy between observed and expected results led us to investigate this effect in greater detail. Since the green component had absorption maxima at about 720 mμ it was thought desirable to make measurements not only with the no. 420 filter but with the no. 660 filter as well. Thus for a simple transition from amber to green the galvanometer deflection should fall steadily using the no. 420 filter and should increase for the no. 660 filter, as the hydrochloric acid concentration was progressively increased, i. e., if the two-component mechanism were all that was involved.

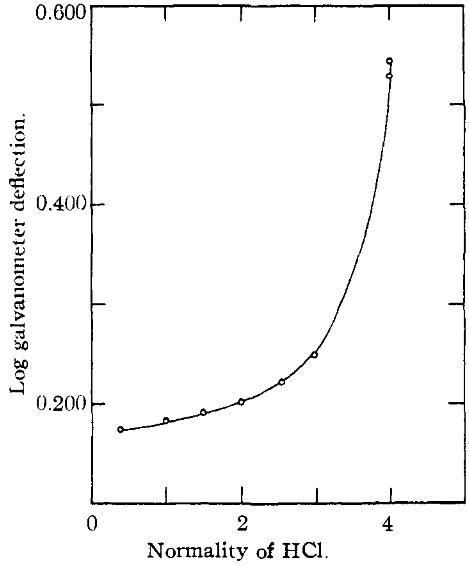


Fig. 1.—Effect of HCl concentration on quinquevalent molybdenum.

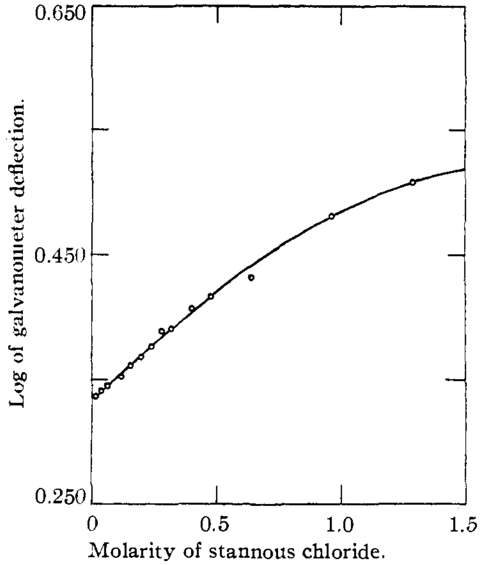


Fig. 2.—Effect of stannous chloride on quinquevalent molybdenum.

Despite the fact that the no. 660 filter had its maximum transmittance about 40 mμ below the absorption maxima of the green component that was being studied, it was not possible for us to obtain a better filter for the colorimeter. Nevertheless the transmitting region of this filter was separated sufficiently from the absorption maxima of the amber component so that there would be little overlap.

The experimental technique used in these studies was similar to that in the preceding ones in which the effect of the hydrochloric acid concentration was determined. Thus in all cases a fixed amount of quinquevalent molybdenum solution was diluted with a fixed amount of hydrochloric acid of varying molarity, and from a knowledge of the method of preparation, the final molarity of hydrochloric acid was calculated.

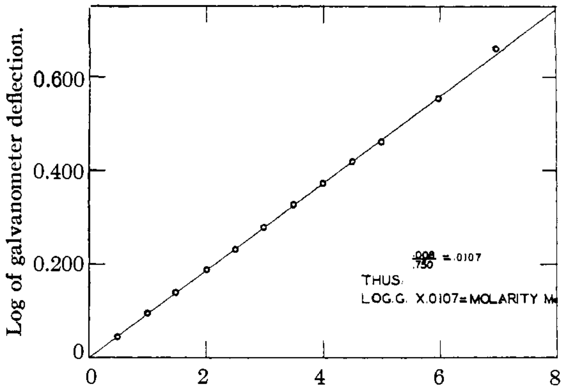


Fig. 3.—Calibration curve for Mo determination.

The necessary data were obtained by first measuring the galvanometer deflection using the no. 420 filter followed by similar observation using the no. 660 filter. In Fig. 4 these data are plotted and are shown in comparison with curves which one might ordinarily expect if a simple two-component mechanism was involved. For these experimental curves the following interpretations were made:

1. As the hydrochloric acid concentration is increased to about 5 *N*, the concentration of the amber component as measured by the no. 420 filter shows a pronounced increase, and this increase is, very roughly, more than fifteen times the molybdenum concentration obtained by extrapolation to zero acid concentration.[11]

2. Above 5 *N* there is a very sudden decrease in the concentration of the amber component as manifested by a 60-fold reduction in the light absorption of the 420 region.

3. Using the no. 660 filter to measure the concentration of the green component, it is apparent that below 2.5 *N* hydrochloric acid there is virtually none present, but above 2.5 *N* and up to 5 *N* there is a very abrupt increase in its concentration. As is quite evident from the curve there is no detectable amount of the green component in the lower acid concentrations until a normality above 2.5 is reached. The effect of increasing the amount of acid from 5 to 10 *N* is to decrease the concentration of the green component to about two-thirds of its maximum value.

4. Although it is not too apparent in these data, the peaks of these curves do not come at the same normalities but are separated somewhat. Studies made using substances other than hydrochloric acid to induce this color change have shown a greater separation of these peaks.

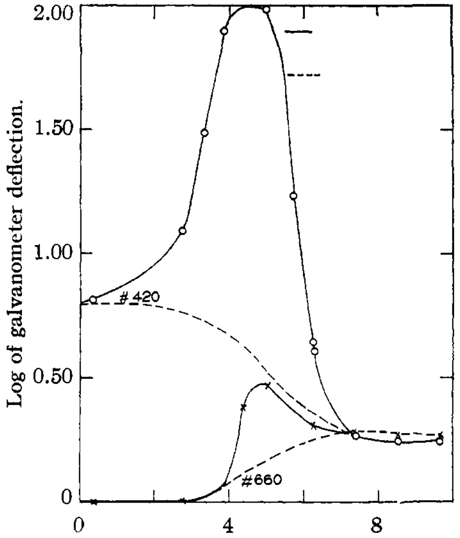
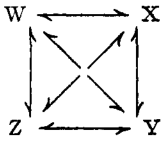


Fig. 4.— ——Experimental; - - - expected curves.

From such considerations it becomes evident that a more elaborate explanation of this color transition must be postulated. A possible mechanism for this equilibrium seems to require not less than four components which we might designate as W, X, Y and Z, existing in equilibrium with each other according to the following sketch:



Let us define the X component as corresponding to that substance which has its maxima at 460 mμ, and the Y component as that substance having its absorption maxima at 720 mμ. Then the simple amber to green transition may be written X $\rightleftarrows$ Y. But in order to explain the fact that the concentration of the component X as well as Y increases as the hydrochloric acid concentration is raised from 0.0 to 5 *N*, it becomes necessary to predicate the existence of at least another substance in solution. This substance is designated as W. In a similar fashion, reasoning from the fact that as the hydrochloric acid concentration is increased above 5 *N* the concentration of X and Y component decreases, it becomes necessary to assume that they are transformed

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[11] At 0.0 *N* the logarithm of the galvanometer deflection is about 0.8, whereas at 5 *N* it is 2.0. This ordinarily would indicate a 15-fold change in concentration, except that 2.0 is a limiting value of the Evelyn colorimeter and in this region the accuracy of the instrument decreases tremendously.

into some other substance or substances and these have been designated as Z. This type of mechanism seems to account for all of the observations which we made in the course of this study. Another mechanism involving much less inter-equilibria and yet accounting for the phenomena observed may be postulated as

$$\underset{\xrightarrow[\text{Increasing HCl Concn.}]{\hphantom{xxxxxxxxxxxxxxxxxxxx}}}{W \leftrightarrows X \leftrightarrows Y \leftrightarrows Z}$$

with the various letters having the same significance as in the preceding formulation.

These two schemes represent the extremes of complexity and simplicity which can be postulated. As yet it is not possible to decide which of these more nearly represents the true state of the system.

In order to establish with greater certainty some of the interpretations which are put on the data listed in Fig. 4, it was decided to make a study of the absorption spectra of these solutions as a function of the wave length and to do this for a number of hydrochloric acid concentrations. The apparatus for this study consisted of a special set-up used in these laboratories and described by James and Birge.[12] For these studies quinquevalent molybdenum solutions containing a fixed concentration of the molybdenum but a variable concentration of hydrochloric acid were prepared. Similar solutions were prepared differing only in that the quinquevalent molybdenum was not present. Using such solutions as solvent standards the percentage of light absorbed could be determined for the quinquevalent molybdenum in solution.

In Figs. 5 and 6 we have plotted the data obtained from these measurements. It will be apparent from these data that the four-component mechanisms as postulated above are confirmed. Thus in the lower acid concentrations the solutions show a light absorption which increases steadily to 5 *N*. At about 4 *N* the 440 mμ peak is clearly evident and remains so for all of the higher acid concentrations. Above 5 *N* a pronounced decrease in the light absorption of this region takes place and at 7 *N* there is only a very small percentage absorption, for the absorption as the acid concentration is increased is much less striking than for the 440 mμ peak. This fact establishes that these two peaks are due to two different components and are not two sets of maxima of one substance.

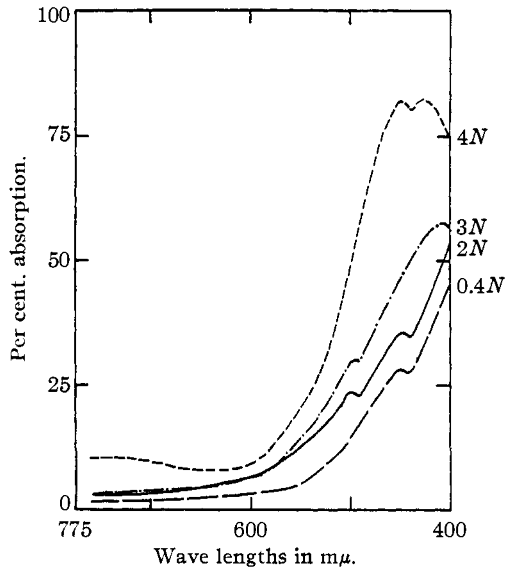

Fig. 5.

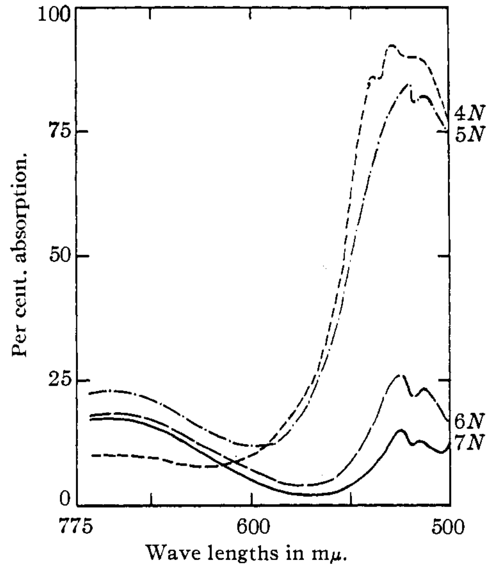

Fig. 6.

Because the concentrations of components X and Y are increased with increase of acid concentrations, it becomes necessary to assume the existence of at least one other absorption maximum somewhere below 400 mμ. Similarly because the concentrations of these two components decrease above 5 *N* hydrochloric acid it becomes necessary again to assume the existence of at least one more absorption maximum somewhere above 800 mμ. These components have been previously designated as W and Z, respectively.

Acknowledgment

The authors would like to express their appre-

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(12) James and Birge, *Trans. Wisconsin Acad.*, **31**, 1 (1938).

ciation to Messrs. Max Wolfe and Warren Olsen for assistance in some of the experiments cited here, to the Work Projects Administration for financial support in carrying out this research and the Brittingham Research Foundation for use of their spectrophotometer.

Summary

1. A colorimetric procedure for the determination of semi-micro amounts of molybdenum is given.

2. The effects of various electrolytes on this procedure are listed.

3. To explain the color phenomena observed a four color component mechanism is offered.

4. Spectrophotometric studies of this system are included.

RECEIVED MAY 2, 1940

[CONTRIBUTION FROM THE T. JEFFERSON COOLIDGE, JR., MEMORIAL LABORATORY, HARVARD UNIVERSITY]

The Specific Gravity of Iodine Pentoxide and the Atomic Weight of Iodine

BY G. P. BAXTER AND W. M. KELLEY

On the basis of a new determination of the specific gravity of iodine pentoxide by Moles and Villan,[1] Moles[2] has recalculated the atomic weight of iodine from the ratio I_2:I_2O_5 determined by Baxter and Butler[3] and from the ratio I_2O_5:Na_2CO_3 determined by Baxter and Hale.[4] The specific gravity found by Moles and Villan, 5.28, differs from that previously found by Baxter and Tilley,[5] 4.80, by nearly 0.5 unit and leads to a vacuum correction somewhat more than 0.002% smaller than that used by Baxter and collaborators. The vacuum corrections corresponding to the two densities are incorrectly calculated by Moles, but the *difference*, which apparently was applied as a correction, is correct. In Moles' paper many of the ratios as well as the atomic weights of iodine are incorrectly calculated. Furthermore Moles arbitrarily rejects the highest result in one series while retaining the lowest which differs nearly as much from the mean.

Apart from the question of the density of iodine pentoxide Moles' treatment of data is incorrect. The weights of iodine pentoxide given in the papers by Baxter, *et al.*, have been subjected to two corrections, one of +0.00011 g./g. for buoyancy of air and one of −0.00001 g./g. for air adsorbed on the powder. The latter correction was found in this Laboratory by weighing iodine pentoxide first in vacuum, then in air of known density. To compute the air displaced by the iodine pentoxide the density 4.80 was employed. If the density 5.00 is used for iodine pentoxide the apparent air adsorption disappears in these experiments, while with the density 5.28 the apparent adsorption is *negative* in sign to the extent of more than 0.001%.

Obviously if the higher density is used in computing the vacuum correction, the correction for air adsorption should be omitted. The correction applied by Moles to the weights of iodine pentoxide of −0.002% should therefore be reduced by the amount of the correction already applied for air adsorption, −0.001%, and therefore is twice too large.

The large difference between the specific gravities of iodine pentoxide found by Baxter and Tilley and by Moles and Villan, nearly 0.5 unit, is hard to understand even when the difficulty of filling with liquid the interstices of the very porous iodine pentoxide, formed by a process of double efflorescence, is taken into consideration. We have therefore made new determinations of the specific gravity of iodine pentoxide by displacement of various liquids. While these new experiments have given results higher than that found by Baxter and Tilley, they are still far lower than that found by Moles and Villan.

Recrystallized iodic acid was carefully dehydrated in two steps in a current of dry air, finally for two hours at 240°. The product was only very slightly discolored, an evidence of considerable purity. It was then rapidly transferred to the pycnometer and weighed. After being covered with the liquid it was placed under a bell jar, which was exhausted, and the air in the powder was dislodged by jarring. This process always required some time. The pycnometer was then set in the usual way and weighed. With xylene the setting remained constant over twelve hours, although there was evidence of slight attack of the xylene by the iodine pentoxide. With mesitylene there

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(1) Moles and Villan, *Anales soc. espan. fis. quim.*, **34**, 787 (1936).

(2) Moles, *ibid.*, **34**, 859 (1936).

(3) Baxter and Butler, THIS JOURNAL, **53**, 968 (1931).

(4) Baxter and Hale, *ibid.*, **56**, 615 (1934).

(5) Baxter and Tilley, *ibid.*, **31**, 213 (1909).