		E (obs.).	E (calc.).	E (obs.)—E cal.
0.2 *n* KCl	—0.2 *n* $KC_2H_3O_2$	—0.0080	—0.0082	0.0002
0.1 *n* KCl	—0.1 *n* $KC_2H_3O_2$	—0.0074	—0.0077	0.0003
0.2 *n* KCl	—0.2 *n* KOH	0.0170	0.0168	0.0002
0.1 *n* KCl	—0.1 *n* KOH	0.0165	0.0165	0.0000
0.2 *n* KCl	—0.2 *n* KBr	0.0004	0.0004[1]	0.0000
0.2 *n* NaCl	—0.2 *n* NaOH	0.0192 ± 0.0003	0.0187	......
0.1 *n* KCl	—0.1 *n* HCl (Sauer, 18°)	—0.0286	—0.0286	0.0000

Summary.

The potentials between six pairs of liquids were determined by a new method. The results agree remarkably well with a modified form of the Planck equation. The conductivities at 25° were accurately determined for all the liquids used.

[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO.]

THE SPEED OF OXIDATION, BY AIR, OF URANOUS SOLUTIONS, WITH A NOTE ON THE VOLUMETRIC DETERMINATION OF URANIUM.

BY HERBERT N. McCOY AND HERBERT H. BUNZEL.

Received December 18, 1908.

The simplest volumetric method for the determination of uranium is that in which the element is converted into uranyl sulphate, UO_2SO_4, reduced with zinc and sulphuric acid to uranous sulphate, $U(SO_4)_2$, and titrated with standard permanganate.[2] The procedure is analogous to the reduction of ferric salts to ferrous and titration of the latter. There is, however, an important difference: uranous solutions oxidize in air far more rapidly than ferrous solutions. In order to learn, quite definitely, what influence atmospheric oxidation might have upon the accuracy of the volumetric determination of uranium, we have made some experiments on the speed of oxidation of uranous sulphate by air.

The uranous solution was prepared just as in the process of analysis: 25 cc. of N/10 uranyl sulphate solution (11.925 grams of uranium per liter) were mixed with 100 cc. of 6 N sulphuric acid (294 grams H_2SO_4 per liter) and reduced with 100 grams of pure stick zinc at 100°, for 15 minutes. The reduced solution was separated from the zinc, diluted to 250 cc. and divided into two portions, each of which was placed in a Drechsel wash bottle and kept at 25° ± 0.01. Air at atmospheric pressure, and satu-

---

[1] Through an oversight the conductivity of KBr was not measured. However, equation (2) will probably in this case give the same result as equation (3). The above calculated value of E was obtained from equation (2), Kohlrausch's values for the ionic mobilities and their temperature coefficients being used.

[2] Kern, THIS JOURNAL, **23**, 685 (1901); Pulman, *Amer. J. Sci.*, **16**, 229 (1903); Goettsch, THIS JOURNAL, **28**, 1541 (1906).

rated with water vapor at 25°, was blown through the first solution at the rate of two bubbles per sec. and through the second at double this rate. Portions, of 25 cc. each, of the solutions were titrated at suitable intervals, with N/40 permanganate. Table I shows the results obtained in the first experiment.

TABLE I.

Time in minutes.	cc. of permanganate, slow air current.	cc. of permanganate, fast air current.	K.
0	9.90	9.90	....
65	9.02	9.00	0.00147
125	8.15	8.20	0.00151
190	7.58	7.50	0.00143
		Mean,	0.00147

It will be seen from Table I that the speed of oxidation was the same for a slow as for a fast current of air. This seems to be due to the fact that even the slow current supplied oxygen about 1000 times as fast as it was used up, so that the solution was always saturated with oxygen. In the last column of Table I, the values of K are those calculated by the monomolecular formula,

$$K = \frac{2.303}{t} \log_{10} \frac{a_0}{a},$$

where t is the time in minutes and a the amount of unchanged uranous salt. Table II represents a duplicate of the experiment summarized in Table I.

TABLE II.

Time.	cc. of permanganate.	K.
0	9.60	0.00244
30	8.92	0.00237
80	7.94	0.00233
145	6.84	0.00244
185	6.10	0.00260
220	5.40	
	Mean,	0.00244

Here again K is a constant; but is nearly twice as great as in the first experiment. It was found, in general, that in any single experiment, like those represented by Tables I and II, K was a good constant, but that the values of K differed capriciously in different experiments carried out with solutions prepared in separate reductions. The cause of the inconstancy was traced to differences in acid content of the reduced solutions due to difference in the extent of the interaction with the zinc used in the reduction.

We prepared a uranous sulphate solution free from zinc sulphate and containing a small known excess of sulphuric acid, by the electrolytic reduction of a solution of uranyl sulphate, a large platinum cathode and a very small anode being used.

Oxidation experiments carried out with dilute (about N/100) uranous solutions, prepared from the electrically reduced solution and containing known concentrations of free sulphuric acid, gave concordant results. Table III gives the data and results for a solution which was 0.3 *N* (equivalent) with respect to free acid.

TABLE III.

Time.	cc. of N/40 permanganate for 25 cc. uranous sol.	*K*.
0	5.32	......
10	3.02	0.0566
15	2.30	0.0567
20	1.64	0.0588
25	1.20	0.0596
30	1.10	0.0525
40	0.48	0.0596
	Mean,	0.0572

Table IV, which gives a summary of the results of several experiments, shows that the addition of an excess of sulphuric acid greatly retards the oxidation; as shown by the last column, the velocity is nearly inversely proportional to the square of the hydrogen ion concentration. The concentration of the total sulphuric acid is expressed in gram equivalents per liter.

TABLE IV.

Conc. H_2SO_4.	Conc. H ion.	*K*.	$10^5K \times H^2$.
0.30	0.164	0.0572	154
0.75	0.40	0.0110	176
1.35	0.69	0.0041	195
2.70	1.18	0.00131	182

The effect of zinc sulphate on the speed of oxidation was also tried. It was found that about 5 grams of zinc dissolve during the reduction of a uranium solution in the regular process of analysis. A solution having approximately the same uranium and sulphuric acid concentrations as solutions prepared in analyses was made from electrically reduced material. The solution was divided into two parts to one of which an amount of zinc sulphate was added corresponding to that present in solutions reduced by zinc. Oxidation experiments made with these two solutions showed that the zinc sulphate produced but a small effect, *K* being reduced about 5 per cent.

There are several possible ways to explain the fact that the speed is inversely proportional to the square of the hydrogen ion concentration.

The chemical equation $U(SO_4)_2 + H_2O + O \longrightarrow UO_2SO_4 + H_2SO_4$ becomes $U^{\cdot\cdot\cdot\cdot} + O'' + O \longrightarrow UO_2^{\cdot\cdot}$ or $U^{\cdot\cdot\cdot\cdot} + 2OH' + O \longrightarrow UO_2^{\cdot\cdot} + H_2O$ if expressed in simplest terms, as ions. According to either of the ionic equations, the oxidation should be of the first order provided the acidity of the solution and the concentration of the free oxygen are constant. The speed should be proportional, also, to O'' or to OH^1 and therefore, in either case, inversely proportional to H^2 since $H^2 \times O$ = a constant and $H \times OH$ = a constant.

However, it is possible that it is not uranous ion but uranous hydroxide, formed by hydrolysis, which is the active reducing agent. If so, the addition of free acid would suppress hydrolysis and so decrease the speed of oxidation. This view is in harmony with that held by Manchot[1] in the analogous case of the oxidation of ferrous solutions by free oxygen and by hydrogen peroxide, where it was found that the rate of oxidation was diminished by free acids and accelerated by salts of weak acids. But it is scarcely profitable to attempt a critical discussion of the mechanism of this oxidation without a more exhaustive study of the problem.

The oxidation-reduction potential of a solution is also a measure of its oxidizing or reducing power.[2] The potential difference, π, between a solution and an immersed platinum electrode is a function of the concentrations of both the oxidized and reduced forms of the electrolyte. For a solution of uranous and uranyl salts, the function takes the form

$$\pi = \pi_0 + \frac{\mathrm{RT}}{2 \times 96600} \log_e \frac{UO_2}{U} = \pi_0 + 0.0298 \log_{10} \frac{UO_2}{U}.$$

The second term becomes zero when the concentrations UO_2 and U are equal, in which case π_0 is the observed potential difference. For any pair of oxidized and reduced forms π_0 is therefore the characteristic constant.[3] This constant for uranium solutions was determined by a series of measurements made for us by Mr. Albert W. Evans, to whom we wish here to express our thanks. Mixtures of uranous and uranyl sulphate, which were 0.125 molar with respect to free sulphuric acid and 0.0493 molar with respect to uranium were made from uranyl sulphate and the electrolytically reduced uranous solution previously mentioned. The potential differences between such solutions and a platinized electrode were measured by the aid of a decinormal calomel electrode, the potential of which, at the temperature of the experiments, 27.5°, was taken as 0.6206 volt. The results are shown in Table V.

The mean value of π_0 for uranium solutions in the presence of 0.125 molar free sulphuric acid is +0.615 volt. For iron, Peters found +0.987 for neutral solutions and +0.984 in the presence of 0.05 molar hydrochloric acid. The much lower value for uranium than for iron is in complete accord with the much greater velocity of oxidation by air of uranous than ferrous solutions.

---

[1] *Z. anorg. Chem.*, **27**, 418; *Ber.*, **34**, 2489 (1901).

[2] Bancroft, *Z. physik. Chem.*, **10**, 387 (1892); **14**, 228 (1894).

[3] Peters, *Z. physik. Chem.*, **26**, 193 (1898).

TABLE V.

Percentage of uranyl salt.	Percentage of uranous salt.	Observed e. m. f. against N/10 calomel electrode.[1]	π = e. m. f. of uranium electrode.[1]	π_0.
48.4	51.6	—0.0098	+0.611	+0.612
61.9	38.1	—0.0020	0.619	0.612
68.7	31.3	+0.0020	0.623	0.612
78.6	21.4	0.0118	0.632	0.616
82.8	17.2	0.0138	0.634	0.614
89.5	10.5	0.0235	0.644	0.616
90.7	9.3	0.0254	0.646	0.616
99.8	0.2	0.0464	0.667	0.617
			Mean,	0.615

The Volumetric Determination of Uranium.—The effect of atmospheric oxidation of uranous solutions during the process of analysis may now be considered. The reduced solution, diluted by the wash water, is usually about 1.5 N with respect to free sulphuric acid. At 25°, such a solution, kept saturated with air, would oxidize at the rate of about 0.3 per cent. per minute. However, the warm solution (at say 40°) resulting from the hot reduced solution and the cold wash water might oxidize at a different rate when exposed to air in a dish preparatory to titration; the smaller solubility of oxygen to the higher temperature and the necessarily unsaturated condition of the solution with respect to oxygen would offset more or less the greater activity due to higher temperature. Kern[2] prevented oxidation of the uranous solution by air by working in atmosphere of carbon dioxide; but Pulman[2] found that the reduction with zinc and sulphuric acid may go somewhat beyond the uranous stage and that high values were obtained by working according to Kern. Pulman concluded that contact with the air after reduction is necessary to reoxidize to the uranous condition the portion reduced to the trivalent stage. Goettsch[2] has confirmed Pulman's observation.

We have also found that one per cent. or more of the uranium is in the trivalent form at the time of titration, if the solution, reduced in the usual way, is filtered in an atmosphere of carbon dioxide.

It would now appear that to get exact analytical results it is necessary to start the titration at just that moment when the atmospheric oxidation of the trivalent uranium is complete and that of the tetravalent form has not progressed to a measurable extent. The first oxidation is certainly very rapid compared with the second; and it seems possible, with some experience, to hit this intermediate point with fair accuracy, as several chemists have found.

As our kinetic experiments show, the speed of the atmospheric oxidation is greatly decreased by increasing the acidity of a uranous solution.

---

[1] The sign is that of the platinum electrode in the uranium solution.

[2] *Loc. cit.*

In accord with this, we have found that, in analyses, if 3 N sulphuric acid is used, instead of water, to wash the zinc, after the reduction, and to dilute the solution, the oxidation of the uranous salt by air is negligible. The method of procedure was as follows: 50 cc. of pure uranyl sulphate solution (= about 0.3 g. uranium), 55 cc. of water and 20 cc. of concentrated sulphuric acid (sp. gr. 1.84) were poured upon 100 g. of pure zinc,[1] in sticks 2 cm. long. The solution was heated nearly to boiling, so that there were 5 or 6 mm. of foam on top. During the first two or three minutes the solution changes in color from yellow to green; and within ten minutes assumes a light brown tint, due to the formation of some of the trivalent salt. After 15 min. the solution is filtered into a large porcelain dish; the zinc (of which about 95 g. remains) is washed with *cold*, dilute sulphuric acid (1 volume of concentrated acid to 10 vols. of water = about 3 normal); the final volume is made about 300 cc. The solution, which changes to sea-green in color during the filtration and washing, is titrated with N/10 permanganate. In four such experiments, the volumes of permanganate required were 25.59 cc., 25.49 cc., 25.65 cc. and 25.74 cc. These solutions, at titration, were about 4.2 normal with respect to free acid, at which concentration the velocity of oxidation by atmospheric oxygen is quite small.

The constancy of the foregoing analytical results also indicated the probable accuracy of the method of procedure. In a second series of determinations, 25 cc. portions of a new uranyl sulphate solution, each mixed with 80 cc. of water and then acidified and reduced as described, required 22.83 cc., 22.70 cc., 22.76 cc. and 22.85 cc. of 0.0997 normal permanganate (standardized with pure iron wire). Duplicate 25 cc. portions of the uranyl solution, evaporated and ignited, gave 0.3193 g. and 0.3198 g. of U_3O_8 respectively. The mean weight of uranium in 25 cc. is 0.2708 g. by the volumetric method instead of 0.2710 g. as calculated from the weight of U_3O_8 found.

The separation of uranium from the elements usually accompanying it in minerals is probably best accomplished by the precipitation of the uranium as phosphate. The method has been studied by Brearley[2] and tested in practice by Boltwood[3] and by McCoy and Ross.[4] The latter have found that instead of igniting and weighing the uranium phosphate it may be dissolved in sulphuric acid and determined volumetrically. Heretofore, the volumetric method of determining uranium has not been found wholly satisfactory, for reasons already discussed.

---

[1] The zinc was made active by preliminary treatment with acid containing a little copper sulphate.

[2] "Analytical Chemistry of Uranium" (1903).

[3] *Phil. Mag.*, 9, 603.

[4] *Am. J. Sci.*, 21, 440 (1906).

But now, since the main source of error seems to have been overcome, there appears to be no reason why the volumetric determination of uranium in minerals should present any difficulty.

THE SEPARATION OF TIN AND ANTIMONY.

BY LEROY W. MCCAY.

Received December 26, 1908.

The action of hydrogen sulphide on hydrofluoric acid solutions of arsenic, antimony, tin, and other heavy metals, has been studied by Arthur A. Noyes.[1] He found that although hydrogen sulphide has no action on a solution of stannic fluoride containing free hydrofluoric acid, it does precipitate antimony partially from a similar solution of antimony fluoride. He says nothing about the action of the gas on hydrofluoric acid solutions of arsenic, antimony and tin, *when these elements are present in their different states of oxidation.* His experimental work led him to conclude that it is not possible to separate quantitatively tin and antimony in hydrofluoric acid solution with hydrogen sulphide. My experimental work goes to show that when the hydrofluoric acid solution contains all the tin in the stannic, and all the antimony in the antimonious state, it is possible, by a proper regulation of the conditions, to separate the two elements quantitatively with hydrogen sulphide.

When a current of hydrogen sulphide is passed into (1) a moderately dilute solution of antimonious fluoride, containing some free hydrofluoric acid, or into (2) a moderately dilute solution of an antimonious compound which has been rendered alkaline with sodium hydroxide and then strongly acidified with hydrofluoric acid, the antimony is *almost* completely precipitated as antimonious sulphide. If, however, either solution be mixed with large amounts of sodium acetate, the hydrogen sulphide precipitates the antimony as antimonious sulphide so completely that mere traces of the element remain dissolved. Some colorimetric determinations based on the observation that hydrogen sulphide produces in exceedingly dilute solutions of antimonious compounds a light yellow color, the intensity of which is proportional to the amount of the metal present, indicate that the filtrate from the antimonious sulphide, precipitated from a hydrofluoric acid solution in which large amounts of sodium acetate have been dissolved, contains approximately four-tenths of a milligram of antimony per liter. The determinations were made as follows:

The fluorides in the filtrates from the antimonious sulphide were converted into sulphates by evaporation with concentrated sulphuric acid, and from a solution of the latter salts the traces of antimony were re-

---

[1] A System of Qualitative Analysis, including nearly all the Metallic Elements, Part II, *Tech. Quart.*, 17, 214 (1904).