

2. The velocity constants of the reaction acetyl-chloro-amino-benzene to *p*-chloro-acetanilide, catalyzed by hydrochloric acid, have been determined at 17.65°, 25° and 35° for concentrations of acid from 0.1 to 1.0 *M*.

3. It has been shown that these velocity constants at each temperature are proportional to the product of the activities of the hydrogen and chlorine ions of the catalyzing acid.

4. As far as we are aware, this is the first case in which homogeneous catalysis may be calculated with exactness over a wide concentration range and in concentrated solutions, without uncertainties arising in liquid junction potentials.

5. The temperature coefficient has been considered and the critical increment has been roughly calculated and shown to vary considerably with rise in temperature.

6. The relation  $K_T = \frac{k}{a_H a_{Cl}}$  which holds exactly for solutions of hydrochloric acid alone, fails to hold when acid-salt mixtures are used as catalysts.

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[CONTRIBUTION FROM THE KEDZIE CHEMICAL LABORATORY OF THE MICHIGAN AGRICULTURAL COLLEGE]

## THE ELECTROMETRIC TITRATION OF URANIUM WITH POTASSIUM PERMANGANATE AND POTASSIUM DICHROMATE

By D. T. EWING AND E. F. ELDRIDGE

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When an acid solution of uranium is treated with a reducing agent such as zinc, the product of the reduction is a mixture of tetravalent uranium with smaller and varying amounts of the trivalent form. Although potassium permanganate solution may be used to oxidize either form to the hexavalent state and since the velocity constant of the oxidation of the lowest form is much greater than that of the tetravalent, it becomes advisable for the volumetric determination of uranium to either have all of it in the tetravalent state or to determine, in the case of a mixture, the ratio of the two. McCoy and Bunzel<sup>1</sup> found that when a reduced solution of uranium was filtered and allowed to come in contact with the atmosphere it contained nearly all of the uranium in the tetravalent form, the velocity constant for the oxidation of the trivalent to the tetravalent being very large compared with that for the oxidation of the latter. Such a solution could be titrated with potassium permanganate.

In this investigation we have accomplished three things: first, we have measured the amount of trivalent uranium in solution by oxidizing it to tetravalent uranium both with potassium permanganate in sulfuric

<sup>1</sup> McCoy and Bunzel, *THIS JOURNAL*, **31**, 367 (1909).

acid solution and with potassium dichromate in hydrochloric acid solution, obtaining the end-points by the well-known electrometric method; second, the tetravalent form was thereupon oxidized further and completely to the hexavalent; third, a uranium solution containing iron was reduced and titrated electrometrically and three end-points were obtained.

**Preparation of the Solutions.**—The uranium solution was standardized by evaporating a known volume of the solution in a platinum crucible and igniting to the oxide  $U_3O_8$ , of which 1 cc. of solution gave 0.0131 g.

The potassium permanganate solution was standardized against sodium oxalate certified by the United States Bureau of Standards. The concentration was found to be 0.1011 *N*.

The potassium dichromate solution was prepared from potassium dichromate which had been recrystallized from conductivity water several times. The normality was obtained against U. S. Bureau of Standards iron ore, and found to be 0.09064.

The ferrous sulfate solution used was 0.1001 *N*.

**Apparatus.**—The apparatus was very similar to the forms in general use, with the exception of the titrating vessel (Fig. 1). It became advisable to keep the reduced solution from contact with the atmosphere, especially since the solution was vigorously stirred. Therefore, the titrating cell was constructed so that the reduced solution emptied directly from the Jones zinc reductor, A into the vessel through which carbon dioxide was being passed. The stirrer was provided with a mercury seal, B. There were 4 other openings in the cover of the vessel, namely, a connection for the calomel electrode, one for the platinum electrode, an inlet for carbon dioxide, and one for the buret. The platinum electrode was made by sealing a heavy wire through a glass capillary. This was ground at right angles to the wire until the platinum was exposed. Uniform conditions of the electrode for successive experiments were maintained by drawing the electrode across carborundum paper until a new surface of platinum was exposed.

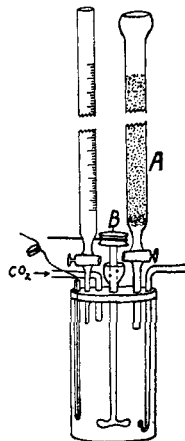


Fig. 1.—Vessel for electrometric titration of uranium solutions.

until a new surface of platinum was exposed.

## Procedure

**Titration of Uranium with Potassium Permanganate.**—Ten cc. of the standard uranium solution was added to 40 cc. of a sulfuric acid solution which contained 2 cc. of conc. sulfuric acid to every 90 cc. of solution. This mixture was warmed to 80–90°. Carbon dioxide was passed through the cell until the air was removed. The solution was then slowly poured through the Jones reductor which was finally rinsed with 50 cc. of the sulfuric acid solution mentioned above. The final solution had a total volume of 100 cc. and contained 2 cc. of sulfuric acid and 10 cc. of uranium solution. The solution at this point was brownish. The intensity of the color was increased by allowing the solution to pass through the reductor more slowly or by decreasing the temperature. Upon the addition of standard potassium permanganate, the color gradually became green and when the first end-point was reached as shown by the galvan-

ometer deflection the brownish color had entirely disappeared. The addition of potassium permanganate was slowly continued and the e. m. f. of the solution changed very little until the second end-point was reached. This second end-point signifies that the tetravalent uranium is changed to the hexavalent form and, as was shown by the electrometric method, was reached just before the end-point was shown by the change in color, due to the excess of permanganate ion in solution.

The interesting thing to note at this point is that the volume of potassium permanganate solution (Fig. 2) added after the first end-point is reached,

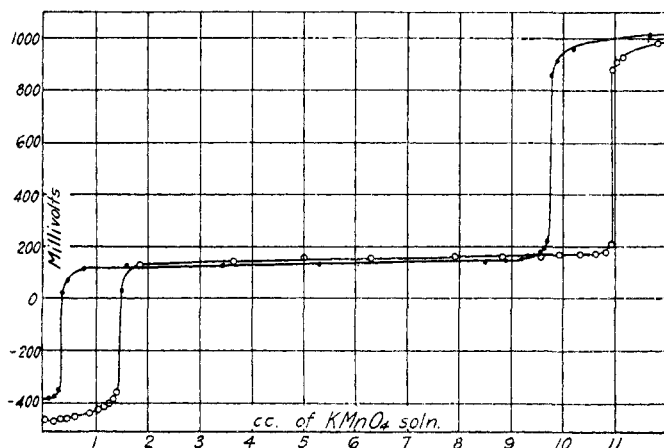


Fig. 2.

in order to reach the second end-point, is equal to the theoretical amount of the oxidizing agent that would be required to oxidize the uranium present from the quadri- to the hexavalent state. The first end-point, then, represents the complete oxidation of the trivalent form to the tetravalent. From the difference between the end-points the total amount of uranium present in a solution can be calculated, whether the uranium is present in the trivalent or tetravalent form, provided only that no hexavalent uranium is present.

The following is a comparison between the measured volume of potassium permanganate solution necessary to produce the second end-point after the first end-point was noted, and the calculated volume. Ten cc. of uranium solution was used.

| Trial | KMnO <sub>4</sub> used<br>Cc. | Calc. amount<br>Cc. | Difference<br>Cc. |
|-------|-------------------------------|---------------------|-------------------|
| 1     | 9.25                          | 9.23                | 0.02              |
| 2     | 9.30                          | 9.23                | 0.07              |

**Titration of a Mixture of Uranium and Iron with Potassium Permanganate.**—The above procedure was followed with the exception that 1

cc. of ferrous sulfate solution was added to the solution before it was poured through the reductor. The solution was titrated immediately after reduction and three end-points were obtained by means of the voltage readings. The first signifies the complete oxidation of the trivalent uranium to the tetravalent, the second the oxidation of the tetravalent to the hexavalent, and the third the oxidation of the ferrous iron to ferric. Each of these end-points checked very well with the theoretical. The results are shown in Fig. 3 where the potential readings in millivolts

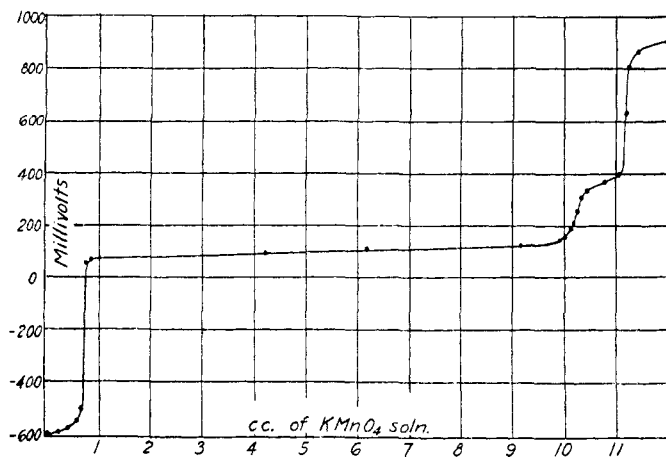


Fig. 3.

are plotted as ordinates and the volume of standard potassium permanganate solution as abscissas.

**Titration of Uranium with Potassium Dichromate.**—Ten cc. of the uranium solution was reduced in the presence of hydrochloric acid and titrated with potassium dichromate. These results plotted as a graph, show the two end-points as in the case of the titration with potassium permanganate in sulfuric acid solution, although the slope of the second end-point does not show as clearly the point of inflection. For this reason the results are tabulated (Table I) using the ratio of the change in millivolts to the change in volume of potassium dichromate solution to designate more accurately the end-points.

From the following table it is noted that 10.25 cc. of the dichromate solution was required to reach the second end-point. The theoretical volume is 10.29 cc.

**Titration of Uranium in Varying Concentrations of Sulfuric Acid.**—Titrations were made using 10 cc. of the uranium solution in solutions containing 2, 3, 5, 10 and 20 cc. of conc. sulfuric acid for each 100 cc. of solution. The results are shown in Fig. 4. The first end-point seemed to be little affected by the concentration of the acid. No attempt was

TABLE I  
TITRATION OF 10 CC. OF URANIUM SOLUTION WITH A STANDARD SOLUTION OF POTASSIUM  
DICHROMATE

| Cc.<br>$K_2Cr_2O_7$ | $\Delta$ Cc.<br>$K_2Cr_2O_7$ | Millivolts | $\Delta$<br>Mv. | $\frac{\Delta Mv.}{\Delta Cc. K_2Cr_2O_7}$ |
|---------------------|------------------------------|------------|-----------------|--|
| 0.0                 | 0.0                          | -570       | 0               | 0  |
| 0.05                | 0.05                         | -565       | 5               | 100  |
| 0.15                | 0.1                          | -560       | 5               | 100  |
| 0.2                 | 0.05                         | -530       | 30              | 600  |
| 0.25                | 0.05                         | -490       | 40              | 800  |
| 0.3                 | 0.05                         | -440       | 50              | 1000                                       |
| 0.35                | 0.05                         | -70        | 370             | 7400                                       |
| 0.4                 | 0.05                         | 50         | 120             | 2400                                       |
| 0.5                 | 0.1                          | 65         | 15              | 150  |
| 2.5                 | 2.0                          | 90         | 25              | 13   |
| 4.4                 | 1.9                          | 110        | 20              | 10   |
| 6.5                 | 2.1                          | 120        | 10              | 5  |
| 8.7                 | 2.2                          | 130        | 10              | 5  |
| 10.3                | 1.6                          | 140        | 10              | 8  |
| 10.4                | 0.1                          | 150        | 10              | 100  |
| 10.5                | 0.1                          | 170        | 20              | 200  |
| 10.6                | 0.1                          | 350        | 180             | 1800                                       |
| 10.8                | 0.2                          | 370        | 20              | 100  |
| 10.9                | 0.1                          | 390        | 20              | 200  |
| 11.1                | 0.2                          | 420        | 30              | 150  |
| 11.55               | 0.45                         | 440        | 20              | 44   |

made to bring about uniform conditions of temperature or rate of reduction, so that the amount of trivalent uranium indicated in the various acid concentrations is not significant.

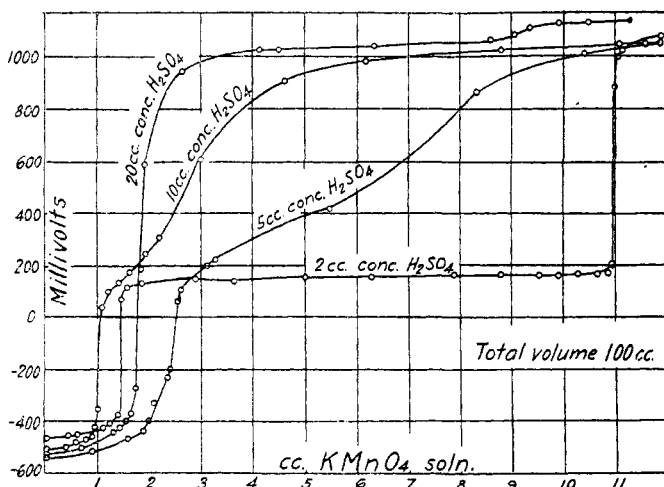


Fig. 4.

The second end-point seems to be greatly affected, however, by the concentration of the acid. The curves readily show that no accurate

end-point was obtained with concentrations above 2 cc. for each 100 cc. of solution, although the color end-points were obtained when the uranium was completely oxidized.

### Summary

When solutions of uranyl sulfate, reduced with zinc, are titrated electro-metrically with permanganate, or when chloride solutions are titrated with dichromate, one change in the oxidation potential occurs when the trivalent uranium is oxidized to the tetravalent and another when the latter is oxidized to the hexavalent form. Thus the total amount of uranium may be calculated.

A third end-point is obtained when iron is present.

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[CONTRIBUTION FROM THE GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 15]

## THE CRYSTAL STRUCTURE OF PHOSPHONIUM IODIDE

BY ROSCOE G. DICKINSON<sup>1</sup>

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### Introduction

The structure of ammonium chloride has been found<sup>2</sup> to be such that each nitrogen atom is surrounded by 8 chlorine atoms at the corners of a cube and each chlorine atom similarly surrounded by nitrogen atoms. Above<sup>3</sup> 184.3° ammonium chloride crystallizes in a second cubic modification which has been found<sup>4</sup> to have the sodium chloride structure. The same relations are true for ammonium bromide whose transition temperature is 137.8°. Ammonium iodide undergoes transition at -17.6°, and above this temperature has the sodium chloride structure.

Phosphonium iodide,  $\text{PH}_4\text{I}$ , readily sublimates, yielding colorless crystals that are cube-like in appearance, but which optical examination has shown<sup>5</sup> to be tetragonal so that the cube-like habit is considered a combination of  $\{110\}$  and  $\{001\}$ . The axial ratio could not be measured. A study of the crystal structure of this substance was undertaken partly with the object of determining whether it bore any relation to either of the structures of the ammonium halides. It has been found possible to account for the X-ray data with a structure which may be considered a modification of

<sup>1</sup> National Research Fellow in Chemistry.

<sup>2</sup> W. H. and W. L. Bragg, "X-rays and Crystal Structure," G. Bell and Sons, Ltd., London, 1916, pp. 110, 158.

<sup>3</sup> The transition temperatures are from Bridgman, *Proc. Am. Acad. Arts Sci.*, **52**, 133 (1916).

<sup>4</sup> Bartlett and Langmuir, *THIS JOURNAL*, **43**, 84 (1921).

<sup>5</sup> Wagner, *Z. Kryst. Mineralog.*, **50**, 47 (1911).