Griffiths[38] appear to be the best; they give 216 and 218 cal. per gram atom, respectively. The agreement between these directly determined values and that computed from the equilibrium measurements is surprisingly good; the discrepancy (shown by Table VII) at the lower temperatures is felt to be due in large part to the great uncertainty in the heat capacity of the two forms of iron in this region.

The heat of solution of graphite in γ-iron may also be determined with the aid of equation 19 and the relation

$$\Delta H_s = -4.575\, d \log a_2/d\,(1/T)$$

where a_2 is activity of carbon in the austenite in equilibrium with graphite and is relative to a standard state such that $a_2 = n_2/n_1$ at infinite dilution. A plot of log a_2 *vs.* $1/T$ for the experimentally determined values of the solubility of graphite is shown in Fig. 10. The slope of this line corresponds to a heat of solution of 9800 cal. in satisfactory agreement with the value (10,100 cal.) obtained previously by a different method.

Summary

By determination of the carbon content of an iron phase which had been definitely equilibrated with one of a series of gas mixtures, each of constant composition, the following equilibria were measured: CH_4–H_2 mixtures with ferrite at 750 and 800°, with austenite at 800 and 1000°, and with graphite at 800 and 1000°; CO–CO_2 mixtures with austenite at 800, 1000 and 1200°, and with graphite at 800 and 1000°.

The limiting solubility of carbon in ferrite at 750 and 800° was found to be 0.020 and 0.0128 weight per cent., respectively, both of which are lower than the data commonly accepted hitherto. Austenite at its lower limit of stability at 800° contains 0.319 ± 0.004% carbon, in good accord with the results of dilatometric measurements.

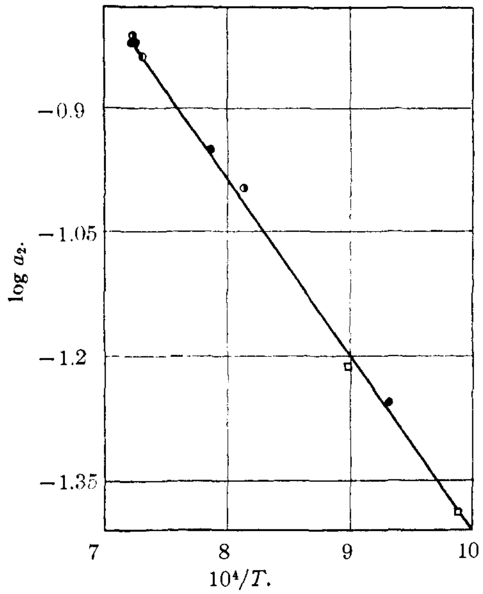

Fig. 10.—Plot of logarithm of activity of carbon in austenite at equilibrium with graphite against $10^4/T$, based on the following solubility measurements: ● Smith, average value of carbon content, determined from plot of austenite equilibria, at which $r_1 = r_1'$ and $r_2 = r_2'$; □ Wells; ◐ Gurry, equilibrium with graphite; ◑ Gurry, equilibrium with carbon from toluene.

The experimental results permitted direct calculation of the activity of carbon in austenite relative to graphite as unity and of the heat of solution of graphite in ferrite and in austenite. There is a slight apparent difference in activity according as it is calculated from the results with one or the other pair of gases; its source is still uncertain.

In the appendix an analytic expression, based on statistical considerations, is developed which reproduces satisfactorily the measurements of activity of carbon in solid solution in γ-iron, austenite, as a function of its concentration.

KEARNY, N. J. RECEIVED JANUARY 8, 1946

---

[38] J. H. Awbery and E. Griffiths, *Proc. Roy. Soc.* (London), **174**, 1 (1940).

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

The Polarography of Uranium. II. Polarography in Strongly Acid Solution[1]

BY I. M. KOLTHOFF AND W. E. HARRIS

In a previous paper[2] the polarography of hexavalent uranium in 0.01 to 0.2 *N* hydrochloric acid was discussed. Two reduction waves were obtained, the first one corresponding quantitatively to the reduction of hexavalent uranium to the pentavalent state and the second to the reduction to the trivalent state.

Herasymenko[3] briefly states that a high concentration of strong acid in the uranyl solution changes the relative magnitudes of the reduction waves obtained. He attributes this to a decomposition of pentavalent uranium into hexavalent and tetravalent uranium, the hexavalent uranium formed being reduced at the dropping electrode. We have made a systematic study of the effect of acidity on the polarographic waves of uranyl uranium. The first diffusion current

---

[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] W. E. Harris and I. M. Kolthoff, THIS JOURNAL, **67**, 1484 (1945).

[3] P. Herasymenko, *Trans. Faraday Soc.*, **24**, 272 (1928).

was found to increase with increasing acidity. Moreover, the sum of the two reduction waves ($U^{VI} \rightarrow U^{V}$ and $U^{V} \rightarrow U^{III}$) was unaffected by the acidity of the solution. The effect of the acid is a function not only of the hydrogen ion concentration but also of the anion of the acid.

In agreement with Herasymenko the effect of acids on the first diffusion current is attributed to a decomposition of the U^{V} into U^{VI} and U^{IV}. Based on the experimental evidence we postulate the following equations as representing the U^{V} decomposition equilibrium.

$$2UO_2^+ + H^+ \rightleftharpoons UO_2^{++} + UO^+OH \qquad (1)$$

or dependent upon the acidity

$$2UO_2^+ + 2H^+ \rightleftharpoons UO_2^{++} + UO^{++} + H_2O \qquad (2)$$

The equilibrium constant K_{eq} of reaction (1) is

$$K_{eq.} = \frac{a_{UO_2^{++}}\, a_{UO^+OH}}{a^2_{UO_2^+}\, a_{H^+}} \qquad (3)$$

From an approximation of the order of magnitude of $K_{eq.}$ (*v. i.*) it is quite apparent that UO_2^+ is very unstable at all acidities. If decomposition equilibrium were established readily at the dropping mercury electrode one would find at various acidities two reduction waves, one corresponding to $U^{VI} \rightarrow U^{IV}$ and a second $U^{IV} \rightarrow U^{III}$.[4] Dependent upon the experimental conditions a "steady state" is attained in the region of potentials corresponding to the first diffusion current in which the net result is reduction of U^{+6} partly to U^{+5} and partly to U^{+4}.

Equation (1) cannot be used for the quantitative calculation of the steady state ion concentrations at the surface of the mercury drop in the potential range of the first diffusion current but experimental evidence is given that it allows a qualitative prediction of the effect of various factors affecting the steady state conditions.

As an alternative hypothesis it may be argued that the UO_2^+ formed at the dropping mercury electrode is partly present as such and partly as UO_2OH and that only one of the two forms is reducible at the dropping mercury electrode, and further that equilibrium between the two forms is established slowly. The equilibrium between UO_2^+ and UO_2OH should be shifted in favor of UO_2^+ with increasing hydrogen ion concentration. Since the first diffusion current increases with increasing acidity the UO_2^+ should be reducible at the dropping electrode and the UO_2OH should not be reducible.

For the following reasons the above interpretation is not probable and we attribute the increase of the first diffusion current to a disproportionation of the UO_2^+.

(a) It is known that U^{V} is unstable at all acidities and that under equilibrium conditions the disproportionation of U^{V} into U^{VI} and U^{IV} is virtually complete. (b) The increase of the diffusion current corresponding to the first wave with increasing negative potential at relatively high acidities (see experimental part) is qualitatively accounted for by the disproportionation but it cannot be interpreted on the basis of the alternative assumption. Similarly the effect of tetravalent uranium on the first diffusion current cannot be interpreted on the basis of the alternative assumption.

Experimental

The apparatus, materials and technique used in making the polarographic measurements have been described previously.[2] All diffusion currents have been corrected for the residual current of the medium. Unless stated otherwise, the temperature was maintained at 25 ± 0.1°. All values of the potential refer to the saturated calomel electrode (S. C. E.).

Effect of Various Factors on Pentavalent Uranium Decomposition as Observed at the Dropping Mercury Electrode

(1) **Uranyl Concentration.**—The diffusion currents obtained with the dropping mercury electrode at potentials in the region of the first diffusion current have been used as an indication of the extent of pentavalent uranium decomposition. It is convenient to express the extent of decomposition in the "steady state" found at the dropping electrode in terms of the ratio, R, of reduction of uranium to the tetravalent and pentavalent states respectively.

$$R = C_{U^{4+}}/C_{U^{5+}} \qquad (4)$$

Previously[2] it has been found, with the capillary of characteristics used in this work, the diffusion current in moderately acid medium is 4.08 microamperes per millimole per liter of uranyl chloride. If reduction stopped at the pentavalent state the diffusion current would be equal to $4.08\,C$, in which C is the millimolar concentration of uranyl in the bulk of the solution. As the other extreme, if reduction proceeded completely to U(IV) the diffusion current would be twice as great or $8.16\,C$. Suppose that the fraction of the U(VI) reduced to U(IV) is f, which is equal to $R/(1 + R)$, then the observed diffusion current will be

$$i_d = 4.08C + 4.08fC \qquad (5)$$

or

$$i_d = (4.08C + 8.16RC)/(1 + R) \qquad (6)$$

from which

$$R = \frac{i_d - 4.08C}{8.16C - i_d} \qquad (7)$$

in which i_d is the diffusion current corresponding to the first reduction wave.

Table I shows that with increasing total concentration of uranium the value of R increases,

---

(4) In a private communication H. G. Heal indicates that he has carried out a study, on the polarography of uranium, similar in many respects to that carried out by the authors. Dr. Heal states he has "made many experiments which put the existence of the ion UO_2^+, for short periods, beyond doubt and (has) data concerning the velocity constants for its disproportionation under various conditions." He intends to publish his results shortly.

indicating more extensive disproportionation. According to equation (1) the fraction of pentavalent uranium decomposing should become greater with increasing uranium concentration.

The first diffusion current is not proportional to the concentration of uranium in solutions of high acidity (Table I).

TABLE I

DIFFUSION CURRENT OF URANIUM AS A FUNCTION OF CONCENTRATION IN 2 M HCl; 2 × 10^{-4} THYMOL

Uranyl chloride, moles per liter	i_d at −0.5 v., microamperes	i_d/C microamperes per millimole per liter	R
3.6 × 10^{-5}	0.21	6.1	0.7
1.04 × 10^{-4}	0.70	6.7	2.0
2.11 × 10^{-4}	1.50	7.11	2.9
3.48 × 10^{-4}	2.51	7.22	3.3
5.63 × 10^{-4}	4.09	7.27	3.6
9.12 × 10^{-4}	6.66	7.31	3.7
2.13 × 10^{-3}	16.00	7.52	5.3
4.34 × 10^{-3}	35.0	8.06	40

(2) **Potential.**—At the surface of the mercury drop the uranyl ion concentration decreases continually as the (negative) potential increases. According to equation (1) a decreasing uranyl ion concentration at constant hydrogen ion concentration should cause the equilibrium to shift toward the right. This shift would manifest itself in a continuously increasing current at the dropping mercury electrode with increasing potential. This is found experimentally when the hydrochloric acid concentration is greater than about 0.5 N. In 1.5 M hydrochloric acid containing 10^{-3} M uranyl chloride the diffusion current at −0.3 v. was 6.08 microamp.; at −0.40 v. 6.33; at −0.5 v. 6.53; at −0.6 v. 6.68 and at −0.7 v. 6.97 microamperes (see also Fig. 1). In moderately acid solution the region from −0.3 to −0.7 v. (*vs.* S. C. E.) is one of constant diffusion current.

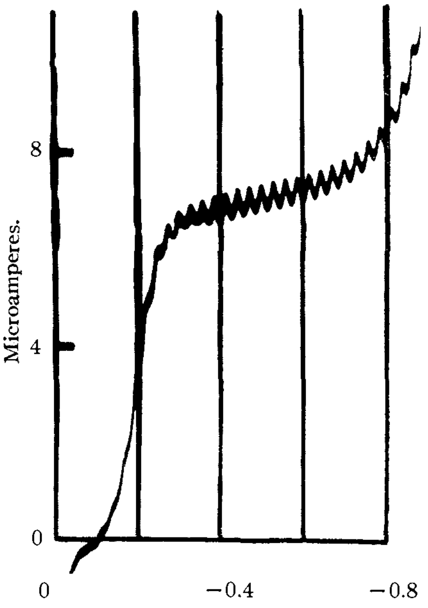

Fig. 1.—Polarogram of 10^{-3} M uranyl chloride in 1.5 M hydrochloric acid, 10^{-4} % thymol.

(3) **Acid Concentration.**—The effect of acid concentration upon diffusion current was studied with the non-complex forming perchloric acid. For a given concentration of uranium the rate of pentavalent uranium decomposition increases with increasing acid strength (Table II).

TABLE II

DIFFUSION CURRENT OF MILLIMOLAR URANYL CHLORIDE IN VARIOUS PERCHLORIC ACID SOLUTIONS, 10^{-4}% THYMOL

$HClO_4$, moles/liter	i_d at −0.4 v., microamperes	R
0.90	4.38	0.08
1.89	4.75	0.19
3.78	5.56	0.57

(4) **Temperature.**—The rate of pentavalent uranium decomposition increases as the temperature increases. This effect is shown qualitatively in Fig. 2. Results of a quantitative investigation of the effect of temperature are summarized in Table III.

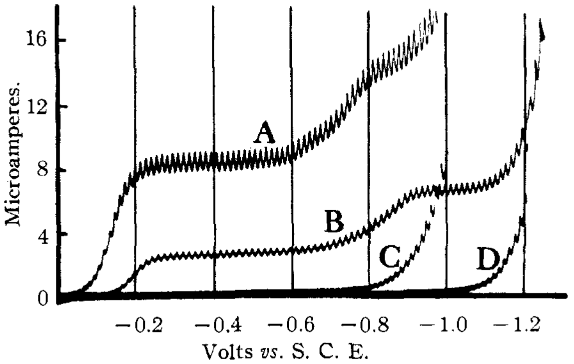

Fig. 2.—Effect of temperature upon polarogram of 10^{-3} M uranyl chloride in 1 M hydrochloric acid: A, polarogram at 60°; B, polarogram at 0°; C, residual current at 60°; D, residual current at 0°.

TABLE III

EFFECT OF TEMPERATURE ON PENTAVALENT URANIUM DISPROPORTIONATION

Solution examined	R		
	0°	25°	60°
0.1 M HCl + 10^{-3} M UO_2Cl_2	0.01		0.09
0.25 M HCl + 4 × 10^{-4} M UO_2Cl_2	0.0	0.02	0.13
1 M HCl + 10^{-3} M UO_2Cl_2	0.21	0.60	4.61

Table III shows that even in 0.1 M hydrochloric acid a small amount of decomposition is found at 60°. In 1 M hydrochloric acid at 60° such extensive decomposition takes place there is almost complete reduction of the uranyl ion to the tetravalent state at potentials more positive than those corresponding to reduction of U^{+4} to U^{+3}. Even at 0° the decomposition of U^{+5} is appreciable at the dropping electrode in 1 *M* hydrochloric acid.

(5) **Tetravalent Uranium.**—According to equation (1) the decomposition of pentavalent uranium should be retarded if an excess of tetravalent uranium were present in the solution. This retardation of the decomposition would be evidenced polarographically by a decreased diffusion current at a given acid strength. This effect has been found (Table IV).

TABLE IV

EFFECT OF TETRAVALENT URANIUM UPON FIRST DIFFUSION CURRENT OF 10^{-3} *M* UO_2Cl_2 IN 1 *N* H_2SO_4; 10^{-4}% THYMOL

Uranous sulfate, moles per liter	Diffusion current in microamperes at potential −0.3 v.	−0.4 v.	−0.5 v.	−0.6 v.
0	7.06	7.13	7.15	7.18
10^{-2}	6.69	6.74	6.59	6.51

However, an anomaly appears in polarograms of strongly acid solutions containing both hexavalent and tetravalent uranium in that the diffusion current actually decreases with increasing negative potential instead of increasing as one would normally expect (see Table IV). Figure 3 shows a slight maximum in the current voltage curve at about −0.35 v. *vs.* S. C. E. of a solution of uranyl chloride containing tetravalent uranium.

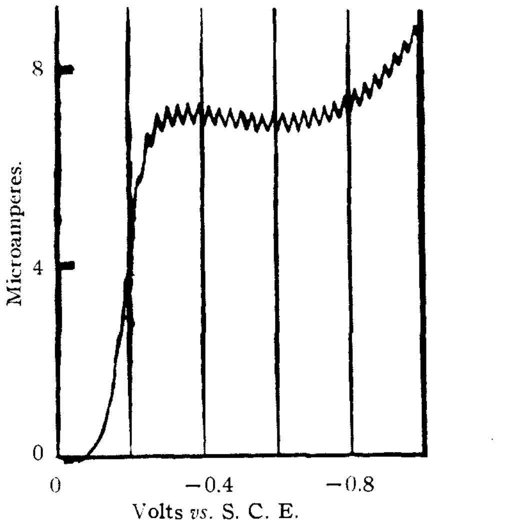

Fig. 3.—Polarogram of 10^{-3} *M* uranyl chloride in 1 *M* sulfuric acid containing 10^{-2} *M* uranous sulfate, 10^{-4} % thymol.

From equation 2 one would expect that in a solution containing a mixture of hexavalent and tetravalent uranium the amount of pentavalent uranium present should correspond to its equilibrium concentration.

If a fairly large amount of tetravalent uranium is added to hexavalent uranium in relatively weakly acid solution a decrease of the first diffusion current can be observed only when a polarographically measurable amount of pentavalent uranium is formed. When enough uranous sulfate was added to 5×10^{-4} *M* uranyl chloride in 0.1 *M* hydrochloric acid to make it 2×10^{-2} *M* in uranous sulfate, no decrease in the diffusion current at −0.4 v. *vs.* S. C. E. was observed. From this experiment it would appear that the equilibrium constant for equation 1 must be greater than 10^6.

(6) **Drop Time.**—Apparently the amount of pentavalent uranium decomposition as observed at the dropping mercury electrode does not change with a change in drop time (Table V).

TABLE V

EFFECT OF DROP TIME ON DIFFUSION CURRENT OF URANIUM IN WEAKLY AND STRONGLY ACID SOLUTION CURRENT MEASURED AT −0.5 V. IN 10^{-3} *M* URANYL CHLORIDE, 10^{-4}% THYMOL

Drop time	Diffusion current, microamperes 0.1 *M* HCl	1.9 *M* HCl	$\frac{i_d(1.9\ M\ HCl)}{i_d(0.1\ M\ HCl)}$
6.86	2.61	4.74	1.82
4.46	3.47	6.01	1.73
3.16	4.17	7.47	1.79
2.64	4.76	8.43	1.77
2.18	5.38	9.48	1.76
1.85	6.18	11.00	1.78
1.62	7.46	12.87	1.74

(7) **Complex Formation.**—Heidt[5] from *p*H measurements of uranyl chloride–oxalic acid solutions calculated that the equilibrium constant for the decomposition of the complex $UO_2H_2C_2O_4^{++}$ is

$$K_{\text{eq.}} = \frac{C_{UO_2^{++}} \times C_{H_2C_2O_4}}{C(UO_3H_2C_2O_4)^{++}} = \frac{1}{370}$$

According to equation (1) the complex formation of hexavalent uranium with oxalic acid should favor the disproportionation of the pentavalent uranium provided that the latter does not form a more stable complex with oxalic acid than uranyl does. The results of Table VI show that oxalic acid increases the rate of pentavalent uranium decomposition.

TABLE VI

DIFFUSION CURRENT OF URANIUM AS A FUNCTION OF OXALIC ACID CONCENTRATION IN 1.89 *M* $HClO_4$; 10^{-4}% THYMOL, 1.182×10^{-3} *M* UO_2Cl_2, 25°

Oxalic acid, moles per liter	i_d at −0.5 v., microamperes	*R*
0	5.68	0.21
1.86×10^{-3}	6.35	0.46
3.79×10^{-3}	6.72	0.64
6.3×10^{-3}	7.31	1.06
9.61×10^{-3}	7.64	1.39
2.67×10^{-2}	8.67	3.95
0.4	9.51	31

In 0.4 *M* oxalic acid the rate of pentavalent uranium decomposition is great enough to allow all but about 5% of the uranyl to be reduced to the tetravalent state. The remaining 5% is

---

[5] L. J. Heidt, *J. Phys. Chem.*, **46**, 624 (1942).

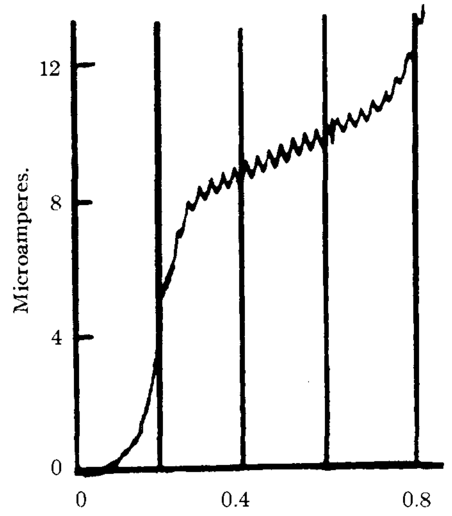

Fig. 4.—Polarogram of 1.18×10^{-3} *M* uranyl chloride in 1.89 *M* perchloric acid, 2.67×10^{-2} *M* oxalic acid, 10^{-4} % thymol.

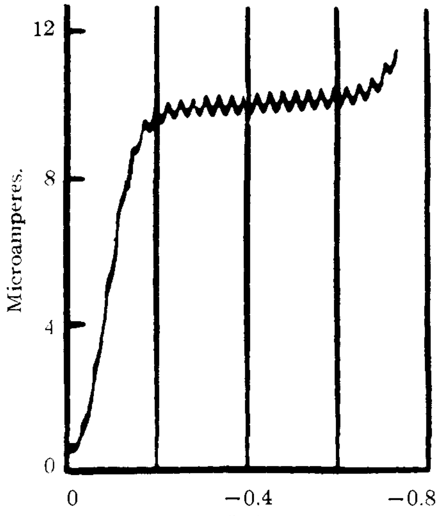

Fig. 5.—Polarogram of 1.18×10^{-3} *M* uranyl chloride in 1.89 *M* perchloric acid, 0.4 *M* oxalic acid, 10^{-4} % thymol.

reduced to pentavalent uranium. As the state of complete reduction to tetravalent uranium is approached the current voltage curves begin to show a region of constant diffusion current instead of a gradually increasing current with increasing potential (compare Figs. 4 and 5). In Fig. 4 reduction to tetravalent uranium is quite incomplete; hence the current in the region between −0.3 and −0.7 volt is increasing continuously. In Fig. 5 where reduction to the tetravalent state is nearly complete the current is practically constant in this same region.

A number of anions form complexes of varying degree of stability with uranyl. If the value of *R* with the various anions may be used as a qualitative indication of the stability of the complex with the uranyl ion, these complexes become more stable in the order perchlorate, chloride, sulfate, oxalate (Table VII).

TABLE VII

SUMMARY OF *R* VALUES IN VARIOUS MEDIA

Concentration of uranyl chloride	Medium	*R* at 0.5 v.
10^{-3} *M*	1.89 *M* $HClO_4$	0.19
10^{-3} *M*	1.5 *M* HCl	1.5
10^{-3} *M*	0.5 *M* H_2SO_4	3.0
1.18×10^{-3} *M*	1.89 *M* $HClO_4$, 0.027 *M* Oxalic Acid	3.9

Summary

In strongly acid solution (greater than about 1 *M* hydrochloric acid) pentavalent uranium decomposes at the dropping mercury electrode probably according to the equation

$$2UO_2^+ + H^+ \rightleftarrows UO_2^{++} + UO^+OH$$

The polarographic steady state does not correspond to the equilibrium state of the pentavalent uranium. The effect of the concentration of strong acid and of other factors, is accounted for qualitatively by the above equation.

The rate of disproportionation of the pentavalent uranium at the dropping mercury electrode increases with increasing concentration of pentavalent uranium, decreasing uranous ion concentration, increasing acid concentration, increasing temperature and addition of complex forming ions.

MINNEAPOLIS, MINN.

RECEIVED MARCH 2, 1946