of this unstable zinc is given by the equation

$$0.001T \log p_{2o} = 0.946 + 7.811\,(0.001T - 1) \quad (13)$$

If liquid zinc be chosen as the standard state, the equation for its vapor pressure must be subtracted from equation 11. Over the range of our measurements the vapor pressure in atmospheres of liquid zinc may be expressed as

$$0.001T \log p_{2l} = -0.843 + 8.282\,(0.001T - 1) \quad (14)$$

If the unstable solid hexagonal zinc is chosen, its vapor pressure may be obtained by temperature extrapolation as

$$0.001T \log p_{2h} = -0.461 + 9.212\,(0.001T - 1) \quad (15)$$

It will be seen that the vapor pressure of hypothetical face-centered zinc is well above that of either the liquid or the unstable hexagonal zinc. Equation 9 gives

$$0.001T \log p_{2o} = -0.134 + 7.811\,(0.001T - 1) \quad (16)$$

which still indicates instability relative to liquid or to hexagonal zinc. Equation (10) for brass, however, gives

$$0.001T \log p_{2o} = -0.672 + 17.104\,(0.001T - 1) \quad (17)$$

If the extrapolation could be trusted, this would indicate that face-centered cubic zinc was the stable form.

The standard state of pure liquid zinc is particularly appropriate for the liquid alloys. The last column of Table II presents $-\log p_{2l}/x_2p_{2lo}$ which is equal to $-\log \gamma_2$ for this standard state.

Probably the most useful reference state for solid alloys is that of unit activity coefficient in an infinitely dilute solution of zinc in silver. By subtracting the value at $x_1 = 1$ from eq. 11 we obtain for $\gamma_2 = a_2/x_2$

$$0.001T \log \gamma_2 = [4.137 + 3.300(0.001T - 1)](1 - x_1^2) + 1.744[1 - x_1^2(3 - 4x_1)] \quad (18)$$

The corresponding equation for the activity coefficient of silver $\gamma_1 = a_1/x_1$

$$0.001T \log \gamma_1 = -[4.137 - 1.744(3 - 4x_2) + 3.300(0.001T - 1)]x_2^2 \quad (19)$$

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[CONTRIBUTION FROM THE ARGONNE NATIONAL LABORATORY]

The Chemistry of Niobium and Tantalum. I. Reduction in Solution[1]

BY R. E. ELSON[2]

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Polarographic and spectrophotometric evidence is presented for the existence of the +3 and +4 oxidation states of niobium and tantalum in solution. Irreversible, one electron reductions are observed at potentials ranging from −1.05 to −1.95 v. *vs.* S.C.E. for niobium and −1.16 to −1.58 for tantalum. Spectral changes in the visible and ultraviolet produced by reduction, are attributed to the (IV) and (III) states.

Wohler, Osborne and others[3] have shown that niobium(V) in sulfuric or hydrochloric acid can be reduced electrolytically or by zinc to a brown or blue solution. The color has been shown to be a function of acid concentration. Titration of this solution has established it to be Nb(III), and potential measurements by Grube and Grube[4] have given values of 0.344 v. for the Nb(III)–Nb(V) couple in 2–6 *N* hydrochloric and 0.342 v. in 3–6 *N* sulfuric.

Zeltzer[5] reported niobium to be polarographically reduced to the III state at −0.8 v. *vs.* S.C.E. in 1 *M* HNO_3 but was unsuccessful in obtaining reduction in other media. Several workers have reported the possible existence of Nb(IV). Ott[6] reduced sodium niobate electrolytically in hydrochloric acid and obtained a green color which he attributed to Nb(IV). He also reduced niobium pentachloride in concentrated sulfuric acid and obtained a blue solution from which a compound was isolated which he postulated to be the mixed oxide $Nb_2O_5 \cdot NbO_2$. No direct evidence of the oxidation state in solution was presented and it is probable that he was working with the (III) state.

There are no data available on the direct reduction of tantalum in solution but lower valence chlorides have been prepared in the dry state by reduction of tantalum pentachloride with aluminum. Ruff and Thomas[7] report that tantalum trichloride dissolves in water to give an intensely green colored aqueous solution which is fairly stable. Tantalum dichloride is also reported by these workers to dissolve with the evolution of hydrogen and the production of the green Ta(III) solution. Zeltzer[5] could not obtain any reduction wave for tantalum in hydrochloric or strong alkali solutions by polarographic techniques.

In this work, evidence was obtained for the existence of the (IV) and (III) states of niobium and tantalum by means of polarographic and spectrophotometric techniques. Most of the reductions were carried out in oxalate and tartrate solutions. It has been found that niobium and tantalum are difficultly soluble in most acids and tend to hydrolyze in these except at high acid concentrations. It was therefore felt advisable to work with strong complexing solutions such as oxalate and tartrate. Some additional polarograms

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(1) Presented in part before the XIIth International Congress of Pure and Applied Chemistry, New York, New York, Sept., 1951.

(2) California Research and Development Co., P. O. Box 751, Livermore, Calif.

(3) (a) F. Wohler, *Pogg. Ann.*, **48**, 93 (1839); (b) W. J. Osborne, *Am. J. Sci.*, [3] **30**, 331 (1885); (c) F. J. Metzger and C. E. Taylor, *J. Soc. Chem. Ind.*, **28**, 818 (1909); (d) S. J. Kiehl and A. Hart, THIS JOURNAL, **50**, 2337 (1928); (e) W. D. Treadwell and R. Nieriker, *Helv. Chim. Acta*, **25**, 474 (1942).

(4) G. Grube and H. L. Grube, *Z. Electrochem.*, **44**, 771 (1938).

(5) S. Zeltzer, *Collection Czechoslov. Chem. Communs.*, **4**, 319 (1932).

(6) F. Ott, *Z. Elektrochem.*, **18**, 349 (1912).

(7) (a) O. Ruff and F. Thomas, *Ber.*, **55B**, 1466 (1922); (b) O. Ruff and F. Thomas, *Z. anorg. Chem.*, **148**, 1 (1925).

were obtained in citrate, fluoride, chloride and nitrate solutions.

Experimental

Polarograms were obtained using a Sargent XX automatic recording polarograph. A conventional H-type cell was used for the electrolysis at 24.5 ± 0.5° and the agar bridge connecting the electrolysis compartment with the calomel reference electrode was prepared using solutions of the same composition as the electrolyte. Drop times were 3 to 5 seconds and *m* values, 0.881 mg./sec. The apparatus was checked by running Fe(III) in oxalate, giving $E_{1/2} = -0.243$ v. *vs.* S.C.E. compared with the value of −0.242 in the literature.[8] Solutions were prepared by dissolving weighed quantities of spectroscopically pure niobium and tantalum metals in a mixture of sulfuric and hydrofluoric acids. The hydrated oxide was precipitated with ammonia; the precipitate was washed thoroughly and dissolved in the desired acid. The acidity was then adjusted by the addition of alkali, and the *p*H was determined with a Beckman *p*H meter. Polarograms were also obtained from blank solutions of the reagents at the same acidity and electrolyte concentrations.

Confirmatory evidence for the existence of lower oxidation states in solution was obtained by noting the changes in spectra that occur in these solutions on reduction. The spectra were observed with a Beckman Model DU spectrophotometer. Conventional 10-mm. silica cells were used which also served as mercury cathode reduction cells. The desired niobium or tantalum solution was placed in the reduction cell, the solution reduced electrolytically in a hydrogen atmosphere, the cells sealed, and the change in spectrum determined using the original solution as the blank. Short periods of reduction could be employed to study the growth of the spectrum of each reduced state.

Discussion

The values obtained for the half-wave potentials are given in Tables I and II. Some difficulty was encountered in the analysis of the Nb(V)–(IV) and Ta(V)–(IV) waves, particularly in oxalate and tartrate solutions, owing to the concurrent discharge of hydrogen. Some typical polarograms are reproduced in Figs. 1–3. Reversibility was tested by Tomes' criterion[9] and by a plot of log $i(i_d - i)$ *vs.* potential,[9] and the reductions were found to be irreversible. Half-wave potentials were obtained from the logarithmic plots which were essentially straight lines. In each case, a one-electron reduction appears to be taking place.

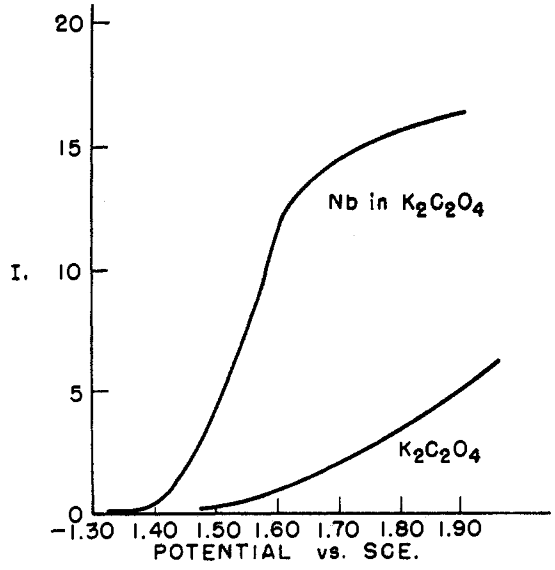

Fig. 1.—3.0 × 10^{-3} Nb in 0.1 *M* $K_2C_2O_4$, *p*H 5.5.

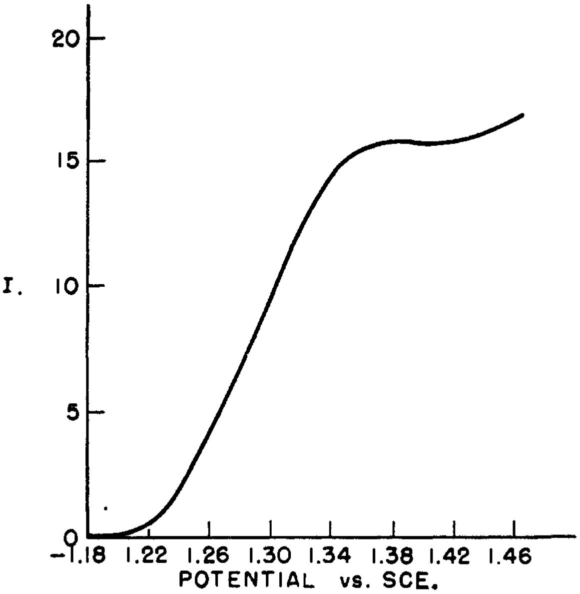

Fig. 2.—1.3 × 10^{-3} *M* Nb in 0.1 *M* KCl, *p*H 2.6.

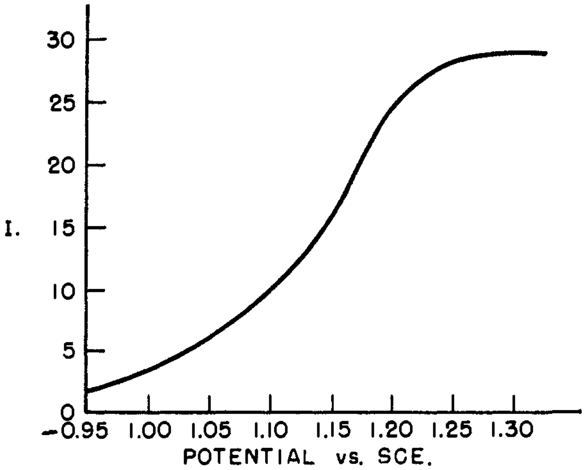

Fig. 3.—7 × 10^{-3} *M* Ta in 0.06 *M* HCl.

The half-wave potential appears to shift to more negative values with increasing *p*H but accurate values for the potentials have not been obtained as yet. However, it is probable that an oxygenated or hydroxylated species is being reduced. The dependency on anion concentration is being studied.

The reduction of niobium to the +3 state was noted in two of the more concentrated solutions noted in Table I. A second and more poorly defined wave was obtained at more negative potentials. These waves, as yet, have not been analyzed for electron change or reversibility but the brown color characteristic of Nb(III) was obtained in these solutions.

The absorption of Nb(V) in oxalate solutions in the ultraviolet was largely obscured by the strong absorption of the oxalate and the acid oxalate ions. There was, however, evidence of a peak at 274 mμ which was shifted to longer wave

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[8] M. v. Stackelberg and H. v. Freyhold, *Z. Elektrochem.*, **46**, 120 (1940).

[9] For a discussion of the principles involved see I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Publishers, Inc., New York, N. Y., 1941.

TABLE I

HALF-WAVE POTENTIALS OF Nb SOLUTIONS

Nb concn., mM	Supporting electrolyte	Concn., M	pH	$E_{1/2}$ vs. S.C.E.
1.0	$K_2C_2O_4$	0.1	1.2	−1.52
3.0	$K_2C_2O_4$	0.1	5.5	−1.53
60	$K_2C_2O_4$	2.0	5.5	−1.53, −2.18[a]
3	$K_2C_2H_4O_6$	0.1	4.7	−1.93
10	$K_2C_4H_4O_6$	1.0	5.2	−1.96
3	$K_2C_4H_4O_6$	1.0	6.5	−1.96
10	$K_2C_4H_4O_6$	1.0	7.0	−2.00
20	$K_3C_6H_5O_7$	0.3	6.8	−1.73, −2.03[a]
1	NH_4F	3.0	7.4	−1.90
4.3	KCl	0.1	2.6	−1.28
1.3	KNO_3	0.1	2.6	−1.03

[a] Second wave attributed to Nb(IV) → Nb(III). A brown color was produced in each case.

TABLE II

HALF-WAVE POTENTIALS OF Ta SOLUTIONS

Ta concn., mM	Supporting electrolyte	Concn., M	pH	$E_{1/2}$ vs. S.C.E.
1.0	$K_2C_2O_4$	1.0	0.5	−1.40
1.0	$K_2C_2O_4$	0.5	2.8	−1.40
3.0	$K_2C_2O_4$	1.5	4.2	−1.47
3.0	$K_2C_2O_4$	2.0	5.4	−1.48
5.0	$K_2C_4H_4O_6$	0.1	2.8	−1.58
7.4	$K_2C_4H_4O_6$	.1	5.0	−1.56
7.3	HCl	.86	...	−1.16

lengths with increasing oxalate concentration. Reduction for 5 to 10 minutes gave two new maxima at 292 and 320 mμ with no absorption in the visible. Further reduction increased the intensity of these two peaks and one new peak appeared in the visible at 435 mμ. Upon further reduction the light absorption in the visible increased more rapidly and attained greater intensity than in the ultraviolet. These changes were accompanied by a reduction in intensity of the peak at 274 mμ ascribed to Nb (V). Upon standing in contact with air, all three peaks slowly decreased, the one at 435 mμ decreased more rapidly and disappeared first. These changes are shown in Table III. As Nb(III) is known to be colored, the peak at 435 mμ is ascribed to Nb(III) and those at 292 and 320 mμ to Nb(IV). The stability of Nb(IV) in these solutions in contact with air appears to be of the same order of magnitude as Nb(III), a half-time of about 10–15 minutes. The wave length of these maxima, particularly the one at 435 mμ, was dependent upon oxalate concentration. Similar results were obtained for Nb in tartrate solutions. Figure 4 reproduces the spectra of Nb(IV) and (III) in oxalate solutions: Nb(V) shows no absorption in the region indicated.

TABLE III

CHANGE IN OPTICAL DENSITY OF NIOBIUM WITH TIME

Time of reduction, min.[a]	Wave length, mμ 320	435	On standing in contact with air, min.	Wave length, mμ 320	435
5	0.145	0	15	0.290	0.790
10	.180	.060	25	.250	.700
30	.275	.700	35	.220	.330
60	.360	1.40	45	.185	.090

[a] 10^{-2} M Nb in $H_2C_2O_4$ reduced in spectrophotometric cell at 0,6 ma.

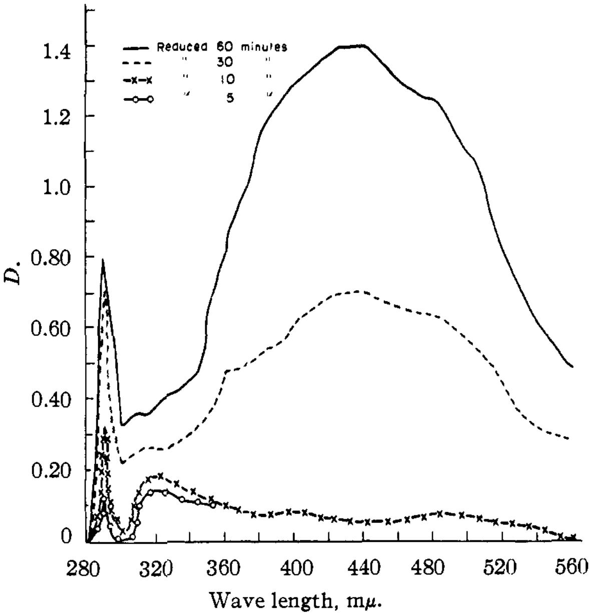

Fig. 4.—Reduction of niobium in oxalic acid: 0.1 M Nb in 0.5 M oxalic acid.

When a solution of Ta(V) in oxalic acid was reduced and the spectrum determined, similar results were obtained. A new absorption maximum is observed at 315 mμ with smaller peaks at 275 and 355 mμ. Further reduction results in a pale yellow-green solution. The peak at 275 mμ increases at a considerably faster rate than those at 315 and 355. It is postulated that the color and maximum at 275 mμ are due to Ta(III) and those at 315 and 355 mμ to Ta(IV). These spectra are reproduced in Fig. 5. These solutions have not been studied thoroughly as yet but the stability to air oxidation appears to be considerably greater than for Nb, of the order of magnitude of hours.

Fig. 5.—Reduction of tantalum in oxalic acid, 5.4 × 10^{-2} M Ta in 0.5 M $H_2C_2O_4$: -o—o-, red. 1 hr. at 0.5 ma. and 2.5 v.—colorless; -x—x-, red. 3 hr. at 0.5 ma. and 2.5 v.—pale yellow-green.

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