[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

The Polarography of Uranium. I. Reduction in Moderately Acid Solutions. Polarographic Determination of Uranium

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This paper will be confined to a discussion of the polarography of uranium in moderately acid solutions and to applications of the findings to the polarographic determination of uranium. Several complications in the polarographic determination of uranyl arise when dealing with solutions which contain no free acid, or only minute amounts of acid, and also in the presence of very large amounts of acid. These more complicated cases will be discussed in subsequent papers.

A procedure is also given for the polarographic determination of traces of uranium. This method is based on the catalytic effect of uranium on the polarographic nitrate reduction.

Herasymenko[2] published the first account of the polarographic reduction of uranium. He found three reduction waves of uranium in neutral or weakly acid medium with half wave potentials of about −0.15, −0.8 and −1.0 v. *vs.* S.C.E. (S.C.E. designates the saturated calomel electrode). In not too acid medium he observed that each of the three successive diffusion currents were of the same magnitude, and he concluded that the three reduction waves corresponded to the reduction of the U^{6+} (UO_2^{++}) to the +5, +4 and +3 states. He supported these assumptions by photochemically reducing a uranyl solution to the quadrivalent state. A current voltage curve of this reduced uranium solution gave very small first and second reduction waves while the magnitude of the third wave was the same as before reduction.

Herasymenko found that the "reduction potential" of the first wave was independent of the acidity of the solution, but that it varied with the concentration of the uranyl salt in solution. Half wave potentials were not considered by him. Strubl[3] found that in a medium of 2 *N* hydroxylamine hydrochloride two polarographic reduction waves of uranium were obtained with half wave potentials of −0.28 and −1.08 v. *vs.* S.C.E. The diffusion current of the first wave was found to be directly proportional to the concentration of uranium present. On the other hand, the diffusion current of the second wave was not proportional to the uranium concentration and the height of the second wave was about two and one-half times as great as that of the first. No interpretation of this anomaly was offered.

Recently Carruthers[4] in connection with a micromethod for the quantitative determination of sodium determined uranyl uranium polarographically in 0.5 *M* hydrochloric acid by measuring its diffusion current at −0.5 v. *vs.* S.C.E. He mentions only one polarographic reduction wave with a half wave potential of −0.22 to −0.26 v. *vs.* S.C.E., and states that the diffusion current of the first wave is proportional to the concentration. However, an examination of his data shows an increasing value of the ratio i_d/c with increasing concentration of uranium.

Kolthoff and Cohn[5] in connection with the determination of phosphate determined the diffusion current of uranium in solutions containing acetic acid and sodium acetate. They found that proportionality between diffusion current and concentration became better as the amount of acetic acid in solution was increased. The current voltage curves obtained in general gave poorly defined diffusion currents at the relatively high *p*H of their solutions.

Experimental

Qualitative observations and work of an exploratory nature were carried out with the aid of a type IX Heyrovsky recording polarograph. For quantitative measurements the manual method for obtaining current voltage curves was used.[6] The saturated calomel electrode was used as reference electrode and as anode.[7]

Prior to making polarographic measurements all solutions were made air-free by bubbling purified nitrogen through them. All solutions were made by dilution with conductance water and all experiments were carried out in a thermostat at 25.0 ± 0.1°.

The current voltage curves of uranium salts were often found to give acute maxima similar to those found with many other substances. These maxima were readily eliminated by making the solution about 10^{-4}% in thymol. In cases where agar was used in the salt bridge the addition of thymol was unnecessary for the elimination of maxima. Unless stated otherwise a capillary was used consisting of a 14-centimeter length of Corning marine barometer tubing, with $m^{2/3}t^{1/6}$ = 2.70 mg.$^{2/3}$ sec.$^{-1/2}$ at −0.4 v. Diffusion currents obtained at potentials other than −0.4 v. have been corrected for the change of $m^{2/3}t^{1/6}$ with potential.[8] All the values of the current reported have been corrected for the residual current.

Materials

Uranyl Chloride.—Solutions in conductivity water of two samples of uranyl chloride, one from Eimer and Amend and another of unknown origin, were analyzed for uranium by the method of Kolthoff and Lingane.[9]

Uranous Sulfate.—To an approximately 0.5 *M* solution of uranyl sulfate, made by heating uranyl acetate to fum-

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(1) From a thesis submitted by W. E. Harris to the Graduate School of the University of Minnesota in partial fulfillment of the requirements for the Ph.D. degree, June, 1944.

(2) P. Herasymenko, *Trans. Faraday Soc.*, **24**, 272 (1928).

(3) R. Strubl, *Coll. Czechoslov. Chem. Commun.*, **10**, 466 (1938).

(4) C. Carruthers, *Ind. Eng. Chem., Anal. Ed.*, **15**, 70 (1943).

(5) I. M. Kolthoff and G. Cohn, *ibid.*, **14**, 412 (1942).

(6) I. M. Kolthoff and J. J. Lingane, *Chem. Rev.*, **24**, 1 (1939).

(7) D. N. Hume and W. E. Harris, *Ind. Eng. Chem., Anal. Ed.*, **15**, 465 (1943).

(8) I. M. Kolthoff and E. F. Orlemann, THIS JOURNAL, **63**, 2085 (1941).

(9) I. M. Kolthoff and J. J. Lingane, *ibid.*, **55**, 1871 (1933).

ing with excess sulfuric acid, alcohol was added to about 40%. After this had stood several days in sunlight to bring about photochemical reduction, the resulting uranous sulfate precipitate was washed several times with alcohol and air dried. For analysis, 0.2- to 0.3-g. samples were dissolved in 5 ml. of 85% phosphoric acid and after cooling 50 ml. of 2 *N* sulfuric acid and 5 ml. of 4% ferric chloride in 2 *N* sulfuric acid were added and the solution titrated with 0.1 *N* potassium dichromate using two drops of diphenylamine sulfonate as indicator. These analyses showed 49% tetravalent uranium, which corresponds approximately to the 48.2% calculated for the salt $UOSO_4 \cdot 8H_2O$.

A. Polarography of Uranyl Chloride in Moderately Acid Solutions

The shape of the current voltage curve shown in Fig. 1 is one typical of a dilute uranium solution containing a moderate concentration of hydrochloric acid (10^{-2} to 0.2 *M*). The two polarographic waves A and B correspond to reductions of uranium and the third rising portion C of the curve corresponds to the discharge of hydrogen. The half wave potentials of the first and second waves in Fig. 1 are designated as $E'_{1/2}$ and $E''_{1/2}$, respectively, and the diffusion currents of the first and second waves as i'_d and i''_d, respectively. The diffusion current at about −1.2 v. *vs.* S.C.E. has been designated $i_{d_{total}}$ and is the sum of the diffusion currents of the first and second waves.

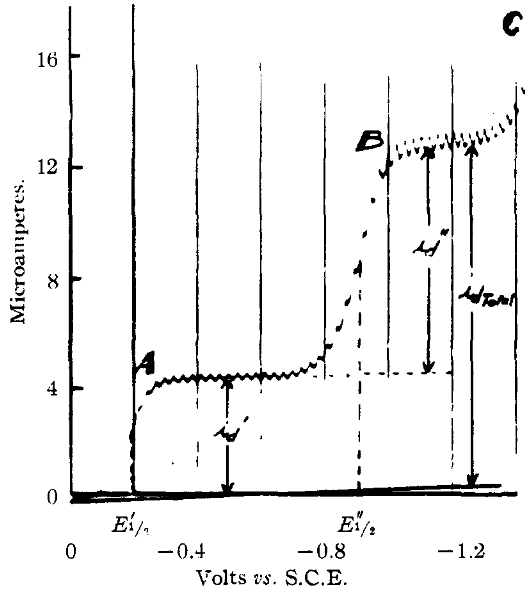

Fig. 1.—A typical polarogram of uranyl chloride in moderately acid solution: 10^{-3} *M* uranyl chloride, 0.1 *M* hydrochloric acid, 10^{-4} % thymol.

Analysis of the Reduction Waves.—The equation of the polarographic wave derived by Heyrovsky and Ilkovic[10] has been applied to the uranium reduction waves. Figure 2 is a typical example of a log $i(i_d - i)$ *vs.* $E_{d.e.}$ plot. In agreement with equation 1 the experimental points fall on a straight line for the first reduction. The slope of the line is 0.062 v. which is in close agreement with the theoretical value of 0.059 for $n = 1$. On the other hand, the experimental points of the second reduction do not fall upon a straight line (see Fig. 2). As became apparent in later work one reason for this deviation from a straight line is that the second reduction wave is composed of two separate reduction waves both with very nearly the same half wave potentials.

$$E_{d.e.} = E_{1/2} - \frac{0.0591}{n} \log \frac{i}{i_d - i} \qquad (1)$$

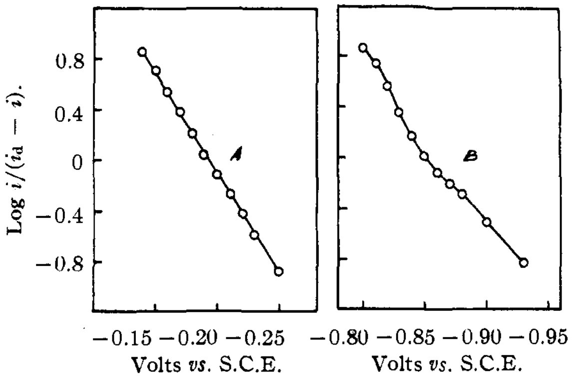

Fig. 2.—Analysis of uranyl chloride polarographic waves in moderately acid solution: 10^{-3} *M* uranyl chloride, 0.1 *M* hydrochloric acid, 1.0 *M* potassium chloride: A is analysis of the first wave; B is analysis of the second wave.

Calculation of the Diffusion Coefficient of UO_2^{++} from Polarographic Data.—When a value of 4.08 microamperes per millimole per liter for the first diffusion current of uranium (see Table IV), a capillary constant $m^{2/3}t^{1/6}$ equal to 2.70 mg.$^{2/3}$ sec.$^{-1/2}$ and $n = 1$ are substituted in the Ilkovic equation

$$i_d = 605nD^{1/2}\text{cm.}^{2/3}T^{1/6} \qquad (2)$$

a value of $D_{UO_2^{++}} = 0.62 \times 10^{-5}$ cm.^{2} sec.$^{-1}$ is found. For $n = 2$ the value $D_{UO_2^{++}}$ would be 0.15×10^{-5} cm.^{2} sec.$^{-1}$. The value of the diffusion coefficient 0.62×10^{-5} cm.^{2} sec.$^{-1}$ is in fair agreement with the value of 0.5×10^{-5} cm.^{2} sec.$^{-1}$ estimated from measurements of the conductance of uranyl chloride solutions.[1] The value of the diffusion coefficient of the uranyl ion calculated from the first diffusion current provides almost conclusive evidence that only one electron is involved in the first polarographic reduction wave. Calculation of the conductance[11] at infinite dilution from the diffusion coefficient yields

$$D_{UO^{++}} = \frac{RT}{2Fy^2} \lambda_{UO_2^{++}} \qquad (3)$$

a value of 46.5 ohm^{-1} sec.^{2} equiv.$^{-1}$ for the equivalent ionic conductance uranyl ion, which seems reasonable.

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[10] J. Heyrovsky and D. Ilkovic, *Coll. Czechoslov. Chem. Commun.*, **7**, 198 (1935).

[11] I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Publishers, Inc., New York, N. Y., 1941.

Half-Wave Potential.—The dependence of the half-wave potentials $E'_{1/2}$ and $E''_{1/2}$ upon hydrogen, chloride and uranyl ion concentrations has been investigated and the results are shown in Table I.

TABLE I

HALF WAVE POTENTIALS (*vs.* S.C.E.) OF URANIUM AT VARIOUS HYDROGEN AND URANIUM ION CONCENTRATIONS

Uranyl chloride, moles/liter	Indifferent electrolyte	$E'_{1/2}$, volt	$E''_{1/2}$, volt
10^{-3}	0.01 *N* HCl 0.1 *N* KCl	−0.179	−0.93
10^{-3}	0.1 *N* HCl	− .183	− .94
10^{-3}	0.5 *N* HCl	− .202	− .92
10^{-3}	1.5 *N* HCl	− .213	....
2×10^{-3}	0.01 *N* KCl	− .173	....
2×10^{-3}	0.1 *N* KCl	− .180	....
2×10^{-3}	1.0 *N* KCl	− .192	....
2.07×10^{-4}	0.01 *N* HCl 0.1 *N* KCl 2×10^{-4}% thymol	− .188	− .92
3.43×10^{-4}		− .181	− .91
6.72×10^{-4}		− .175	− .90
1×10^{-3}		− .179	− .93
1.536×10^{-3}		− .180	(− .88)
3.36×10^{-3}		− .182	− .93

Neither $E'_{1/2}$ nor $E''_{1/2}$ changes with concentration of uranium while $E''_{1/2}$ is independent of hydrochloric acid concentration and $E'_{1/2}$ is practically independent. The slight shift to more negative values with increasing acid present is in the opposite direction to that which one would expect if hydrogen ions were involved in the electrode reaction.

Ratio of Two Reduction Wave Heights.—The ratio i''_d/i'_d of the two reduction waves of uranium has been determined for a number of concentrations of uranyl chloride and has been found to be approximately two (see Table II). This indicates that twice as many electrons are involved during the second reduction as during the first reduction.

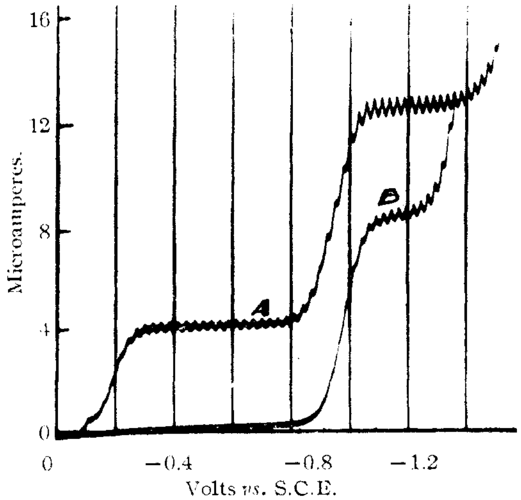

Fig. 3.—Polarograms of hexavalent and tetravalent uranium: A, polarogram of 10^{-3} *M* uranyl chloride, 0.1 *M* potassium chloride, 0.01 *M* hydrochloric acid; B, polarogram of 2.08×10^{-3} *M* uranous sulfate, 0.1 *M* potassium chloride, 0.1 *M* hydrochloric acid.

TABLE II

RATIO i''_d/i'_d OF UO_2Cl_2 IN SOLUTION CONTAINING 0.1 *N* KCl, 0.01 *N* HCl, 2×10^{-4}% THYMOL

Uranyl chloride, moles/liter	i_d at −0.5 v., microamp.	i_d total at −1.0 v., microamp.	i''_d, microamp.	i''_d/i'_d
2.07×10^{-4}	0.90	2.69	1.79	1.99
3.43×10^{-4}	1.46	4.46	3.00	2.05
4.80×10^{-4}	2.00	6.66	4.66	2.32
6.72×10^{-4}	2.73	8.52	5.79	2.11
9.18×10^{-4}	3.73	11.62	7.89	2.10
9.46×10^{-4}	3.82	12.08	8.16	2.13

B. Polarography of Uranous Sulfate in Moderately Acid Solutions

A solution of uranous sulfate in acid medium gives only one polarographic reduction wave, which has the same half wave potential as that of the second one of uranyl chloride. Figure 3 shows the relationship between the polarograms of uranyl chloride and uranous sulfate. No anodic or oxidation wave is given by uranous sulfate to at least a potential of +0.4 v. at the dropping mercury electrode.

Half Wave Potential.—From Table III it appears that the half wave potential in the reduction of tetravalent uranium is independent of hydrogen ion concentration, while it appears to be shifted toward slightly more negative values with increasing uranous ion concentration. This non-constancy of half wave potential is probably due to irreversibility of the reaction.

TABLE III

DEPENDENCE OF HALF WAVE POTENTIAL OF URANOUS SULFATE UPON HYDROGEN AND URANOUS ION CONCENTRATIONS

Uranous sulfate, moles/liter	Concn. of acid, *N*	$E_{1/2}$ volts *vs.* S.C.E.	i_d at −1.15 v., microamp.	i_d, in microamp. per mm./liter
8×10^{-4}	0.1 $HClO_4$	−0.93		
8×10^{-4}	1.0 $HClO_4$	− .93		
4.22×10^{-4}	0.1 $HClO_4$	− .92	1.52	4.29
7.22×10^{-4}	0.1 $HClO_4$	− .93	2.78	4.30
1.134×10^{-3}	0.1 $HClO_4$	− .95	4.50	4.34
1.806×10^{-3}	0.1 $HClO_4$	− .96	7.19	4.17
2.08×10^{-3}	0.1 HCl 0.1 KCl	− .96		

Diffusion Current and Analysis of the Wave.—Analysis of the reduction wave of tetravalent uranium gives a straight line whose slope is 0.08 (Fig. 4). This value of 0.08 for the slope is in poor agreement with the theoretical value of 0.059 for one electron and it indicates the irreversibility of the reduction.

The diffusion current per millimole of tetravalent uranium is 4.30 microamperes (Table III). This value is very close to the value of 4.08 microamperes per millimole obtained for the first reduction of hexavalent uranium. Hence the same number of electrons must be involved in both reactions since the diffusion coefficients of the uranyl and uranous uranium ions must be of the same order of magnitude. The fact that the diffusion current per millimole for tetravalent uranium is one-third the total diffusion current per millimole for hexavalent uranium is the most conclusive evidence that the final reduction product of both uranyl and uranous salts must be a trivalent uranium compound.

C. The Polarographic Determination of Uranium

I. Determination by Measurement of Diffusion Current in Moderately Acid Solution.—In moderately acid solution (0.01 to 0.1 *N* hydrochloric acid) the diffusion current measured at potentials in the first constant diffusion current region is proportional to the concentration of uranium. A potential of −1.2 v. *vs.* S.C.E. might be suggested as a desirable one at which to measure the diffusion current since at this potential it is three times the magnitude at −0.5 v. However, this is undesirable since a greater number of substances may interfere at this higher potential. In addition the diffusion current cannot be measured so accurately due to the discharge of hydrogen very near this potential.

As may be seen from Table IV the concentration of uranium can be varied about one hundredfold without deviation of proportionality between current and concentration beyond experimental error from the value of 4.08 microamperes per millimole per liter. Between concentrations of 5×10^{-4} and 4×10^{-3} *M* uranyl chloride, the uranium can be determined with an accuracy of about 2%.

TABLE IV

DIFFUSION CURRENT OF URANIUM (U^{6+} TO U^{5+}) AS A FUNCTION OF CONCENTRATION IN 0.1 *N* KCl, 0.01 *N* HCl, 2×10^{-4}% THYMOL

Uranyl chloride, moles/liter	Diffusion current of uranium at −0.5 v. *vs.* S.C.E., microamp.	$K = i_d/c$ Diffusion current per millimole uranyl chloride, microamp. millimole/liter
2.4×10^{-5}	0.11	4.6
1.06×10^{-4}	.44	4.15
2.07×10^{-4}	.90	4.34
3.43×10^{-4}	1.46	4.26
4.80×10^{-4}	2.00	4.16
6.72×10^{-4}	2.73	4.07
9.18×10^{-4}	3.73	4.12
9.46×10^{-4}	3.82	4.04
1.536×10^{-3}	6.25	4.07
2.366×10^{-3}	9.56	4.04
3.36×10^{-3}	13.71	4.08

For the determination of uranium in solutions in which the uranium concentration is in the range 10^{-4} to 5×10^{-3} *M* the following procedure is recommended. Prepare a stock solution which is 0.5 *M* in potassium chloride and 0.05 *M* in hydrochloric acid.

Procedure.—Measure a suitable volume of the unknown uranium solution (*p*H 2 to 3) into a 50-ml. volumetric flask and add 10 ml. of stock solution. Add enough 0.1% thymol solution to give a final concentration of about 10^{-4}% thymol (see section on interferences). Dilute to volume in the 50-ml. flask. Place the solution in a polarographic cell, make air-free with nitrogen and measure the apparent diffusion current at a potential of −0.5 v. *vs.* S.C.E. Subtract the residual current found for a solution containing no uranium. The proportionality constant, $K = i_d/c_{\text{uranium}}$ is found by determining the diffusion current of a known uranium solution.

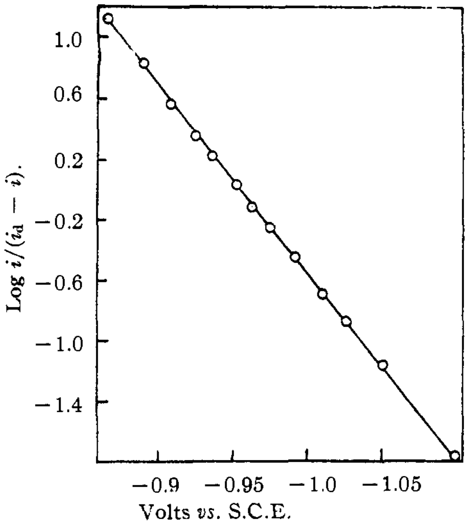

Fig. 4.—Analysis of tetravalent uranium polarographic wave in moderately acid solution: 2.08×10^{-3} *M* uranous sulfate, 0.1 *M* hydrochloric acid, 0.1 *M* potassium chloride.

Interferences.—One of the most commonly occurring reducible interfering ions is ferric ion. Strubl[8] eliminated the interference by iron by boiling with hydroxylamine hydrochloride. Ferrous iron is not reduced below potentials of about −1.3 v. *vs.* S.C.E. and so causes no interference in the determination of uranium. In this Laboratory it has been found that up to a concentration of at least 2 *M* hydroxylamine hydrochloride the diffusion current of uranium is proportional to uranyl concentration and equal in magnitude to the values shown in Table IV. It was also found that boiling with hydroxylamine hydrochloride is unnecessary to reduce the ferric iron. For example, a solution which was 0.2 *M* in ferric chloride, 10^{-3} *M* in uranyl chloride, 2 *M* in hydroxylamine hydrochloride and 10^{-4}% in thymol was merely warmed to 50° for ten minutes. The diffusion current was then determined at −0.5 v. *vs.* S.C.E. and was found to be 4.05 microamp. per millimole per liter. This is in good agreement with the value of 4.08 microamp. found in Table IV.

Basic solutions precipitate the uranium, while in neutral or very slightly acid solutions the diffusion current usually is greater than the values given in Table IV and under some conditions it is less.[1] In more strongly acid solutions than 0.2 N hydrochloric acid the diffusion current increases. In either too acid or too basic solutions the diffusion current is not proportional to the concentration.

A number of substances although not reducible or oxidizable at −0.5 v. *vs.* S.C.E. alter the characteristics of the first polarographic wave of uranium and so cause interference in its determination. Among these substances there are a large number of organic compounds, especially acids, which may change both the diffusion current and the half-wave potential. Therefore it is recommended that, before carrying out the polarographic analysis, the sample be ashed if it contains organic matter.

Thymol used as a maximum suppressor reduces the diffusion current obtained in moderately acid solution. Evidently the thymol ties up the uranium in a complex and it shifts the half-wave potential to more negative potentials.

In a 8.2×10^{-4} M uranyl chloride, 0.1 M hydrochloric acid solution containing $2 \times 10^{-4}\%$ thymol the diffusion current was 3.35 microamp. while with $10^{-3}\%$ thymol the diffusion current was 3.31 microamp. at −0.5 v. Since only about $10^{-4}\%$ to $2 \times 10^{-4}\%$ thymol is recommended for use as maximum suppressor, the error due to this amount of thymol is less than 0.01 microamp.

Carruthers[4] used caffeine as maximum suppressor and found that it reduced the diffusion current obtained in 0.5 M hydrochloric acid. In this laboratory caffeine, even in amounts up to 1%, has been found to have no serious effect upon the diffusion current measured at −0.5 v. in solutions containing 0.01 N hydrochloric acid plus 0.1 N potassium chloride. Caffeine, therefore, is probably to be preferred to thymol as a maximum suppressor in the determination of uranium.

Examination of Fig. 5 indicates that no region of constant diffusion current is obtained with uranium in the presence of 0.1 M phosphoric acid. At −0.5 v. *vs.* S.C.E. the diffusion current is about 6 microamperes instead 4.08 microamperes obtained under the recommended conditions for the determination of uranium. Also, as will be seen in a subsequent paper, the diffusion current is not proportional to the concentration of uranium in the presence of phosphoric acid. Chemical separation of the phosphate is therefore necessary before determining uranium polarographically.

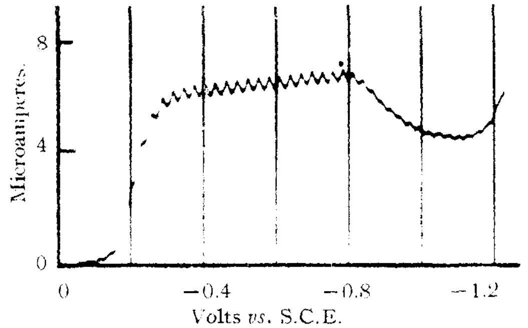

Fig. 5.—Polarogram of 10^{-3} M uranyl chloride in 0.1 M hydrochloric acid, 0.1 M phosphoric acid.

II. Determination of Very Small Amounts of Uranium by its Catalytic Effect on the Nitrate Reduction Wave

It has been reported[12] that either uranyl or uranous uranium catalyzes the reduction of nitrate at the dropping mercury electrode. Nitrate can be determined polarographically in the presence of small amounts of uranium. Use of this catalytic effect can be made in the polarographic determination of traces of uranium.

When the nitrate to uranium ratio is much greater than one there is only partial reduction of the nitrate and the polarographic reduction waves have no region of constant diffusion current (see Fig. 6). However, a small amount of uranium causes a relatively large nitrate reduction current and this reduction current can be used as a measure of the amount of uranium present if the nitrate concentration is large.

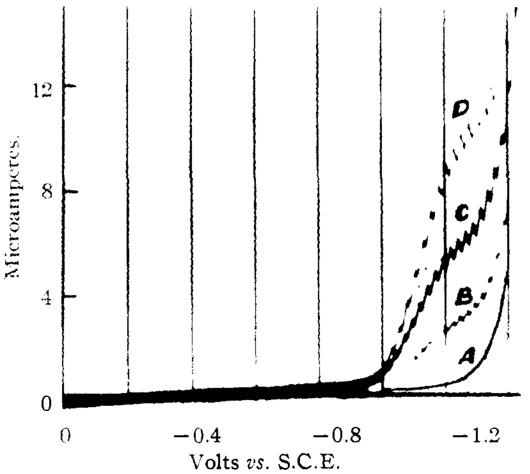

Fig. 6.—Polarogram of 10^{-3} M potassium nitrate, 0.1 M hydrochloric acid, 0.1 M potassium chloride containing varying amounts of uranyl chloride: A, no uranyl chloride; B, 2×10^{-6} M uranyl chloride; C, 10^{-5} M uranyl chloride; D, 2×10^{-5} M uranyl chloride.

The diffusion current obtained at −1.2 v. *vs.* S.C.E. is not directly proportional to the uranium concentration (see Table V). Therefore, a procedure for the determination of uranium based upon the apparent nitrate diffusion current is empirical, but it has the great advantage that the diffusion current obtained is about one hundred times the magnitude of the uranium diffusion current obtained at −0.5 v. *vs.* S.C.E. By making use of the catalytic effect the limit of polarographic determination of uranium can be extended to

(12) I. M. Kolthoff, W. E. Harris and G. Matsuyama, THIS JOURNAL, **66**, 1782 (1944).

TABLE V

"APPARENT" DIFFUSION CURRENT *vs.* CONCENTRATION OF URANIUM AT −1.2 v. *vs.* S.C.E. IN A MEDIUM OF 10^{-3} *M* KNO_3, 0.1 *M* KCl, 0.01 *M* HCl

Uranyl chloride, moles/liter	Diffusion current at −1.2 v. *vs.* S.C.E., microamp.	Diffusion current per millimole of uranyl chloride, microamp./millimole
3.1×10^{-7}	0.26	840
9.6×10^{-7}	0.62	650
1.90×10^{-6}	1.10	580
3.09×10^{-6}	1.66	537
4.64×10^{-5}	2.33	503
7.30×10^{-6}	3.29	462
9.50×10^{-6}	4.32	455
1.261×10^{-5}	5.56	441
1.654×10^{-5}	6.88	416
2.11×10^{-5}	8.31	396
2.58×10^{-5}	9.71	377

concentrations as small as 10^{-6} or 10^{-7} molar (see Fig. 7).

For the determination of uranium in solutions in which the final uranium concentration is in the range of 10^{-6} *M* to 3×10^{-5} *M*, the following procedure is recommended. Prepare a stock nitrate solution which is 0.005 *M* potassium nitrate, 0.5 *M* potassium chloride and 0.05 *M* hydrochloric acid.

Procedure.—Measure a suitable volume of unknown uranium solution into a 50-ml. volumetric flask and add 10 ml. of stock nitrate solution. Dilute to volume and make the resulting solution air-free in a polarographic cell. Measure the diffusion current at −1.2 v. *vs.* S.C.E. Subtract the residual current found for a solution containing no uranium to obtain the "apparent" diffusion current due to uranium.

The amount of uranium in solution is found from a calibration curve (see Fig. 7), with known amounts of uranium. For most purposes a satisfactory calibration curve can be drawn from the "apparent" diffusion currents obtained at the following uranium concentrations: 0, 2×10^{-6}, 5×10^{-6}, 10^{-5}, 2×10^{-5} and 3×10^{-5} *M*.

Since the interferences in this determination, in general, will be the same as in the polarographic determination of nitrate, reference is made to our previous paper.[12]

Discussion

From the foregoing experimental evidence presented in Sections A and B, there seems little doubt that the first polarographic reduction of a uranyl salt involves one electron as Herasymenko had already concluded. Furthermore, since the half wave potential of the reduction is independent of hydrogen ion concentration the first reduction must be according to the reaction

$$UO_2^{++} + e \longrightarrow UO_2^{+} \qquad (4)$$

The half-wave potential found for this reaction is −0.18 v. (*vs.* S.C.E.) which agrees fairly well with the values found by Herasymenko[2] but it is

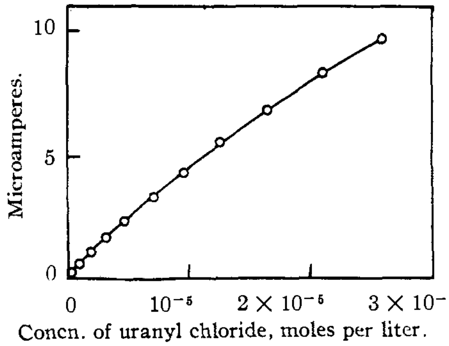

Fig. 7.—Relation between concentration of uranyl chloride in 10^{-3} *M* potassium nitrate, 0.1 *M* potassium chloride, 0.01 *M* hydrochloric acid and diffusion current at −1.2 v. *vs.* S.C.E.

more positive than the value of −0.28 v. reported by Strubl[3] and the value of −0.22 to −0.26 reported by Carruthers.[4] The half-wave potential does not agree with the value of +0.16 v. of the oxidation potential of a mixture of uranous and uranyl salt solution at the platinum electrode. This difference indicates a different reaction mechanism at the platinum and mercury electrodes since Treadwell[13] finds the oxidation potential at the platinum electrode to be dependent upon hydrogen ion concentration according to the equation

$$UO_2^{++} + 2H^+ + 2e \rightleftarrows UO^{++} + H_2O \qquad (5)$$

However, we do not find the uranyl–uranous potential reversible at a platinum electrode. Little can be said of the second reduction wave except that there are two electrons involved in the reaction or reactions occurring during this reduction.

From the fact that the half wave potential of the uranous reduction to trivalent uranium is independent of the concentration of hydrogen ion, it is concluded that the potential determining reaction is not represented by the equation

$$UO^{++} + 2H^+ + e \rightleftarrows U^{3+} + H_2O \qquad (6)$$

It seems more plausible that the first step of the reaction is either

$$UO^{++} + e \longrightarrow UO^{+} \qquad (7)$$

or

$$UOOH^{+} + e \longrightarrow UOOH \qquad (8)$$

and that the UO^+ or UOOH reacts with hydrogen ions present to form trivalent uranium.

Summary

1. A polarogram of uranyl chloride in 0.01 to 0.2 *M* hydrochloric acid shows two distinct reduction waves. The first wave corresponds to a reduction of U^{6+} to U^{5+} and the second to a reduction of U^{5+} to U^{3+}. The equation of the first polarographic wave corresponds to an electron

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[13] W. D. Treadwell, *Helv. Chim. Acta*, **5**, 732 (1922).

transfer of one. The second wave corresponds to an irreversible reduction.

2. The half-wave potential of the first wave in 0.01 to 0.1 *N* hydrochloric acid is −0.18 v. (*vs.* S.C.E.). Its value is independent of the uranyl concentration and is hardly affected by the acidity of the solution or the concentration of potassium chloride. The half-wave potential of the second wave is −0.92 v.; it is independent of the uranium and hydrochloric acid concentration in the solution. The independency of both half wave potentials of the acidity indicates that hydrogen ions are not involved in the electrode reactions. An explanation of this fact has been presented.

3. The diffusion coefficient of the UO_2^{++} at 25° ion has been calculated to be 0.62×10^{-5} cm.^{2} sec.$^{-1}$. This corresponds to a mobility of the uranyl ion of 46.5 ohm^{-1} sec.^{2}.

4. Uranous uranium in 0.1 *N* HCl gives one reduction wave corresponding to a reduction of U^{4+} to U^{3+}. The half wave potential is equal to that of the second uranyl wave.

5. For the polarographic determination of uranyl it is recommended that the first diffusion current be measured at a potential of −0.5 v. (*vs.* S.C.E.) in 0.01 to 0.1 *N* hydrochloric acid. The solution contains $10^{-4}\%$ thymol as an eliminator of the maximum. The diffusion current was found proportional to the uranyl concentration in a range between 5×10^{-4} and 4×10^{-3} *M*. Ferric iron is made harmless by warming the solution at 50° for ten minutes with an excess of hydroxylamine hydrochloride.

6. Use is made of the catalytic effect of uranium upon the polarographic reduction of nitrate. An empirical procedure has been developed which allows the polarographic determination in a concentration range between 2×10^{-7} and 3×10^{-5} *M*.

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[CONTRIBUTION OF THE COÖPERATIVE X-RAY LABORATORY, UNIVERSITY OF PITTSBURGH]

X-Ray Diffraction Studies of Anhydrous Sodium and Potassium Ferric Sulfates. I. The Disulfates and Trisulfates[1]

BY RICHARD C. COREY[2] AND S. S. SIDHU[3]

When a mixture of sodium or potassium sulfate and ferric oxide is exposed to dry sulfur trioxide, the entire system being at 538°, a change of phase occurs. This transition is indicated by an increase in weight and a noticeable change in color of the reaction product. For a given mixture the equilibrium percentage increase of weight is constant for partial pressures of sulfur trioxide between 0.15 to 0.50 mm. Neither sodium nor potassium sulfate, nor ferric oxide alone undergoes any such changes under the same conditions of temperature and range of partial pressures of sulfur trioxide. An X-ray diffraction pattern of the reaction product is entirely different from either of the original constituents.

This paper gives (1) the identification of the unknown phase formed, and (2) the methods for the preparation of the anhydrous alkali metal ferric sulfates and their X-ray diffraction data used for the identification of the newly formed phase.

Experimental

Alkali metal ferric disulfates and trisulfates were prepared by two methods. In the first method the sulfates were crystallized from solution and heated to a relatively high temperature, and in the second method they were obtained from a solid–solid reaction between the anhydrous salts at a high temperature.

The equations for the reactions involved in the first method are as follows

$$M_2SO_4 + Fe_2O_3 + 3H_2SO_4 \longrightarrow 2MFe(SO_4)_2 + nH_2O \quad (1)$$

$$3M_2SO_4 + Fe_2O_3 + 3H_2SO_4 \longrightarrow 2M_3Fe(SO_4)_3 + nH_2O \quad (2)$$

where M = Na or K

Reagent grade anhydrous Na_2SO_4, K_2SO_4, Fe_2O_3 and concentrated H_2SO_4 in the proper mole proportions were mixed in water, evaporated to dryness and the final product heated to a constant weight at 300°. The proportions that were used are given in Table I.

TABLE I

MOLE PROPORTIONS OF ANHYDROUS Na_2SO_4, K_2SO_4, Fe_2O_3 AND SO_3 FOR PREPARATION OF ALKALI METAL FERRIC SULFATES

Compound	Materials used	Moles	Wt. %
$NaFe(SO_4)_2$	Na_2SO_4	1	26.2
	Fe_2O_3	1	29.5
	SO_3	3	44.3
$KFe(SO_4)_2$	K_2SO_4	1	30.7
	Fe_2O_3	1	27.8
	SO_3	3	41.5
$Na_3Fe(SO_4)_3$	Na_2SO_4	3	51.6
	Fe_2O_3	1	19.3
	SO_3	3	29.1
$K_3Fe(SO_4)_3$	K_2SO_4	3	56.7
	Fe_2O_3	1	17.3
	SO_3	3	26.0

For each mole of sulfur trioxide required, 55 ml. of concentrated sulfuric acid was used. This amount was slightly in excess of the stoichiometric requirement, but it was used to minimize hydrolysis.

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