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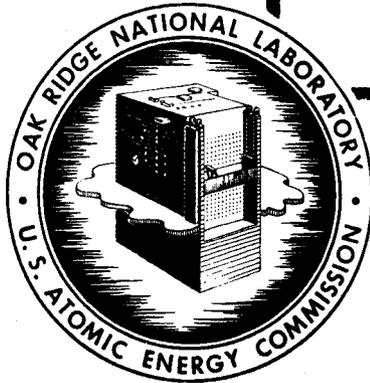


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THE REDUCTION OF URANIUM (VI) BY
FERROUS IRON IN PHOSPHORIC ACID SOLUTION:
THE FORMAL ELECTRODE POTENTIAL OF THE
U (IV) / (VI) COUPLE

C. F. Baes, Jr.



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ELECTRODE POTENTIAL OF THE U(IV)/(VI) COUPLE

C. F. Baes, Jr.

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ABSTRACT

The extent of reduction of U(VI) by Fe(II) in phosphoric acid solution has been measured as a function of the phosphoric acid concentration (1.9 - 7.7M) and as a function of the Fe(II)/Fe(III) ratio. Kinetic measurements of the slow redox equilibrium involved conform to a first order rate law. The introduction of fluoride ion into these solutions considerably increases both the reaction rate and the extent of reduction. The formal electrode potential of the U(IV)/(VI) couple, $E_{U4,6}$ has been estimated in the range 1.85 - 4.8M H_3PO_4 , from measured $E_{Fe2,3}$ values in combination with the redox equilibrium data.

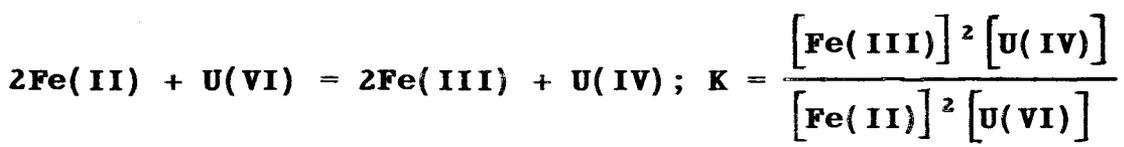
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THE REDUCTION OF URANIUM(VI) BY FERROUS IRON
IN PHOSPHORIC ACID SOLUTION: THE FORMAL
ELECTRODE POTENTIAL OF THE U(IV)/(VI) COUPLE

On the basis of some preliminary studies conducted by investigators at the Armour Fertilizer Works, it has been proposed that uranium(VI) is slowly reduced by iron(II) in 6M phosphoric acid solution.* Such a suggestion is of particular interest since it has been noted⁽¹⁾ that uranium(IV) is oxidized by iron(III) in 1 to 2M phosphoric acid.

An examination of the U(IV)/(VI) - Fe(II)/(III) redox system in phosphoric acid has been carried out in this laboratory, and the results confirm that uranium(VI) is extensively reduced by ferrous iron in high phosphoric acid concentrations. The concentration equilibrium quotient for the reaction

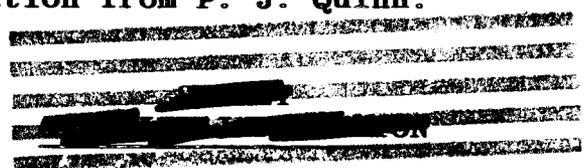


has been determined as a function of the phosphoric acid concentration, and these results, along with e.m.f. measurements of the Fe(II)/(III) couple in phosphoric acid, have permitted the approximate evaluation of the formal electrode potential for the U(IV)/(VI) couple in these solutions.

Redox Equilibrium Measurements

The spectrophotometric method of U(IV) analysis was used in these measurements. The experimental procedure consisted

*Private communication from P. J. Quinn.



in preparing two series of solutions, all of which were 0.36M in H_2SO_4 and initially ca. 0.01M in UO_2SO_4 . In the first series each solution was brought to 0.05M in Fe(II) and 0.05M in Fe(III) (added as the sulfates), and the phosphoric acid concentration was varied as shown in Table 1. The extent of reduction was followed by measuring the increase in the optical density at wavelengths of 630 $m\mu$ and 670 $m\mu$ (wherein U(IV) adsorbs strongly and U(VI) shows zero adsorption), (2) the reaction being followed in each case until constant readings were obtained. Due to the slowness of the reduction, it was necessary to wait several days in some cases for the attainment of equilibrium. In these experiments, no attempt was made to control the temperature and the results must be considered to correspond only approximately to 25°C. The total reducing power of these solutions was determined in a series of titrations against standard dichromate, the results of which established that air oxidation in these solutions (stored in glass-stoppered flasks) was negligible.

In the second series of experiments, the phosphoric acid concentration was held constant at 3.68M (22% P_2O_5) and the $[Fe(II)]/[Fe(III)]$ ratio varied in order to confirm the form of the equilibrium quotient (Tables 2 and 4).

The molar extinction coefficients of U(IV) in these solutions were found to be:

$$\epsilon_{U(IV),630} = 31.6; \quad \epsilon_{U(IV),670} = 38.2$$

A slight increase was noted for the more concentrated phosphoric acid solutions, but this effect was barely beyond experimental error, hence the above values were used throughout in the calculation of percent reduction. A correction was necessitated by the appreciable absorption of Fe(III) in these solutions*,

$$\epsilon_{Fe(III),630} = 0.16; \quad \epsilon_{Fe(III),670} = 0.20$$

The expression used to calculate the percent reduction was:

*When not obscured by other colored solutes, phosphoric acid solutions containing Fe(III) were pink in color.

$$\text{Percent reduction} = 100 \left[\frac{d - \epsilon_{\text{Fe(III)}} [\text{Fe(III)}]}{\epsilon_{\text{U(IV)}} [\Sigma \text{U}]} \right] \quad (2)$$

wherein d is the optical density of 1 cm of solution and $[\Sigma \text{U}]$ denotes the total concentration of uranium ($[\text{U(IV)}] + [\text{U(VI)}]$). The value of $[\text{Fe(III)}]$ used in the correction term in Eq. 2 was estimated with sufficient accuracy from a preliminary calculation of the uncorrected absorbancy data.

The experimental results are summarized in Tables 1 and 2, and plotted in Figure 1. The equilibrium quotients, K (Eq. 1), are calculated in Tables 3 and 4.

Effect of Fluoride

Additional equilibrium measurements were performed at 25°C on a series of solutions of the following composition:

$[\text{H}_3\text{PO}_4]$	=	3.7M
$[\text{H}_2\text{SO}_4]$	=	0.36M
$[\text{Fe(II)}]$	=	0.02M (initial concentration)
$[\text{Fe(III)}]$	=	0.08M (initial concentration)
$[\text{U(VI)}]$	=	0.01M (initial concentration)
$[\text{F}^-]$	=	0.08M - 0.8M

The results are summarized below:

$[\text{F}^-]$ moles/l	<u>% Reduction at 25°C</u>
0.08	45
0.16	55
0.24	66
0.4	81
0.8	86

Table 1
THE % REDUCTION OF U(VI) BY Fe(II) AS A FUNCTION
OF PHOSPHORIC ACID CONCENTRATION AT ca. 25°C

Initial Sol'n. Comp'n.: $[\text{Fe(II)}] = 0.050\text{M}$
 $[\text{Fe(III)}] = 0.050\text{M}$
 $[\text{U(VI)}] = 0.01036\text{M}$
 $[\text{H}_2\text{SO}_4] = 0.36\text{M}$

$[\text{H}_3\text{PO}_4]$ m/l	Wt.% P_2O_5	d_{630}^*	% Red.	d_{670}^*	% Red.	Ave.% Red.
1.85	11.9	0.013	4.0	0.017	4.3	4.2
2.59	16.1	0.083	25.4	0.105	26.5	26.0
3.33	20.1	0.199	60.9	0.253	63.9	62.4
4.81	27.4	0.313	95.2	0.394	98.5	96.9
7.77	39.6	0.325	99.4	0.421	105	(100)

*These values have been corrected for Fe(III) absorption.

Table 2

THE % REDUCTION OF U(VI) BY Fe(II) AS A FUNCTION
OF $[\text{Fe(II)}] / [\text{Fe(III)}]$ IN 3.7M H_3PO_4 AT ca.25°C

Initial Sol'n. Comp'n.: $[\text{Fe(II)}] + [\text{Fe(III)}] = 0.0500\text{M}$
 $[\text{U(VI)}] = 0.00964\text{M}$
 $[\text{H}_3\text{PO}_4] = 3.68\text{M}$
 $[\text{H}_2\text{SO}_4] = 0.36\text{M}$

<u>Initial</u> <u>$[\text{Fe(II)}]$</u> <u>ΣFe</u>	<u>d_{630}^*</u>	<u>% Red.</u>	<u>d_{670}^*</u>	<u>% Red.</u>	<u>Ave.%</u> <u>Red.</u>
0.20	0.058	19.0	0.073	19.8	19.4
0.40	0.148	48.5	0.183	49.7	49.1
0.60	0.223	73.1	0.273	74.2	73.7
0.80	0.266	87.2	0.334	90.8	89.0
1.00	0.295	96.7	0.362	98.4	97.6

*These values have been corrected for Fe(III) absorption.

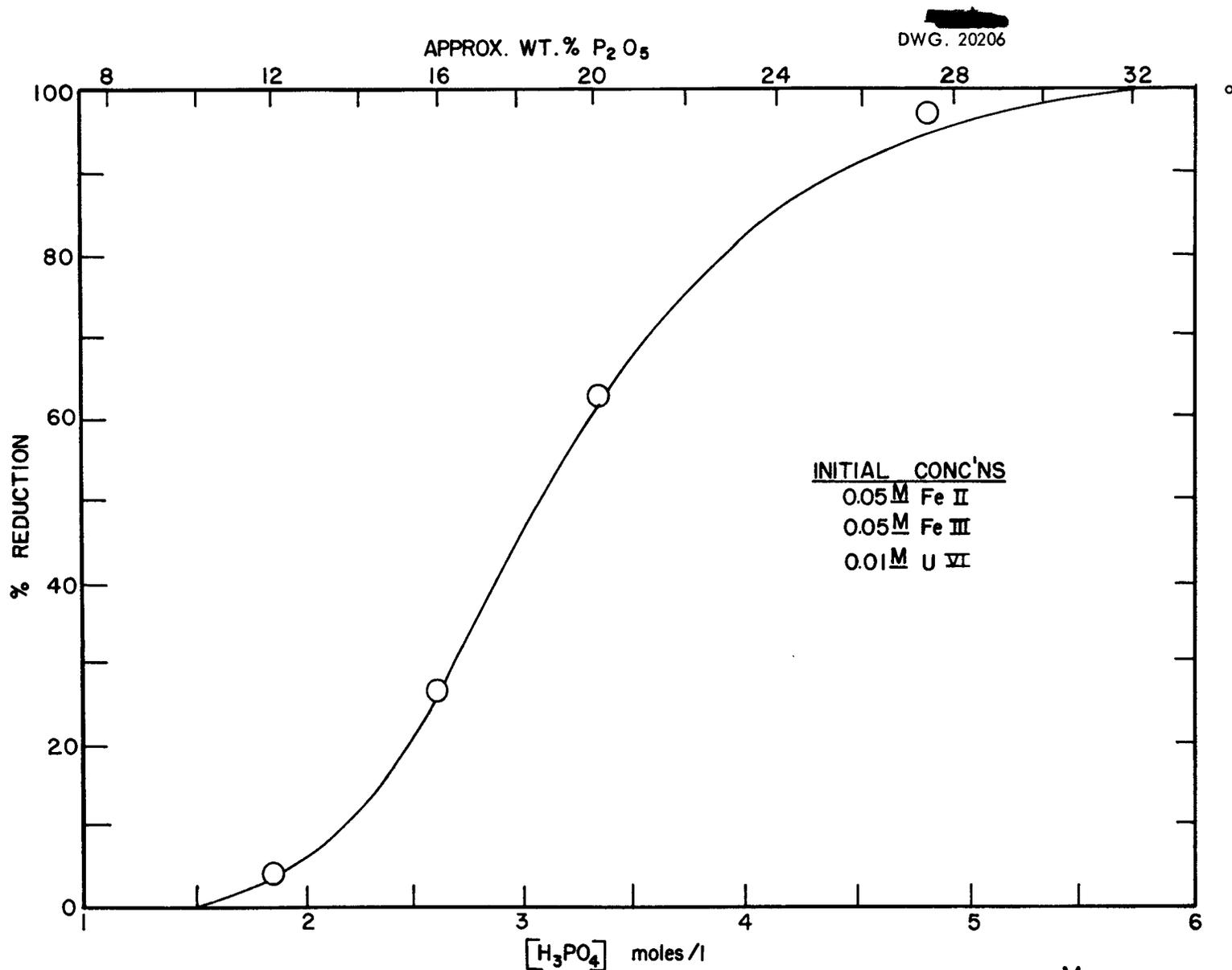


FIGURE 1. REDUCTION OF U(VI) TO U(IV) BY Fe(II) IN PHOSPHORIC ACID (0.36M H₂SO₄) AT ROOM TEMPERATURE

Table 3

CALCULATION OF THE EQUILIBRIUM QUOTIENT

$$K = \frac{[\text{Fe(III)}]^2 [\text{U(IV)}]}{[\text{Fe(II)}]^2 [\text{U(VI)}]}$$

AS A FUNCTION OF $[\text{H}_3\text{PO}_4]$ CONCENTRATION

$[\text{H}_3\text{PO}_4]$ m/l	$[\text{U(IV)}]$ m/l	$[\text{U(VI)}]$ m/l	$[\text{Fe(III)}]$ m/l	$[\text{Fe(II)}]$ m/l	$\frac{[\text{U(IV)}]}{[\text{U(VI)}]}$	$\frac{[\text{Fe(III)}]^2}{[\text{Fe(II)}]^2}$	K	$\frac{K^*}{[\text{H}_3\text{PO}_4]^8}$ $\times 10^4$	$\frac{K^*}{[\text{H}_3\text{PO}_4]^9}$ $\times 10^5$
1.85	0.00044	0.00992	0.0509	0.0491	0.044	1.07	.047	3.4	18.5
2.59	0.00269	0.00767	0.0554	0.0446	0.351	1.54	.54	2.7	10.3
3.33	0.00646	0.00390	0.0629	0.0371	1.66	2.87	4.8	3.2	9.5
4.81	0.01004	0.00032	0.0701	0.0299	31.4	5.50	173	6.0	12.5
3.68							13**	3.9	10.5

*These two columns indicate that the $[\text{H}_3\text{PO}_4]$ dependence of K is approximately 8th or 9th power. The constancy of $K/[\text{H}_3\text{PO}_4]^8$ is perhaps more satisfactory in that the largest deviation occurs for the least accurately known K value.

**This value results from the calculations in Table 4.

Table 4

CALCULATION OF THE EQUILIBRIUM QUOTIENT

$$K = \frac{[\text{Fe(III)}]^2 [\text{U(IV)}]}{[\text{Fe(II)}]^2 [\text{U(VI)}]}$$

AS A FUNCTION OF $[\text{Fe(II)}] / [\text{Fe(III)}]$ IN 3.7M H_3PO_4

<u>Initial</u> <u>$[\text{Fe(II)}]$</u> <u>$\sum \text{Fe}$</u>	<u>$[\text{U(IV)}]$</u> <u>m/l</u>	<u>$[\text{U(VI)}]$</u> <u>m/l</u>	<u>$[\text{Fe(III)}]$</u> <u>m/l</u>	<u>$[\text{Fe(II)}]$</u> <u>m/l</u>	<u>$\frac{[\text{U(IV)}]}{[\text{U(VI)}]}$</u>	<u>$\frac{[\text{Fe(III)}]^2}{[\text{Fe(II)}]^2}$</u>	<u>K</u>
0.20	0.00187	0.00777	0.0437	0.00626	0.241	48.7	11.7
0.40	0.00473	0.00491	0.0395	0.0105	0.963	14.1	13.6
0.60	0.00710	0.00254	0.0342	0.0158	2.80	4.67	13.1
0.80	0.00856	0.00108	0.0271	0.0229	7.93	1.40	11.1
1.00	0.00941	0.00023	0.0188	0.0312	40.9	0.364	14.9

Ave. 13±2

These equilibrium measurements are less accurate than those previously described due to appreciable air oxidation*. In addition to its pronounced effect on the extent of reduction, fluoride was observed to greatly increase the reaction rate. Thus, whereas in fluoride-free solutions, days are required to reach equilibrium, in the presence of as little as 0.08M fluoride virtually complete equilibrium is obtained in a few minutes.

Reaction Rate Measurements

Preliminary kinetic studies were carried out in which the rate of appearance of U(IV) was followed spectrophotometrically during the course of reduction of U(VI) by Fe(II) in fluoride-free 3.7M phosphoric acid. In a second experiment, the change in the Fe(II)/Fe(III) ratio with time was followed potentiometrically. Both sets of rate data conform to a first order rate law within experimental error, i.e.,

$$\frac{d [U(IV)]}{dt} = k([U(IV)]_{eq.} - [U(IV)]_t)$$

and

$$\frac{d Fe(III)}{dt} = k([Fe(III)]_{eq.} - [Fe(III)]_t)$$

wherein the subscripts eq. and t signify concentration values at equilibrium and at a given time, t. At 25°C, the half time of reaction was found to be 160-170 minutes. One potentiometric rate measurement at 48°C gave a half time of approximately 14 minutes.

*Whereas stoppered volumetric flasks, filled to the mark, were used to store fluoride-free solutions, the screw-cap polyethylene bottles used in the present equilibrium measurements contained enough air to result in appreciable oxidation.

E. M. F. Measurements

The e.m.f. of the cell,

Pt/Fe(II), (0.05M); Fe(III), (0.05M); H₂SO₄, (0.36M); H₃PO₄, c//S.C.E.

in which the concentration of phosphoric acid was varied from 0 to 7.4M was measured with a L&N type K-2 potentiometer in conjunction with a high sensitivity reflecting galvanometer. The cell was mounted in a thermostat regulated at $24.7 \pm 0.1^\circ\text{C}$. Argon gas was bubbled through the solution to minimize air oxidation. In all cases, it appeared that constant readings were reached within 12 minutes. The precision of successive measurements on the same sample was usually within 0.1 mv.

The results of these measurements have been corrected to a $\frac{[\text{Fe(II)}]}{[\text{Fe(III)}]}$ ratio of unity (in Table 5), yielding the formal electrode potentials $E'_{\text{Fe}2,3}$ (vs. the H₂ electrode) listed in the last column; $E'_{\text{Fe}2,3}$ is plotted as a function of phosphoric acid concentration in Figure 2.

Formal Electrode Potentials of the U(IV)/(VI) Couple

The formal electrode potentials $E'_{\text{Fe}2,3}$ and $E'_{\text{U}4,6}$ at 25°C are defined by the equations:

$$E_{\text{Fe}2,3} = E'_{\text{Fe}2,3} - 0.0591 \log \frac{[\text{Fe(III)}]}{[\text{Fe(II)}]} \quad (3)$$

and

$$E_{\text{U}4,6} = E'_{\text{U}4,6} - \frac{0.0591}{2} \log \frac{[\text{U(VI)}]}{[\text{U(IV)}]} \quad (4)$$

Since the potentials of the two couples, $E_{\text{Fe}2,3}$ and $E_{\text{U}4,6}$, will be equal when U(IV), U(VI); Fe(II) and Fe(III) are at equilibrium in solution, then

Table 5

ELECTRODE POTENTIAL MEASUREMENTS OF THE Fe(II)/(III) COUPLE

AS A FUNCTION OF PHOSPHORIC ACID CONCENTRATION AT 25°C

Fe(II) + Fe(III) = 0.1005M, H₂SO₄ = 0.36M

$[H_3PO_4]$ m/l	$E'_{Fe^{2,3}}$ vs. S.C.E. v.	$\frac{[Fe(III)]}{[Fe(II)]}$	$E'_{Fe^{2,3}}$ vs. Std. H ₂ Electrode v.
0	-0.4343	1.047	-0.6746
0.00994	-0.4294	"	-0.6697
0.01988	-0.4238	"	-0.6641
0.03976	-0.4136	"	-0.6539
0.05964	-0.4037	"	-0.6440
0.0994	-0.3881	1.043	-0.6285
0.1988	-0.3581	"	-0.5985
0.2982	-0.3407	"	-0.5811
0.3976	-0.3287	"	-0.5691
0.497	-0.3202	"	-0.5606
0.795	-0.3009	"	-0.5413
1.182	-0.2844	"	-0.5248
1.774	-0.2678	"	-0.5082
2.956	-0.2465	"	-0.4869
4.552	-0.2261	"	-0.4665
7.40	-0.1918	"	-0.4322

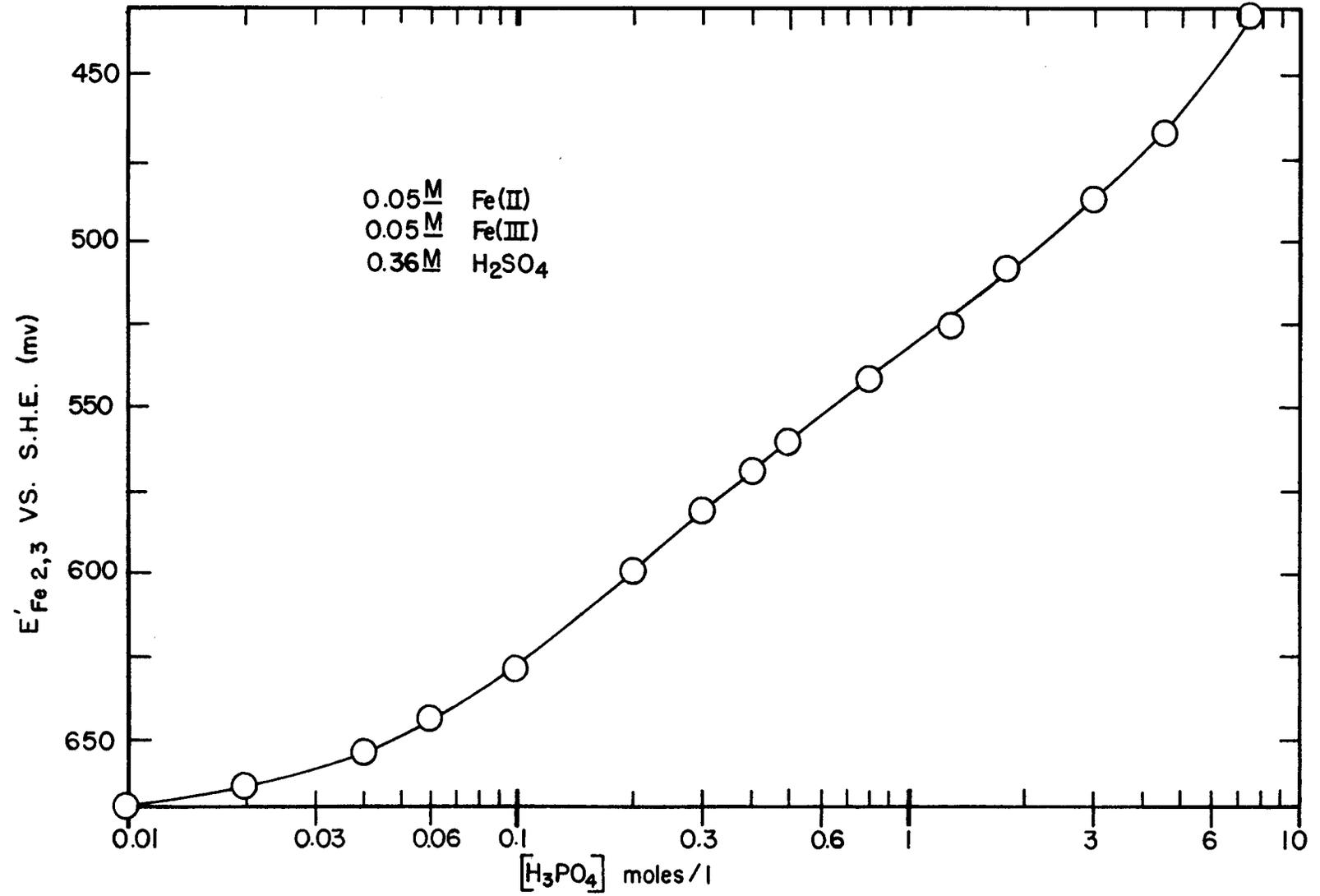


FIGURE 2. FORMAL ELECTRODE POTENTIAL OF Fe (II)/(III) IN PHOSPHORIC ACID SOLUTION AT 25 °C

$$E'_{U4,6} = E'_{Fe2,3} - \frac{0.0591}{2} \log \frac{[Fe(III)]^2 [U(IV)]}{[Fe(II)]^2 [U(VI)]}$$

$$E'_{U4,6} = E'_{Fe2,3} - \frac{0.0591}{2} \log K \quad (5)$$

It is by means of this last equation that the $E'_{U4,6}$ values listed in Table 6 were calculated. The $E'_{Fe2,3}$ values listed in the table were read from the curve in Figure 2, and correspond to the indicated phosphoric acid concentrations. In these calculations, it is assumed that the presence of U(IV) and U(VI) in the redox-equilibrium solutions does not appreciably alter the $E'_{Fe2,3}$ values, through changes in ionic strength and the small change in the amount of uncomplexed phosphoric acid.

It is further assumed in each separate calculation of $E'_{U4,6}$ that all ionic and molecular species of appreciable abundance involving iron and uranium contain but one metal atom and that their activity coefficients remain constant. These assumptions must be made in order to employ Equations 3 and 4. The phosphoric acid concentration dependence of $E'_{U4,6}$ is indicated in Figure 3.

Discussion

The change in the extent of reduction of U(VI) by Fe(II) with increasing phosphoric acid concentration which was suggested by the work done at Armour is shown clearly by the plot in Figure 1. The high dependence of the equilibrium on the phosphoric acid concentration results from the opposite concentration dependence of the two redox couples. Within the rather large experimental error, the K values appear to be proportional to approximately the eighth power of the phosphoric acid concentration over the range covered (Table 3).

Since fluoride is known to complex strongly with uranyl, uranous and ferric ions in aqueous solution, it is not surprising that its presence in phosphoric acid should produce the large effects indicated by the preliminary results presented here. From the direction of the effect, it appears that fluoride increases the relative stability of either Fe(III) or U(IV), or both.

Table 6
CALCULATION OF THE FORMAL ELECTRODE POTENTIAL
OF THE U(IV)/(VI) COUPLE IN PHOSPHORIC ACID AT 25°C

<u>[H₃PO₄]</u>	<u>E_{Fe2,3} vs.</u> <u>Std. H₂ Electrode</u> <u>v.</u>	<u>K</u>	<u>-0.0296 log K</u>	<u>E_{U4,6} vs.</u> <u>Std. H₂ Electrode</u> <u>v.</u>
1.85	-0.5066	0.047	+0.0392	-0.467
2.59	-0.4926	0.54	+0.0079	-0.485
3.33	-0.4819	4.8	-0.0201	-0.502
4.81	-0.4638	173	-0.0661	-0.530

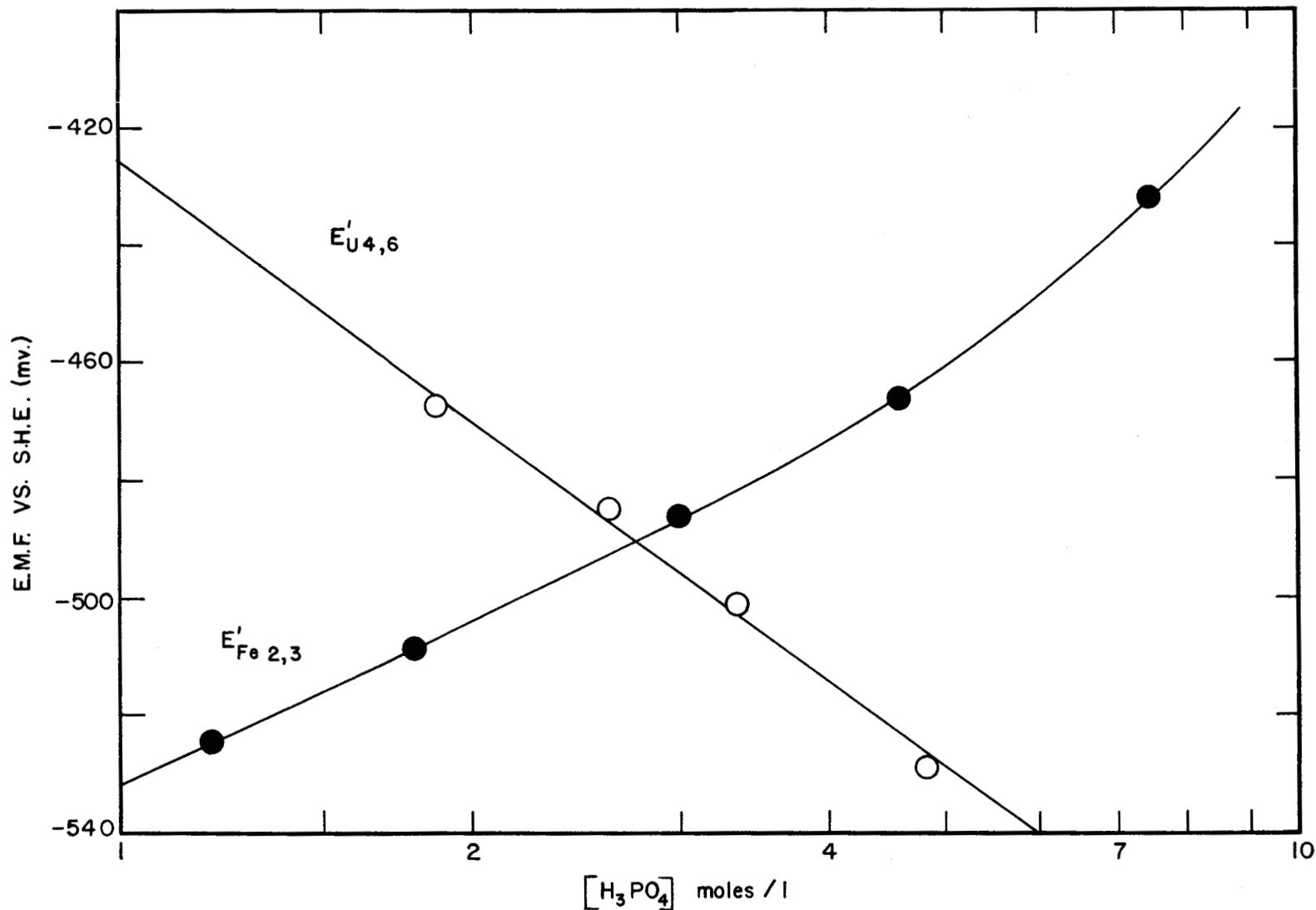


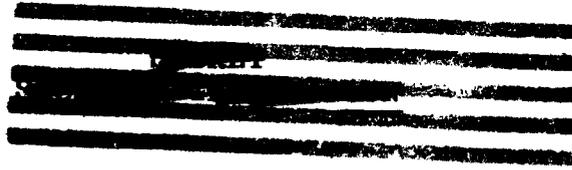
FIGURE 3. THE FORMAL ELECTRODE POTENTIAL OF U(IV)/(VI) IN PHOSPHORIC ACID SOLUTION (0.36 M H₂SO₄) AT 25°C

Since, in the rate measurements, the Fe(II), Fe(III), U(IV) and U(VI) concentrations all underwent appreciable changes during the course of the reduction reaction*, it is somewhat surprising that the data conform to a simple first order rate law. A more detailed study of the kinetics of this reaction is planned.

The solid line which has been fitted to the data in Figure 3, representing the change in $\text{EU}_{4,6}$ with phosphoric acid concentration, has been drawn with a slope of $\frac{5}{2} \times 0.0591$, corresponding to a fifth power dependence of the U(IV)/(VI) couple on $[\text{H}_3\text{PO}_4]$. Since the complex $\text{UO}_2(\text{H}_2\text{PO}_4)_2(\text{H}_3\text{PO}_4)$ has been proposed⁽³⁾ as the most abundant U(VI) species in solution in the concentration range of this data, one may suggest, on the basis of the present data, that a U(IV) phosphate complex is present in these solutions in which the $\text{PO}_4^{-3}/\text{U(IV)}$ ratio is about eight.

*For example, during the course of one measurement, the following approximate concentration changes occurred:

$[\text{Fe(II)}]$,	0.020 to 0.012M	$[\text{U(IV)}]$,	0 to 0.004 M
$[\text{Fe(III)}]$,	0.010 to 0.018M	$[\text{U(VI)}]$,	0.005 to 0.001 M



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