TABLE I

COMPARISON OF CALCULATED WITH OBSERVED INTENSITIES OF Ta_3Sn

hkl	Obs.	Calcd. disord.	Calcd. ord.
110	3	0	10
200	58	60	50
210	184	175	210
211	128	134	110
220	0	0	2
310	0	0	2
222	22	15	25
320	49	38	46
321	68	67	55
400	32	27	35
411, 330	0	0	2
420	24	20	16
421	44	36	43
332	14	17	20
422	0	0	1
510, 431	0	0	2
520, 432	45	42	50
521	22	27	22
440	24	28	28
530, 433	0	0	1
600, 442	16	20	16
610	15	16	19
611, 532	38	51	40
620	0	0	1
541	0	0	2
622	22	30	50
630, 542	106	111	135

coördinated to twelve A atoms at the distance B-A. Each A atom is coördinated to 2 A atoms at distance $(A\text{-}A)_1$, 8 A atoms at distance $(A\text{-}A)_2$ and 4 B atoms at distance B-A.

TABLE II

STRUCTURAL DATA

Compound	a_0, Å.	ρ X-ray, g./cc.	Interatomic distances, Å. B-A	$(A\text{-}A)_1$	$(A\text{-}A)_2$
Nb_3Os	5.121 (±0.002)	11.59	2.862	2.561	3.316
Nb_3Ir	5.131 (±0.001)	11.52	2.869	2.566	3.143
Nb_3Pt	5.153 (±0.003)	11.50	2.880	2.577	3.155
Nb_3Sn	5.289 (±0.002)	8.92	2.956	2.645	3.238
Ta_3Sn	5.276 (±0.001)	8.81	2.949	2.638	3.231
V_3Sn	4.94 (±0.01)	5.39	2.76	2.47	3.02

Reactions of 75 atomic % Ta with 25 atomic % Ir, Pt, and Os were tried. The compounds formed are isomorphous but do not have the A15 type structure. These compounds will be investigated further.

It appears that vanadium will dissolve at least 25 weight per cent. of platinum. The lines on the powder photograph of this alloy were broad and therefore no change in lattice constant of the vanadium could be detected.

Acknowledgment.—The authors wish to thank Mr. E. Corenzwit for helping with the preparation of the compounds and for taking the powder photographs used in this study.

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Some Kinetic Studies of the Tin(II) Reduction of Uranium(VI)[1] in Hydrochloric Acid Media

BY ROBERT LEE MOORE

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Stannous chloride is one of the few common reducing agents which will readily reduce uranium(VI) to uranium(IV) in acid solutions. Furthermore, the potentials are such that no uranium(III) is formed. However, it is found that the rate and degree of reduction are markedly dependent on the conditions and appear to be strongly influenced by the concentrations of the reactants, the temperature and the acidity. A kinetic study of this reaction was accordingly carried out in our laboratory to determine the effect of these variables.

Experimental

The solutions studied were made up from weighed amounts of reagent grade stannous chloride ($SnCl_2 \cdot 2H_2O$), standardized hydrochloric acid and an analyzed stock solution of uranyl chloride which was prepared by dissolving uranium trioxide (UO_3) in hydrochloric acid. Solutions of uranium(VI) and tin(II), which upon mixing would give the desired initial composition, were prepared separately and brought to the reaction temperature in a water-bath maintained to ±0.1° of the desired temperature. Volume changes accompanying mixing were ignored.

The reaction was followed spectrophotometrically. Small aliquots of solution were removed periodically from the stoppered, thermostated reaction vessel. These were chilled with ice to inhibit the reaction and the absorption curves determined on a Model 12M Cary recording spectrophotometer. A complete scan required only about four minutes and the extent of the reaction during this time is believed to have been negligible in most cases. The uranium(IV) absorption peaks at about 555 and 655 mμ, where U(VI) is completely transparent, and the (VI) absorption at 410 mμ, where there is very little overlap, were used to compute the extent of reaction. The excellent agreement obtained between the amount of U(IV) formed and the U(VI) left indicated that no detectable concentrations of the other states (particularly V) were formed. Since the molar extinction coefficients and the exact location of the absorption maxima varied somewhat with the acidity, it was necessary to determine standard absorption curves for pure U(IV) and pure U(VI) for each hydrochloric acid concentration employed. In addition, a curve for U(IV) was also determined for most of the experiments after the reaction had gone to completion.

Discussion of Results

Order of the Reaction.—The rate of the reduction was shown to be first order in U(VI) by means of a series of experiments in which the stannous chloride was present in large excess (10- or 20-fold) and hence essentially constant. The Sn(II) dependence was established by means of a series of experiments in which the initial stannous chloride concentration was varied tenfold, from 0.1 to 1 *M*, as shown in Table I. A plot of the reciprocal of the half time of uranium reduction *versus* the logarithm of the average Sn(II) concentration had a slope of unity. In addition, the rate data were well correlated by means of a second order equation, *i.e.*, first order in U(VI) and first order in Sn(II), as shown by the tabulated rate constants. The second-order rate constants for experiments at the same temperature and acidity generally agreed to within ±15%, which is considered satisfactory in

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view of the large effect of small variations in hydrochloric acid concentration.

TABLE I

DEPENDENCE OF RATE ON Sn(II) CONCENTRATION

Temp. 40 ± 0.1°; 7 M hydrochloric acid; 0.1 M uranium-(VI)

$SnCl_2$, M	$t_{1/2}$(hr.)	k (l. mole^{-1} hr.$^{-1}$)
1	3.45	0.22
0.5	7.6	.19
.25	19	.16
.1	38.5	.23
	Av.	0.20

Effect of Temperature.—The effect of temperature was determined in a second series of experiments. Values of 0.055, 0.124 and 0.299 l. mole^{-1} hr.$^{-1}$ were obtained for the second-order rate constant in 6 M hydrochloric acid at 35, 45 and 55°, respectively. These yield an energy of activation of 18 kcal. for the reaction.

Hydrochloric Acid Dependence.—The pronounced effect of hydrochloric acid on the rate of reduction is well shown by the slope of the curves in Fig. 1 and by the rate constants in Table II. It will be noted that the specific rate increased over a thousand-fold as the acidity was changed from 3 to 9 M at 35°. It was suspected that this effect might be due either to the chloride ion or hydrogen ion, rather than to the hydrochloric acid, since both U(VI) and Sn(II) form chloride complexes and both undergo hydrolysis.

TABLE II

EFFECT OF HYDROCHLORIC ACID CONCENTRATION

Temp. = 35 ± 0.1°

HCl, M	3	6	7	8	9
k, l. mole^{-1} hr.$^{-1}$	0.004[a]	0.055	0.161	0.758	5.9

[a] Extrapolated from value of 0.024 at 55°.

Two series of experiments were carried out in an attempt to elucidate this matter. In one, the chloride concentration and the ionic strength were held constant and the hydrogen ion varied by use of hydrochloric acid–lithium chloride mixtures. Perchloric acid–hydrochloric acid mixtures were used in the other series to vary the chloride concentration at constant acidity (and ionic strength). In this case it was necessary to employ a lower temperature (25°) to minimize reaction between the stannous chloride and perchloric acid. It will be noted from Table III that neither variable had much effect on the rate. Changing the hydrogen ion from 1 to 7 M increased the rate by not more than 70%, while a similar increase in the chloride concentration caused only a 60% increase. These are so small, compared to a thousand-fold effect, that they may be considered as a second-order salt effect. It thus appears that the primary "hydrochloric acid effect" is probably more accurately an ionic strength or activity coefficient effect.

TABLE III

CHLORIDE AND HYDROGEN ION DEPENDENCE

Ionic strength, *ca.* 7 M

H$^+$ Series[a]			Cl$^-$ Series[b]		
HCl, M	LiCl, M	k (l. mole^{-1} hr.$^{-1}$)	HCl, M	$HClO_4$, M	k (l. mole^{-1} hr.$^{-1}$)
7	0	0.216	7	0	0.098
5	2	.206	6	1	.177
3	4	.154	4	3	.119
1	6	.128	1	6	.061

[a] 40°. [b] 25°.

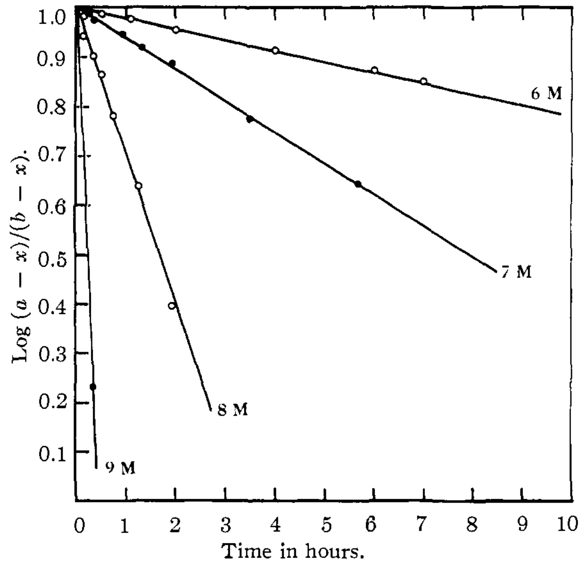

Fig. 1.—Effect of hydrochloric acid on rate of reaction. All initially 0.1 M U(VI), 1 M Sn(II), indicated M HCl.

Interaction Absorption and the U(VI)–Sn(II) Complex.—In the course of the above work it was observed that the color intensity of the initial U(VI) solutions was somewhat enhanced upon addition of Sn(II) and that the molar extinction coefficient of the 410 mμ U(VI) peak, extrapolated to zero reaction time, was larger than when tin was absent. This suggested that some association or complex formation was taking place between the uranium and tin, and this phenomenon was briefly investigated.

The absorption curves of Sn(II), U(VI) and a solution containing both (all in 6 M HCl) are shown in Fig. 2. The curve "D" is absorption of the mixture less that of the U(VI) and Sn(II) alone and represents the contribution due to complex formation. This behavior is very similar to that observed by Norman Davidson[2–6] for the interaction of different valence states of several metal ions in hydrochloric acid solutions and termed by him *interaction absorption*. As with his spectra, a plot of the logarithm of this absorption *versus* wave length was found to be a straight line.

The familiar method of continuous variations of Job[7] was applied to determine the composition of the complex as shown in Fig. 3. It is noted that the location of the maxima, irrespective of wave length, corresponds to a Sn(II) to U(VI) composition in the complex of 1:1. The broad shape of the

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[2] James E. Whitney and Norman Davidson, THIS JOURNAL, **71**, 3809 (1949).

[3] Harden McConnell and Norman Davidson, *ibid.*, **72**, 3168 (1950).

[4] Harden McConnell and Norman Davidson, *ibid.*, **72**, 5557 (1950).

[5] Charles I. Browne, Roy P. Craig and Norman Davidson, *ibid.*, **73**, 1946 (1951).

[6] Roy P. Craig and Norman Davidson, *ibid.*, **73**, 1951 (1951).

[7] P. Job, *Ann. Chim.*, [10] **9**, 113 (1928).

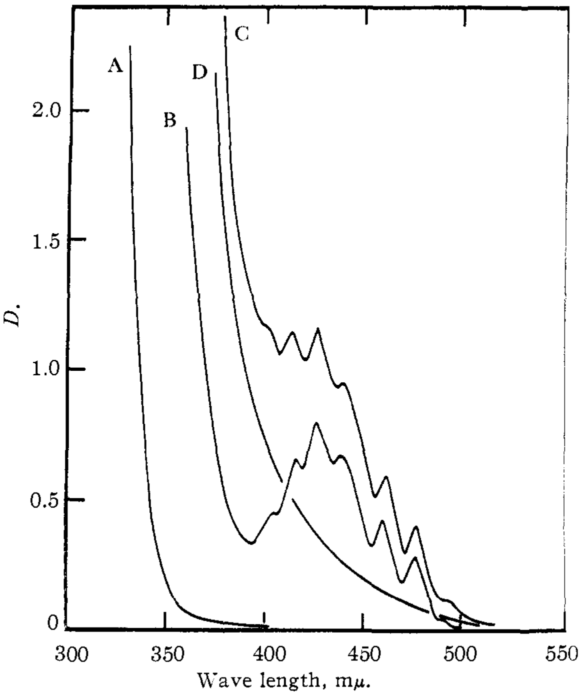

Fig. 2.—Interaction absorption of U(VI) and Sn(II): A, 1 *M* Sn(II); B, 0.1 *M* U(VI); C, 0.1 *M* U(VI); 1 *M* Sn(II); D = C–A–B. All 6 *M* HCl, 5 mm. cells.

maximum indicates that the complex is very largely dissociated.

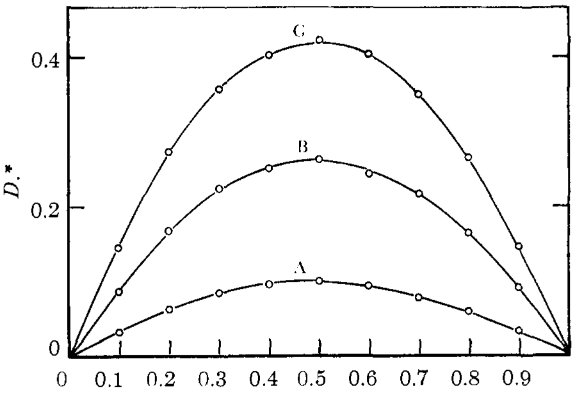

Fig. 3.—Method of continuous variations: total Sn(II) + U(VI) = 1 *M*. All solutions 7 *M* HCl, 1 mm. path length cells. $D^* = D_{\text{total}} - D_{\text{U(VI)}} - D_{\text{Sn(II)}}$. A, 455 mμ; B, 420 mμ; C, 400 mμ.

An analysis of these data by the method of Davidson is shown in Fig. 4 where the interaction absorption is plotted *versus* the product of the total Sn(II) and total U(VI) concentrations. The fact that a straight line is obtained indicates that the complex not only has a 1:1 composition but that it actually contains one U(VI) and one Sn(II) and that its concentration is inappreciable compared to that of the reactants. (Otherwise it would be necessary to correct the tin and uranium concentrations for the amount reacted.) Unfortunately, it is not possible to determine the instability constant of the complex from either analysis, but only the product of this by the extinction coefficient for any given wave length.

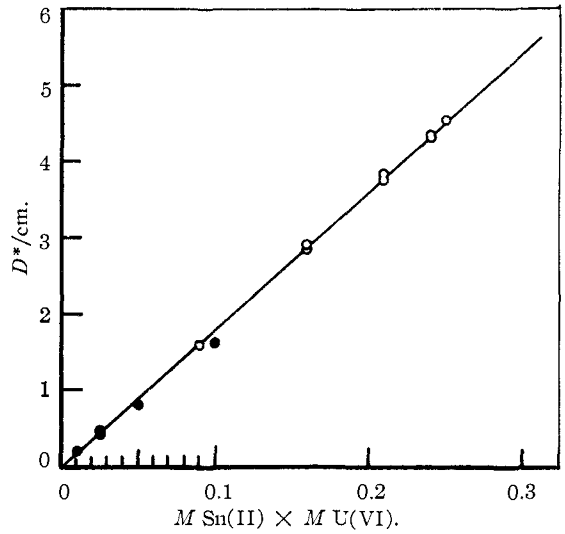

Fig. 4.—Variation of D^* with Sn(II), U(VI) product: ●, 5 mm. cells; ○, 1 mm. cells. All 7 *M* HCl, 400 mμ wave length.

The composition of the interaction complex and the first-order dependence of the reduction reaction on U(VI) and Sn(II) suggests, but does not prove, that the observed complex may be an intermediate in the reduction reaction and that its decomposition may constitute the rate controlling step.

Other Uranium–Tin Complexes.—Addition of either Sn(II) or Sn(IV) to a U(IV) solution (prepared by electrolytic reduction at a mercury cathode) resulted in no change in the U(IV) absorption in the visible region. However a weak interaction between U(IV) and Sn(II) was found in the ultraviolet around 320 to 340 mμ near the Sn(II) cutoff. Here, too, a 1:1 complex was indicated. The intense ultraviolet absorption of traces of U(III), formed by over reduction in the electrolytic cell, or of traces of U(VI), formed by air oxidation of U(IV), prevented the detection of interaction between U(IV) and Sn(IV).

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GENERAL ELECTRIC COMPANY
RICHLAND, WASHINGTON

A Convenient Preparation of Pyridine–Borane

BY MODDIE D. TAYLOR, LOUIS R. GRANT AND CLIFTON A. SANDS

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Pyridine–borane, $C_5H_5NBH_3$, is a pale yellow liquid which freezes to a white solid of melting point 10–11°. It is stable in dry air, nearly insoluble in water, only slightly hydrolyzed by it, and very soluble in alcohol and ether. It is an excellent reducing agent: reducing iron to the ferrous state in slightly acid solution; silver nitrate to silver; and iodine to iodide, giving rise to lower iodides of boron at the same time. Its high solubility in ether coupled with its great stability and low reac-